The Effect of a Tribo-Modified Surface Layer on Friction in Elastomer Contacts

Milad Mokhtari

The effect of a tribo-modified surface layer on friction in elastomer contacts

Milad Mokhtari

De promotiecommissie is als volgt samengesteld:

prof.dr. G.P.M.R. Dewulf, Universiteit Twente, voorzitter en secretaris
prof.dr.ir. D.J. Schipper, Universiteit Twente, promotor
prof.dr.ir. J.W.M. Noordermeer, Universiteit Twente
prof.dr. G.J. Vancso, Universiteit Twente
prof.dr. habil. M. Klüppel, DIK e.V.
prof.dr.ir. L.E. Govaert, Technische Universiteit Eindhoven
prof.dr. A. Pich, RWTH Aachen

Mokhtari, Milad

The effect of a tribo-modified surface layer on friction in elastomer contacts
Ph.D. Thesis, University of Twente, Enschede, The Netherlands,
November, 2015

ISBN: 978-90-365-4001-8

DOI: 10.3990/1.9789036540018

Copyright © M. Mokhtari, Enschede, The Netherlands

THE EFFECT OF A TRIBO-MODIFIED SURFACE LAYER ON FRICTION IN ELASTOMER CONTACTS

PROEFSCHRIFT

ter verkrijging van
de graad van doctor aan de Universiteit Twente,
op gezag van de rector magnificus,
prof.dr. H. Brinksma,
volgens besluit van het College voor Promoties
in het openbaar te verdedigen
op vrijdag 13 november 2015 om 12:45 uur

door

Milad Mokhtari
geboren op 21 mei 1986
te Teheran, Iran

Dit proefschrift is goedgekeurd door:
de promotor: prof.dr.ir. D.J. Schipper

Acknowledgements

It is a pleasure to thank those who made this thesis possible. I owe deep thanks to my promoter, prof.dr.ir. D.J. Schipper. Dik, thank you for our inspiring discussions which kept me sharp. Your guidance and patience helped me a lot in developing over the past four years. Moreover, I would like to thank Matthijn for his useful hints. Matthijn, I appreciate that you helped me get through wherever you could.

During this research, I had the honor to have the support of the tribology group at the University of Twente. I would like to thank Erik, Walter, Jacob, Laura and Ivo for their assistance during the experimental works.

This project was carried out in the framework of the innovation program “GO Gebundelde Innovatie kracht” and funded by the “European Regional Development Fund”, “Regio Twente” and “Provincie Overijssel”. The project partners Apollo Tyres Global R&D B.V., University of Twente (Tire Road Consortium), Reef Infra, Stemmer Imaging B.V. and the Provincie Gelderland are gratefully acknowledged.

To my colleagues with whom I had a nice time in the group: Martijn, Michel, Mattheijs, Dariush, Febin, Aydar and also Agnieszka, Marieke, Nadia, Yibo, Adeel, Adriana, Dinesh, Mahdiar, Jincan, Belinda, Debbie, Piet, Emile, Lydia, Sheng and Mohammad thanks to all of you.

I wish to thank my parents for backing me up through every moment of my life. And thank you, my dearest Niki for your encouragement and support during these years.

Last but not least, I would like to thank my friends, Damon, Hossein, Csaba, Amir, Saghar, Shahrzad, Frederick, Juan, Olga and Frederiek with whom Enschede was a different city.

Summary

Friction between rubber and a counter surface has interested many researchers because of its huge practical importance. Rubber components are applied in various industrial applications such as tires, rubber seals, wiper blades, conveyor belts and syringes. The friction between a rubber surface in contact with a rigid surface is still not fully understood. The complexity lies partially in the viscoelastic nature of elastomers next to various parameters such as roughness, contact pressure and sliding velocity. In addition, several complex phenomena occur at the interface between rubber and the rough rigid body in contact, which can significantly influence the tribological behavior of the system.

The contact and friction of rubber with a focus on the importance and influence of a tribo-modified surface layer is studied both theoretically and experimentally in this work.

Contact and friction models dealing with soft viscoelastic materials are briefly introduced and the complex aspects of the rubber friction problem are reviewed. To understand the dependence of rubber friction on various parameters, the rubber network, structure and morphology are described. The effect of different reinforcement fillers on the mechanical properties of the rubber is analyzed. The main components of the overall friction in elastomeric contacts are studied and the importance of each friction contributor as a function of the tribological conditions is investigated. It is shown that the shearing of a modified surface layer by a rigid counter surface does play an important role in the total friction. However, it has not been studied thoroughly, therefore this modified layer is researched extensively in this thesis.

The contact and friction model of Persson is extended in such a way that it can model the contact and friction of a transversely isotropic viscoelastic solid, i.e. a fiber reinforced material, in contact with a rigid rough surface, and the results are validated experimentally.

Based on AFM nanoindentations, the existence of a modified surface layer on top of rubber that was subjected to frictional energy is shown. The mechanical properties of the modified layer degrade as a function of tribological conditions when compared to the original surface. A physical model is developed which explains the modification due to mechanical degradation. In this model, the mechanical energy exerted on the bulk of the rubber as a function of the tribological conditions is related to the layer formation rate. The effect of wear is considered in the aforementioned model. It is emphasized that wear of the layer is as important as the formation and a high wear rate might even remove the tribologically modified layer. Finally,

based on the formation and wear, the existence of a modified surface layer is discussed as a function of the energy input rate.

Samenvatting

Wrijving tussen rubber en een tegenoppervlak is een veel onderzocht onderwerp vanwege het enorme praktische belang. Rubber componenten worden in verschillende industriële toepassingen gebruikt, zoals banden, afdichtingen, ruitenwisserbladen, transportbanden en spuitens. Het begrip van de wrijving tussen een rubber oppervlak in contact met een stijf tegenoppervlak is nog niet volledig. De complexiteit ligt gedeeltelijk in het visco-elastische karakter van elastomeren, naast verschillende parameters zoals ruwheid, contactdruk en glijnsnelheid. Daarnaast zijn er verschillende complexe verschijnselen die zich voordoen op het grensvlak tussen rubber en het ruwe stijve lichaam, die het tribologische gedrag van het systeem in hoge mate beïnvloeden.

In dit werk wordt het contact en de wrijving van rubber zowel theoretisch als experimenteel bestudeerd, waarbij de focus op het belang en de invloed van een tribo-gemodificeerde laag ligt.

Contact- en wrijvingsmodellen, die met zachte visco-elastische materialen te maken hebben, worden beknopt geïntroduceerd en de complexe aspecten van de wrijving van rubber worden besproken. Om de invloed van verschillende parameters op rubberwrijving te begrijpen, worden het netwerk, de structuur en morfologie beschreven. Het effect van verschillende versterkende vulstoffen op de mechanische eigenschappen van het rubber wordt geanalyseerd. De belangrijkste componenten van de totale wrijving in elastomeer contacten worden bestudeerd en het belang van elke component als functie van de tribologische omstandigheden wordt onderzocht. Het is bewezen dat het afschuiven van een gemodificeerde laag door een stijf tegenoppervlak een belangrijke rol heeft bij de totale wrijving. De reden hiervoor is echter nog niet grondig bestudeerd en daarom is deze gemodificeerde laag in dit proefschrift uitvoerig onderzocht.

Het contact- en wrijvingsmodel van Persson is uitgebreid, zodat het contact en de wrijving van een transversaal isotroop visco-elastisch materiaal, zoals een fiberversterkt materiaal, in contact met een stijf, ruw oppervlak kan worden gemodelleerd. De resultaten worden experimenteel gevalideerd.

Op basis van AFM nano-indentaties is het bestaan van een gemodificeerde oppervlaktelaag bovenop rubber dat werd onderworpen aan wrijvingsenergie aangetoond. De mechanische eigenschappen van de gemodificeerde laag degraderen als een functie van tribologische omstandigheden in vergelijking met het maagdelijke oppervlak. Een fysiek model is ontwikkeld waarmee de modificatie door mechanische degradatie beschreven wordt. In dit model wordt de mechanische energie die uitgeoefend is op de massa van het rubber als een functie van de tribologische

omstandigheden gerelateerd aan de laag formatie snelheid. Verder wordt ook het effect van slijtage beschouwd in het eerder genoemde model. Er wordt benadrukt dat zowel slijtage en formatie van de laag even belangrijk zijn, aangezien een hoge slijtage tot het verwijderen van de tribologisch gemodificeerde laag leidt. Ten slotte, op basis van de vorming en slijtage is het bestaan van een gemodificeerde oppervlaktelaag bediscussieerd als functie van de energie-invoersnelheid.

Contents

Acknowledgements	i
Summary	iii
Samenvatting	v
Nomenclature	xi
I Part I	xi
1 Introduction	1
1.1 Contact and friction between a soft viscoelastic solid and a rigid rough surface	1
1.2 Water as a lubricant in rubber tribo systems	2
1.3 Tribo-modified surface layer	3
1.4 Objectives	4
1.5 Thesis outline	5
2 Contact and Friction Modeling of Rubber as a Soft Viscoelastic Solid	7
2.1 Rubber composition	7
2.2 Mechanical properties	9
2.3 Contact model	12
2.4 Friction model	14
2.4.1 Friction due to hysteresis	14
2.4.2 Friction due to area of contact	15
2.5 Friction measurement	18
2.6 Summary	19
3 Contact Mechanics and Friction for Transversely Isotropic Viscoelastic Materials	21
3.1 Transversely isotropic viscoelastic materials	21
3.2 Modeling contact and friction of transversely isotropic materials	24
3.3 Importance of considering transversely isotropic viscoelasticity in contact and friction	25
3.4 Summary	28
4 Tribologically Modified Surface Layers	29
4.1 Existence of the modified surface layer	29
4.1.1 Controlled formation of the modified surface layer . . .	31

4.1.2	AFM nanoindentations	31
4.2	Formation of a tribologically modified surface layer	35
4.2.1	Application of the formation model to a friction test	37
4.3	Wear of the modified surface layer	43
4.4	Balance between formation and wear of the modified surface layer	47
4.5	Summary	51
5	Conclusions and Recommendations	53
5.1	Conclusions	53
5.2	Discussion	54
5.3	Recommendations for future research	54
	Bibliography	57

Nomenclature

Roman symbols

a	Crack-tip radius	(m)
a_T	Temperature-frequency viscoelastic horizontal shift factor	(-)
A_0	Nominal area of contact	(m^2)
$A(q)$	Area of contact when the surface is smooth on wave vectors $> q$	(m^2)
A_{real}	Real area of contact	(m^2)
$C(q)$	Power spectral density of the roughness	(m^4)
E	Modulus of elasticity	(Pa)
E'	Storage modulus of elasticity	(Pa)
E''	Loss modulus of elasticity	(Pa)
f	Reciprocal of the roughness wavelength	($1/m$)
F_f	Total friction force	(N)
F_N	Nominal normal load	(N)
F_{vis}	Hysteresis contribution of friction force	(N)
$G(\omega)$	Shear modulus of elasticity	(Pa)
$G(v)$	Energy/area to break the interfacial rubber-substrate bond	(J/m^2)
$\hbar$	Reduced Planck's constant	($J.s$)
k	Specific wear rate	(mm^3/Nm)
k_B	Boltzmann's constant	(J/K)
$P(q)$	Real to the nominal contact area ratio	(-)
$\vec{q}$	Roughness wave vector	($1/m$)
q	Amplitude of the roughness wave vector	($1/m$)
q_0	Lower wave vector cutoff related to the longest wave length	($1/m$)
q_1	Higher wave vector cutoff related to the shortest wave length	($1/m$)
Q_f	Formation rate of the modified surface layer	(m/s)
Q_w	Wear rate	(m/s)
T_g	Glass transition temperature	($^{\circ}C$)
T	Temperature	($^{\circ}C$)
u_z	Displacement of a point inside a solid in z direction	(m)
v	Sliding velocity	(m/s)
w	Distributed elastic energy rate per volume inside the bulk	(J/sm^3)
W	Distributed elastic energy rate inside the bulk	(J/s)

Greek symbols

δ_f	Thickness of the modified surface layer neglecting wear	(<i>m</i>)
δ_{total}	Thickness of the modified surface layer at balance	(<i>m</i>)
δ_w	Thickness of the worn layer	(<i>m</i>)
ε	Strain	(-)
ζ	Magnification factor	(-)
η	Areal asperity density	(1/ <i>m</i> ²)
λ	Length scale of the roughness under study	(<i>m</i>)
μ_f	Total coefficient of friction	(-)
μ_{hys}	Viscoelastic or hysteresis coefficient of friction	(-)
μ_f	Total coefficient of friction	(-)
ν	Poisson's ratio	(-)
σ_0	Nominal contact pressure	(<i>Pa</i>)
τ_c	Frictional stress related to energy dissipation at a crack opening	(<i>Pa</i>)
τ_s	Frictional stress with regard to shearing a thin confined film	(<i>Pa</i>)
ϕ	Angle between the velocity vector and the wave vector $\vec{q}$	(<i>rad</i>)
ω	Frequency of the applied load to the rubber	(<i>rad/s</i>)
Ω	Rate of rubber degradation	(1/ <i>s</i>)

Abbreviations

AFM	Atomic Force Microscopy
DMA	Dynamical Mechanical Analysis
phr	weight parts of component per hundred weight parts of the rubber
SEM	Scanning Electron Microscopy
TGA	Thermal Gravimetric Analysis

Part I

Introduction

Introduction

Rubber components are applied in various industrial applications such as tires, rubber seals, wiper blades, conveyor belts and syringes [1–5]. A smart design of the rubber components requires detailed knowledge about friction between rubber and a rough counter surface. For instance, the grip between tire and road evidently plays a crucial role in road safety, which can achieve significant crash reductions by improving friction under wet and dry conditions [6]. It is the friction that determines the stopping distance and gives drivers the ability to control the direction of their vehicles. Therefore, understanding the interaction between tire and road and the main factors contributing to the friction in tire/road contacts is essential in designing safer tire/roads. The tire/road interaction not only determines the (wet) grip, but noise, rolling resistance and dynamical behaviour of the tires are also correlated with this subject. The complex problem of contact between a rigid rough surface and a soft elastomer has been extensively studied. Despite the great interest in studying the tribological behavior of rubber sliding contacts, the friction problem is not yet fully understood. The complexity of the (wet) sliding friction is due to the fact that the contact problem involves the interaction between at least three different mediums; namely, tread compound (soft elastomer behaving as a viscoelastic solid), asphalt road surface and the water in between. The problem gets even more complicated when observing the changes in the mechanical properties of the interface as a function of the working conditions, which can change the friction. Furthermore, several parameters, such as contact pressure, sliding velocity, temperature, surface roughness and morphology of the rubber compounds, all play a role in the friction of an elastomer in contact with solid surfaces. The research described in this thesis focuses on the tire/road interaction.

1.1 Contact and friction between a soft viscoelastic solid and a rigid rough surface

The sliding friction of rubber is of huge importance for various practical applications [7–11]. However, contact mechanics and friction are intensely connected. To understand friction, a deep insight of the contact formation between bodies is necessary. Several parameters like mechanical properties, including loss and storage modulus of elasticity of the elastomer, geometrical specifications of the contact (both micro and macro roughness), sliding velocity and environmental conditions (temperature and humidity) should be considered to model the contact and friction between a soft viscoelastic

material and a rigid rough surface.

It has been shown [12, 13] that for high contact pressures (or when dealing with compliant materials) which develop relatively large contact areas, the contact model of Persson [2] provides more accurate results when compared with multi-asperity contact models. In addition, Persson’s approach does not pre-exclude any roughness scale from analysis. Despite the success of Persson’s theory a detailed investigation of it [13], reveals opportunities for further enhancement.

Several phenomenological models have been presented regarding the friction between rubber and a rigid rough surface [14–17]. The main disadvantage of phenomenological models is that they are mainly based on experiments and need different tests to find the constants presented in their models. Therefore they do not provide physical understanding.

Various components contribute to the friction between a soft viscoelastic solid and a rigid rough surface. The hysteresis component of friction corresponds to the internal damping of the rubber, which is a bulk property of the material [18, 19]. Hysteresis is generated by (cyclic) deformation of the rubber which is exerted by the roughness of the counter surface. Adhesion, another friction contributor, is ascribed to the attractive forces between the contacting bodies [20, 21]. Another origin of energy dissipation in contact of compliant viscoelastic materials is characterized by the energy dissipation at crack openings [22, 23]. In addition to the aforementioned contributors to friction, which are mainly described by the properties of the bulk of the material, the significant role of interfacial interactions should be emphasized [24]. A remarkable amount of energy can be dissipated through shearing of a thin viscous film [25] during frictional contact.

The friction force is divided into two main forces as illustrated in Figure 1.1: the contribution due to deformation of the rubber as well as the contribution from the area of contact as defined in Equation 1.1

$$F_f = F_{vis} + \tau_f A_{real} \quad (1.1)$$

where F_f , F_{vis} are the forces concerning the total friction and the contribution from the hysteresis losses respectively and the product $\tau_f A_{real}$ represents the force in the real area of contact where τ_f , A_{real} are the frictional shear stress and real area of contact.

1.2 Water as a lubricant in rubber tribo systems

Water behaves as a lubricant in contact between soft viscoelastic solids and a rough rigid surface. Different lubrication regimes have been studied both theoretically and experimentally in lubricated soft contacts [26, 27]. To

Figure 1.1. A viscoelastic solid in contact with a rigid rough surface is shown schematically. Several length scales should be considered in contact and friction modeling. Shearing of a tribo-modified surface layer by the rough surface and assymetric pressure distribution are the two main friction contributors.

design safer tire/roads, two different strategies are realized. In Figure 1.2 a typical Stribeck curve is shown schematically where the friction coefficient μ is depicted as a function of velocity. To increase safety by providing higher friction during driving, two solutions are considered (see Figure 1.2). Several studies endeavoured to decrease the sudden friction loss due to a transition from boundary to mixed lubrication regime. This goal is achieved by designing efficient tread patterns [28] and roads [29] which facilitate fast removal of water. Therefore aquaplaning occurs at higher speeds. Another option is to increase the sliding friction by an increment in both contributions from hysteresis and area of contact. In this thesis the second approach is studied.

1.3 Tribo-modified surface layer

As mentioned above, a possible approach to increase wet grip and consequently improve safety is to increase both contributions of friction. Hysteresis is mainly determined by the bulk properties of the tread rubber and roughness of the road. Many studies concern enhancing friction by tuning roughness or rubber bulk properties [30, 31]. An increase in friction contribution from the area of contact increases the friction in both boundary and mixed lubrication regimes. However, the contribution from the area of

Figure 1.2. A typical Stribeck curve for compliant contacts is shown schematically.

contact is not very well established. This is mainly due to the complex phenomena taking place in the contact at the surface in comparison with the bulk of the material, so that Wolfgang Pauli said, “*God made the bulk, surfaces were invented by the devil*”. It has been shown that the mechanical properties of the rubber surface in contact with a rough surface are modified and consequently, friction varies [32]. To characterize the modifications occurring at the interface, more research is required.

1.4 Objectives

Improving various practical aspects of a tire in contact with an asphalt road (such as wet grip, rolling resistance and noise generation) requires a thorough knowledge of the tribological phenomena occurring not only in the bulk of the rubber but also at the interface between the tire tread and the road asperities. To design safer tire/roads, the dependence of friction on various factors should be known. This research aims at understanding the friction behavior of rubber in contact with a rough surface on different length scales. In addition, the mechanical properties of the surfaces in contact are prone to modifications. These changes occur depending on the tribological conditions like temperature, load and type of motion. The modified surface layers can significantly alter the overall friction. Therefore the dynamics of the tribo-modified surface layer are specifically of importance in modelling the friction. This requires a predictive model capable of modeling the friction, taking into consideration the dynamic process of changes in the rubber

interface besides the other friction contributors. The objective of this research is to study how the rubber interface is modified. Furthermore, inclusion of such modification in to a present friction model is researched.

1.5 Thesis outline

This thesis is divided into two parts: in Part I an overview of the theory and some important experimental results of the articles appended in Part II are demonstrated.

Figure 1.3. Schematic overview of the thesis.

In Part I, Chapter 2 describes the mechanical properties of rubbers and reviews the present contact models, discussing their (dis)advantages when applied to soft viscoelatic solids. In addition, the importance of shearing a modified surface layer in the total friction is emphasized. In Chapter 3, the contact and friction model of Persson is extended in such a way that it can model the contact and friction of transversely isotropic viscoelastic solids in contact with a rigid rough counter surface. Chapter 4 discusses the existence of a tribo-modified surface layer. Furthermore, the importance of the wear besides the formation of a modified surface layer is demonstrated in accordance with determining the existence and thickness of the tribo-modified layer. In addition, a physical model which illustrates how the rubber surface layer degrades is presented. Finally, the main conclusions of this research and some recommendations for future studies are presented in Chapter 5.

An overview of this thesis is shown in Figure 1.3 schematically, illustrating the connections between the chapters in Part I and the corresponding articles in Part II.

Contact and Friction Modeling of Rubber as a Soft Viscoelastic Solid*

In this chapter, rubber as a viscoelastic solid is introduced and its general properties are reviewed. Contact models, when applied to viscoelastic solids, are compared and the friction model of Persson is briefly summarized. The importance of shearing a modified surface layer in friction is emphasized. Feasible methods to improve rubber friction and contact modeling, which are discussed in later chapters, are briefly deliberated.

2.1 Rubber composition

Elastomers, a unique group of polymers, are composed of long hydrocarbon polymer chains. Elastomers are distinctive from polymers by weak intermolecular forces which bring about a low Young's modulus and high failure strain. If an elastomer is modified to a stable state (stable state means that it cannot be easily moulded to another permanent shape by the application of heat and pressure after modification), it is called a rubber. However, the words rubber and elastomer are used correspondingly. Rubbers themselves are divided into two groups of thermosets and thermoplastics. The chemical bonds between the elastomer chains is characteristic for thermosets, while thermoplastic chains are connected physically. In the rubber industry, the process of chemical modification of elastomers is called vulcanization. In Figure 2.1 the chemical bonds between rubber chains (cross-links) are shown. Cross-linked chains cannot move independently. Thermosets have been recognized as the ideal choice for tire applications. In this thesis, the words rubber and elastomers are used interchangeably.

In practice, rubbers are too weak to be used in their genuine form, particularly for tire applications. The mechanical properties of the rubbers are enormously improved by addition of reinforcement fillers. The cross-linking agent, anti-degradates, process aids, extenders and other special additives such as colorants are typical additives other than reinforcement fillers. Carbon black and silica, with completely different surface chemistries, are widely used as the main reinforcing agents in rubber compounds. Silica

*Paper-A

Figure 2.1. In a cross-linked rubber, individual elastomer chains are bonded chemically. Cross-linking is performed under pressure and at higher temperatures. Cross-linked chains cannot move independently anymore.

particles, because of their surface polarity, are eager to aggregate tightly. In addition, most of the rubber compounds are less polar, therefore, a coupling agent is required to improve filler dispersion. After the introduction of the Green tire [33] since the early 1990s, the effect of fillers on wet friction has been investigated in many researches [34, 35]. Rubber compounds reinforced with precipitated silica *can* exhibit improved wet skid resistance when compared with corresponding compounds, filled with carbon black particles [36]. Mainly bulk properties are used to explain the superiority of silica to carbon black as a reinforcement filler in wet friction. However, it has been shown that solely considering bulk properties is unable to explain the wet friction trends and interfacial interactions should be taken into account in explaining wet friction [37].

By properly adding fillers to the rubber network, two extra networks are made between filler particles and the rubber chains. As shown in Figure 2.2, fillers can bond to the cross-links or directly to a rubber chain. In a generalized network decomposition model [38], it is assumed that the breakage and the recreation of aggregates occur in the filler-cross-link network. Moreover, chain debonding and chain sliding takes place in the filler-polymer network and results in Mullins or stress softening [39].

The interaction between both the elastomer matrix and reinforcement fillers and between fillers themselves plays a crucial role in determining the tribological behaviour and mechanical properties of rubbers. In Figure 2.3, Scanning Electron Microscopic (SEM) images of the wear debris from carbon black and silica reinforced rubbers are shown. The difference between the

Figure 2.2. A filler reinforced rubber matrix is decomposed to different networks.

two systems is remarkable. The carbon black reinforced debris has the tendency to attach together and form a smear film, while the silica-filled debris stays apart from each other. Such differences can severely change the friction behavior of rubber tribo systems.

(a) Carbon black filled rubber.

(b) Silica filled rubber.

Figure 2.3. Scanning electron microscopic images of rubber wear particles.

2.2 Mechanical properties

Rubbers are viscoelastic solids, therefore on the one hand they behave viscously, as a liquid, and on the other hand, elastically, as a solid. Thus the elastic modulus of viscoelastic materials is a complex number which consists of the loss modulus (E'') and the storage modulus (E') respectively:

$$E = E' + iE'' \quad (2.1)$$

Viscoelastic materials exhibit some phase lag in strain. The phase lag, δ is related to the loss and storage moduli by $\tan\delta = E''/E'$.

The elastic modulus of rubber-like materials is a complex matter; not only do they strongly depend on the frequency of the applied load ω and temperature T , but they also depend on the strain, dynamic strain rate, static pre-load, time effects, aging and other irreversible effects. A sample of the measured storage and loss moduli as a function of temperature is shown in Figure 2.4. To study the effect of the filler and its content on the mechanical properties, the elastomer matrix is kept the same, however, the filler and its content are changed. Rubber samples are filled with 100, 85, 70 (namely high, medium and low content) parts per hundred rubber (phr) of carbon black and silica which are named HC, MC, LC, HS, MS, LS respectively. An overview of the different rubber compounds prepared with the corresponding amounts (phr) of the components is given in Table 1 of Paper A. The storage and loss moduli of elasticity of the rubber samples are measured using dynamical mechanical analysis (DMA) in temperature sweep mode at a fixed frequency of 10 Hz , under dynamic and static strains of 0.1 and 1 %, respectively.

It is shown that carbon black filled samples are less elastic than silica filled compounds. In addition, an increase in the filler content results in an increase in both loss and storage modulus of elasticity.

Because the roughness of the rough surfaces contains many decades of wave lengths, the mechanical properties of rubbers are required to be known for many decades of frequencies. However, the measurement equipment is usually unable to apply such high frequent cyclic loads. Time-temperature superposition principle can be used to determine the mechanical properties of a linear viscoelastic solid at a desired temperature (frequency), provided from known properties at a reference temperature (frequency). The Williams-Landel-Ferry (WLF) equation [40] is an empirical equation associated to time-temperature superposition that can be used for linear rubbers to predict time-temperature dependencies. However, filled rubbers (especially at high strains) are not linear and therefore the WLF equation is inadequate to fully explain the mechanical behavior of the rubbers at typical strains applied in the tire application. A new procedure has been proposed [41] to calculate the time-temperature dependencies, however it is not possible to conduct direct measurements corresponding to high frequencies and at high strains to validate the aforementioned method.

The procedure of obtaining a master curve is explained below; the shear modulus G is measured in oscillatory shear mode at a constant strain

(a) Storage modulus of elasticity.

(b) Loss modulus of elasticity.

Figure 2.4. Young's storage and loss modulus of elasticity as a function of temperature for different samples. Effect of filler type and its content on mechanical properties of the elastomers is illustrated.

amplitude of 0.1 %. The sample is fixed at both interfaces and sheared at different frequencies between 1 and 200 Hz . The whole procedure is repeated

then for different temperatures (the temperature is varied between -20 and 85 °C). To obtain master curves from the measurements, covering several frequency decades, the WLF equation is applied to shift the measurements performed corresponding to each temperature horizontally. Because of the nonlinear behavior of the filled rubbers, unrestricted vertical shifting is also performed to govern smooth master curves. The master curve corresponding to LS is shown in Figure 2.5.

Figure 2.5. Shifted loss and storage shear modulus of elasticity as a function of frequency for the sample LS.

2.3 Contact model

Contact between rough surfaces is generally modeled by two different approaches; namely, analytical models and numerical methods. Analytical models are classified into two categories; multi-asperity approaches initiated by Greenwood and Williamson (GW) [42] and division of models initially addressed by Persson [2].

In the initial version of the GW model, the roughness was reduced to a set of identical asperities which are incorporated with a Hertzian punch. Little is gained by refining geometrical and statistical aspects of the GW model in the modified versions of it [43–46]. The achieved results through multi-asperity contact models are simple and neat and therefore of practical worth. Consequently, they have attracted the attention of a number of researchers for quite some time now. However, neglecting the interactions

between neighbouring micro contacts is the main disadvantage of these models, especially when dealing with compliant materials such as rubbers or soft biological tissues and/or high contact pressures. Even though the interaction between the asperities can be added to the current asperity models [47, 48], the complication of the interaction between neighbouring micro contacts is not accurately solved [12]. All in all, as Greenwood mentioned in a self critical article entitled “*Surface Roughness and Contact: An Apology*” [49], the initial definition of a peak corresponding to the asperities was wrong and, instead, a pioneering Archard’s concept in which roughness consists of “protuberances on protuberances on protuberances” should be used.

On the other hand, the second category of the analytical models (following the approach presented by Persson [2]) does not suffer from the deficiency of ignoring interaction between neighbouring micro contacts. Unlike the multi-asperity contact models the roughness is not simplified to asperities but, in contrast, all of the length scales of roughness are included in the analysis. In the model developed by Persson, the exact solution for the case of full contact is obtained. Furthermore, the partial contact problem is handled by imposing a boundary condition which is an approximate solution. The applied boundary conditions have been subject to criticism by Manners and Greenwood [50]. In addition, the ill-posed boundary conditions bring about an overestimation in the asperity elastic energy and consequently an underestimation in the calculated real area of contact [48]. A correction has been applied to the model subsequently [51]. Both asperity contact models and the models based on Persson’s approach have been investigated and the results have been compared [12, 13, 52].

Rubber behavior as a hyperelastic material that can bend and fill out the roughness on at least small wave lengths is more analogous to Persson’s analysis than the asperity contact models (where it is assumed that contact occurs on segregated islands, far from each other, which are named asperities and do not have any influence on each other because of the far distances in between). Therefore, the contact and friction model introduced by Persson is investigated and possible improvements (when applied to rubber friction) are suggested. The contact model of Persson has been extended in such a way that it can also handle surfaces with anisotropic statistical properties [53]. In Chapter 3, the contact model of Persson is extended to model contact between transversely isotropic viscoelastic solids and rough surfaces. This is important for modeling contact of unidirectionally fiber reinforced rubbers or when dealing with induced anisotropy by the Mullins effect [54].

2.4 Friction model

Once the contact between two bodies is known, friction should be modeled. Hysteresis is calculated via Persson's model. Because surfaces are rough with roughness on many different length scales λ , the contact and friction are calculated as a summation of contributions from each wavelength of the rough surface. If the rough surface is isotropic, just the amplitude of the wave vector $|\vec{q}| = q = 2\pi/\lambda$ is considered.

2.4.1 Friction due to hysteresis

In this section the main formulations to calculate the hysteresis contribution of friction are reviewed [2].

$$\mu_{hys} \approx \int_{q_0}^{q_1} dq q^3 C(q) P(q) \int_0^{2\pi} d\phi \cos \phi \operatorname{Im} \frac{E(qv \cos \phi)}{(1 - \nu^2)\sigma_0} \quad (2.2)$$

The function $P(q) = \frac{A(q)}{A_0}$ is given by

$$P(q) = \frac{2}{\pi} \int_0^\infty dx \frac{\sin x}{x} \exp \left[-x^2 G(q) \right] = \operatorname{erf} \left(\frac{1}{2\sqrt{G}} \right) \quad (2.3)$$

where

$$G(q) = \frac{1}{8} \int_{q_0}^q dq q^3 C(q) \int_0^{2\pi} d\phi \left| \frac{E(qv \cos \phi)}{(1 - \nu^2)\sigma_0} \right|^2 \quad (2.4)$$

In the formulations presented above, E is the complex elasticity modulus, C is the power spectral density of roughness which is a function of the wave vector q , ν is the Poisson's ratio of the elastomer, σ_0 is the nominal contact pressure and v is the sliding velocity.

$P(q)$ is the ratio between the real area of contact $A(q)$, when the surface is assumed to be smooth on all wave vectors larger than q and the apparent contact area A_0 . Persson suggests that the power spectral density of roughness, $C(q)$, contains all the necessary information regarding oscillating forces exerted by asperities. Most natural surfaces and surfaces of engineering interest are self-affine fractal. The power spectral density of roughness [55] and the fractal dimension of rough surfaces have been studied closely [56]. In the presented equations, ϕ is the angle between the wave vector $\vec{q}$ and the velocity vector $\vec{v}$, ν is the Poisson's ratio of the viscoelastic body and σ_0 is the nominal contact pressure.

To study the effect of roughness on hysteresis, two different roughnesses, namely smooth and rough, i.e., with arithmetic average roughness of 0.52 and 2.28 μm , respectively, were used. The Eqs. 2.2 to 2.4, together with the mechanical properties of the rubber samples, filled with carbon black or silica

(see Section 2.2 and Figure 2.4) are used to calculate the hysteresis contribution to friction. The effect of roughness and mechanical properties on the hysteresis component of friction in the studied system is illustrated in Figure 2.6.

Figure 2.6. Hysteresis coefficient of friction as a function of sliding velocity for carbon black and silica filled samples in contact with relatively smooth and rough spheres.

Among the carbon black and silica filled samples, the elastomers reinforced with carbon black show a higher level of hysteresis. In addition, a higher content of filler (both carbon black and silica) induces a higher hysteresis in the bulk of the material.

2.4.2 Friction due to area of contact

When soft materials are in contact with rigid surfaces, larger contact areas are formed and therefore the contribution from the real area of contact becomes more important in the overall friction. The contributions from real area of contact have been investigated in various studies [1, 57], however, the physical mechanism of their characteristics is not understood well. Recently some physical models were proposed to model the real area of contact contribution to the sliding friction of elastomers on the basis of crack opening and crack propagation processes and the rate processes of molecular bonds [58–61]. The shear stress τ_f introduced in Equation 1.1 is connected to

shearing of a thin modified layer, energy dissipation at crack opening or bond breaking due to wear [25]. The effects of all factors are added together and summarized in τ_f [62]. The real area of contact contribution to the total friction is determined by two factors. As illustrated in Equation 1.1, both the real area of contact A_{real} and the shear stress τ_f regulate the contribution of real area of contact to friction. Hence, the properties of the top rubber layer and the real area of contact both deserve attention.

The real area of contact depends on both the surface roughness and the mechanical properties of the rubber compounds. To investigate the effects of roughness, filler type and content on the real area of contact, the mechanical properties of the carbon black and silica reinforced samples presented in Figure 2.4 together with the two rough surfaces previously used to calculate the hysteresis component of friction (Figure 2.6) are used. The calculated real area of contact for each tribo system is depicted in Figure 2.7 as a function of magnification factor ζ . The magnification factor $\zeta = q/q_L$ is defined as the ratio between the wave vector of which the contact is being studied q and the shortest wave vector q_L corresponding to the length of the nominal contact.

It is shown that the real area of contact decreases with an increase in the filler content (which consequently increases the Young's modulus of elasticity). This argument is also valid in comparing silica and carbon black filled samples; silica filled compounds, due to their lower moduli of elasticity, make larger contact areas than carbon black reinforced composites. In addition, the real area of contact for all rubber samples increases approximately 3-5 times when a smooth ball is in contact with rubber compared to the rough one.

Furthermore, in most tribological contacts, the composition and tribological properties of the original interface changes during use [63]. These modified surfaces play an important role in determining the tribological behavior. As mentioned in Chapter 1, a possible solution to improve wet grip is to increase the contribution from the real area of contact. Therefore the dynamics of the formation, removal and the stability of the tribo-modified surface layers on rubbers (which play an important role in the overall friction) should be studied. However, there are not many studies on the existence and the properties of the modified surface layer in elastomeric contacts. The existence of a tribo-modified surface layer as a function of tribological conditions and identical importance of wear and formation of the modified layer are studied in Chapter 4. The formation of a modified surface layer, or a *dead layer* as named by Persson is rationalized by thermal and stress-induced degradation of the top rubber layer [64]. Persson uses the standard expression describing activated processes to model the formation process. The presented model is indirectly in qualitative agreement with experiments. However, it seems that the formation process should be

(a)

(b)

Figure 2.7. Variation of real area of contact $A(\zeta)$ over nominal contact area A_0 as a function of magnification factor ζ for sliding velocity of $v = 5 \text{ mm/s}$ in contact with (a) smooth and (b) rough granite surfaces.

modeled considering microscopic phenomena occurring underneath the contact. In addition, several parameters are introduced that are hard to measure precisely. In Chapter 4, the modification of the top rubber layer is explained and modeled.

2.5 Friction measurement

Friction in sliding contact is measured by a pin-on-disk apparatus. The advantage of the lab measurements is that friction can be measured under controlled conditions. A pin-on-disk setup is illustrated schematically in Figure 2.8. The contact pressure is controlled by the external load F for various rubber samples, while the disk rotates with an angular velocity of ω . In a pin-on-disk setup, both the macro geometry and the micro roughness of the pin can be defined. Therefore, one can focus on the effect of the micro roughness on friction by selecting a nicely shaped pin (a sphere as an example). In the pin-on-disk measurements, a granite sphere with a diameter of 30 mm and different values of micro roughness is used.

Figure 2.8. A pin-on-disk apparatus is shown schematically where a rubber disk is in sliding contact with a granite sphere.

The friction between tire and road on the real scale can be measured using different methods. These methods are categorized into three different classes; namely, vehicle based [65], tire based [66] and wheel based systems. In a vehicle based measurement system, the lateral and longitudinal motions of the vehicle are used for estimating the tire/road friction. Thanks to the tire/road models, the deflection of the tire (which is measured directly using different intelligent sensors) can be related to the tire/road friction in tire based measurement systems. In a wheel based system, a redundant wheel is attached to a car and pulled with a specific speed. The friction is measured while a braking torque

is applied to the additional wheel. Moreover, the slip angle of the tire can be changed. To study the roughness and tread material influence on wet friction, a wheel based system is used.

2.6 Summary

In this chapter, the main properties of the rubbers as soft viscoelastic elastomers were reviewed. The role of the reinforcement fillers in enhancing mechanical properties of the rubber articles and their significance on adjusting mechanical properties were indicated. The contact and friction models for the contact between soft elastomers and rigid rough surfaces were mentioned and the (dis)advantages of them were briefly summarized. The main contributors to elastomer friction were introduced and the importance of each one in determining the total friction was studied. Furthermore, the influence of several parameters such as mechanical properties of the rubbers, roughness, filler types and sliding velocity on the contact and friction of elastomers was investigated both theoretically and experimentally. The importance of shearing a modified surface layer on the total friction was emphasized.

Contact Mechanics and Friction for Transversely Isotropic Viscoelastic Materials*

The theory of contact mechanics developed by Persson is extended in such a way that it can model the contact and friction of a transversely isotropic viscoelastic solid in contact with a rigid rough surface.

As discussed earlier in Section 2.3, the contact and friction model of Persson is more compatible for elastically soft materials. The contact between an isotropic viscoelastic solid and a randomly rough surface, with statistical properties which are translationally invariant and isotropic, has been modeled by Persson [2]. This model has been extended to handle surfaces with anisotropic statistical properties (like unidirectional polished surfaces) [53]. Several soft materials behave differently along principal axes. Moreover, rubbers are prone to change their mechanical properties as a function of loading direction [54, 67]. In other words, an initially isotropic rubber might evolve to a transversely isotropic solid due to the loading conditions. Therefore, in this chapter, the contact model of Persson [2] is extended so it can model the contact between a transversely isotropic viscoelastic solid and a rigid rough surface.

3.1 Transversely isotropic viscoelastic materials

Transversely isotropic materials are a unique group of materials whose properties are the same along two of the three principal axes. Several materials can be classified as transversely isotropic materials including crystals, rocks, piezoelectric materials, some biological tissues such as muscles, skin, cartilage tissue and fibrous composites. Viscoelasticity, which makes the contact problem even more complex, is crucial in modeling rubber-like materials and biological tissues and should not be ignored. Consider a transversely isotropic solid, with symmetry plane x - y . The relations between stresses and strains applied to a transversely isotropic body are determined by 5 independent elastic constants E_p , E_z , G_{zp} , ν_p , ν_{pz} ; the Young's modulus and Poisson's ratio in the x - y symmetry plane are given by E_p , ν_p , the Young's modulus and Poisson's ratio in the z direction are E_z , ν_{pz}

*Paper-B

and the shear modulus in the z direction is G_{zp} . The Poisson's ratios must satisfy $\frac{\nu_{pz}}{E_p} = \frac{\nu_{zp}}{E_z}$. The generalized Hook's law, in the stiffness form, reads:

$$\begin{bmatrix} \sigma_x \\ \sigma_y \\ \sigma_z \\ \tau_{yz} \\ \tau_{zx} \\ \tau_{xy} \end{bmatrix} = \begin{bmatrix} A_{11} & A_{12} & A_{13} & 0 & 0 & 0 \\ A_{12} & A_{11} & A_{13} & 0 & 0 & 0 \\ A_{13} & A_{13} & A_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & A_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & A_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & A_{66} \end{bmatrix} \begin{bmatrix} \frac{\partial u_x}{\partial x} \\ \frac{\partial u_y}{\partial y} \\ \frac{\partial u_z}{\partial z} \\ \frac{\partial u_z}{\partial y} + \frac{\partial u_y}{\partial z} \\ \frac{\partial u_z}{\partial x} + \frac{\partial u_x}{\partial z} \\ \frac{\partial x}{\partial u_x} + \frac{\partial z}{\partial u_y} \end{bmatrix} \quad (3.1)$$

In Equation 3.1, the following relations hold:

$$\left\{ \begin{array}{l} A_{11} = \frac{1 - \nu_{pz}\nu_{zp}}{E_p E_z \Delta}, \quad A_{12} = \frac{\nu_p + \nu_{pz}\nu_{zp}}{E_p E_z \Delta} \\ A_{13} = \frac{\nu_{zp} + \nu_p \nu_{zp}}{E_p E_z \Delta}, \quad A_{33} = \frac{1 - \nu_p^2}{E_p E_z \Delta} \\ A_{44} = G_{zp}, \quad A_{66} = \frac{E_p}{2(1 + \nu_p)} \\ \Delta = \frac{(1 + \nu_p)(1 - \nu_p - 2\nu_{pz}\nu_{zp})}{E_p^2 E_z} \end{array} \right.$$

Consider a transversely isotropic half-space whose surface is parallel to the planes of isotropy. Take a rectangular coordinate system $(\mathbf{x}, z) = (x, y, z)$, where z is perpendicular to the planes of isotropy. If a concentrated load $F(\mathbf{x}, 0) = F_0$ is applied on the free surface of the transversely isotropic solid, the displacement at any point on the surface, $u_z(\mathbf{x}, 0)$ can be calculated by the equation below [68], substituting $z = 0$:

$$u_z(\mathbf{x}, z) = \sum_{i=1,2} \frac{\alpha - \gamma s_i^2}{s_i^2} \frac{\partial \varphi_i}{\partial z} \quad (3.2)$$

The functions $\varphi_{1,2}(\mathbf{x}, z)$ are defined as,

$$\begin{aligned} \varphi_{1,2}(\mathbf{x}, z) = & -\frac{s_{1,2} \left[\alpha + (1 - \gamma) s_{2,1}^2 \right]}{s_2 k_2 \left[\alpha + (1 - \gamma) s_1^2 \right] - s_1 k_1 \left[\alpha + (1 - \gamma) s_2^2 \right]} \left(\frac{F_0}{2\pi B_{66}} \right) \\ & \times \log \left(\sqrt{x^2 + y^2 + s_{1,2}^2 z^2} - s_{1,2} z \right) \end{aligned} \quad (3.3)$$

In Equations 3.2 and 3.3 the constants α, γ, k_1 are determined by

$$\begin{cases} \alpha = \frac{B_{11}}{B_{13}}, \gamma = \frac{B_{44}}{B_{13}}, k_i = \frac{1 - \gamma - \beta(\alpha - \gamma s_i^2)}{\gamma s_0^2} \\ \text{where } \beta = \frac{B_{33}}{B_{13}}, s_0^2 = \frac{B_{66}}{B_{44}} \end{cases} \quad (3.4)$$

In addition,

$$s_{1,2}^2 = \frac{B_{44}^2 + B_{11}B_{33} - B_{13}^2 \pm \sqrt{(B_{44}^2 + B_{11}B_{33} - B_{13}^2)^2 - 4B_{11}B_{33}B_{44}^2}}{2B_{33}B_{44}} \quad (3.5)$$

The B_{ij} constants in Eqs. 3.3 to 3.5 are related to the 5 elastic constants by the following relations:

$$\begin{cases} B_{11} = A_{11}, & B_{33} = A_{33}, & B_{44} = A_{44}, \\ B_{66} = A_{66}, & B_{12} = A_{12} + A_{66}, & B_{13} = A_{13} + A_{44} \end{cases}$$

Substituting $z = 0$ in Equation 3.2 and after some simplifications, the displacement at the interface is written as

$$u_z(\mathbf{x}, 0) = \frac{DF_0}{2\pi|\mathbf{x}|} \quad (3.6)$$

where D is a function of 5 independent elastic constants of a transversely isotropic solid,

$$\begin{aligned} D = & \left[2\alpha^2 + \alpha(1 - 2\gamma) \left(\frac{B_{44}^2 + B_{11}B_{33} - B_{13}^2}{B_{33}B_{44}} \right) - 2\gamma(1 - \gamma) \frac{B_{11}}{B_{33}} \right] \\ & \times \left(\frac{1}{B_{66}} \right) \frac{1}{s_2 k_2 \left[\alpha + (1 - \gamma) s_1^2 \right] - s_1 k_1 \left[\alpha + (1 - \gamma) s_2^2 \right]} \end{aligned} \quad (3.7)$$

Equation 3.6 shows that the displacement field is symmetric. The displacement at each point is dependent on the distance from the location of the applied (point) load and elastic properties of the infinite half-space.

In the presented equations, if the transversely isotropic solid has viscoelastic properties, at least the elastic and shear moduli of elasticity are complex numbers and a function of temperature and excitation frequency. In this case, D is a complex function of frequency ω and temperature T .

3.2 Modeling contact and friction of transversely isotropic materials

Consider a rough rigid surface sliding at a constant velocity $\mathbf{v}$ on a transversely isotropic viscoelastic half-space. The normal stress and displacements applied by the asperities of the counter surface to the transversely isotropic viscoelastic solid repeat themselves in the time domain or in other words $\sigma_z(\mathbf{x}, t) = \sigma_z(\mathbf{x} - \mathbf{v}t)$ and $u_z(\mathbf{x}, t) = u_z(\mathbf{x} - \mathbf{v}t)$. The Fourier transforms of the normal stress σ_z and the normal displacement u_z (shown simply as σ, u from now on, because only a normal force is applied on the free surface of the transversely isotropic viscoelastic solid) are related by the response function M :

$$M(\mathbf{q}, \omega) \sigma(\mathbf{q}, \omega) = u(\mathbf{q}, \omega) \quad (3.8)$$

After transforming Equation 3.6 into Fourier domain and substituting in Equation 3.8, the M function is obtained:

$$M(\mathbf{q}, \omega) = \frac{2D}{|\mathbf{q}|} \quad (3.9)$$

With regard to simplicity, it is assumed that the rough surfaces are isotropic. Therefore the amplitude of the wave vector $|\vec{q}| = q = \frac{2\pi}{\lambda}$ is important and not its direction. However, the presented formulations are general and they can be combined with the model presented in [53] to include roughness anisotropy in addition to the material anisotropy. Considering the calculated M function in Equation 3.9 and following Persson's approach, the hysteresis component of friction is obtained by

$$\mu_{hys} = \frac{-i}{\sigma_0} \int_{q_0}^{q_1} dq \, q^2 C(q) P(q) \int_0^{2\pi} d\phi \, \cos \phi \, M^{-1}(q, q.v) \quad (3.10)$$

The function $P(q) = \frac{A(q)}{A_0}$ is given by

$$P(q) = \frac{2}{\pi} \int_0^\infty dx \, \frac{\sin x}{x} \exp[-x^2 G(q)] = \operatorname{erf} \left(\frac{1}{2\sqrt{G}} \right) \quad (3.11)$$

where

$$G(q) = \frac{1}{2} \int_{q_0}^q dq \, q \, C(q) \int_0^{2\pi} d\phi \left| \frac{M^{-1}(q, q.v)}{\sigma_0} \right|^2 \quad (3.12)$$

Once the hysteresis component of friction and the real area of contact are known (using Eqs. 3.10 to 3.12) together with Eqs. 3.7 and 3.9, the total friction can be modeled using Equation 1.1.

3.3 Importance of considering transversely isotropic viscoelasticity in contact and friction

The effect of mechanical properties anisotropy (in the form of transverse isotropy) on the contact area and the hysteresis contribution of a viscoelastic material is examined by comparing the presented contact and friction model with the model of Persson [2]. To do this, the dynamical mechanical properties of a tire tread compound are used. The normalized modulus of elasticity of the tread compound is depicted in Figure 3.1. The contact and friction model of Persson together with the isotropic rubber properties are used to calculate the hysteresis component of friction, as well as the real area of contact.

Figure 3.1. Normalized modulus of elasticity of an isotropic viscoelastic material (tire tread).

Two transversely isotropic materials are introduced; the presented isotropic material is virtually reinforced (reinforcement is performed by increasing both the storage and loss modulus independently, by a factor of

2.5, for the whole frequency range, in the direction of indentation z) while all the other mechanical properties (such as Poisson's ratio) are kept constant. In other words, for the isotropic solid illustrated in Figure 3.1, $E_x = E_y = E_z = E' + iE''$. The elastic moduli for the first transversely isotropic solid are governed by:

$$(E_x)_{R1} = (E_y)_{R1} = E' + iE'', \quad (E_z)_{R1} = 2.5E' + iE'' \quad (3.13)$$

The mechanical properties of the second transversely isotropic solid are determined by the following relations:

$$(E_x)_{R2} = (E_y)_{R2} = E' + iE'', \quad (E_z)_{R2} = E' + 2.5iE'' \quad (3.14)$$

The surface roughness power spectral density presented in Figure 3.2 and the mechanical properties of the isotropic solid and the two transversely isotropic rubbers are used to calculate the hysteresis coefficient of friction as a function of sliding velocity. The calculated hysteresis coefficient of friction is shown in Figure 3.3.

Figure 3.2. The fitted power spectral density of a rigid surface roughness.

The friction is not only determined by the hysteresis but the real area of contact is also playing an important role in determining the overall friction. It is known that the real area of contact decreases with an increase in the sliding velocity. The ratio between the real area of contact to the apparent contact area is shown for a sliding velocity of 5 mm/s to study the effect of transversely isotropy. The results are demonstrated in Figure 3.4.

Figure 3.3. Hysteresis coefficient of friction as a function of velocity for an isotropic viscoelastic solid and two transversely isotropic viscoelastic solids.

Figure 3.4. Variation of real area of contact over nominal contact area as a function of magnification for sliding velocity of 5 mm/s for an isotropic viscoelastic solid and two transversely isotropic viscoelastic solids.

The numerical results show that anisotropy in the class of transversely isotropy has a significant effect on both the hysteresis coefficient of friction and the real area of contact and should not be neglected.

Figure 3.4 shows that any increase in the elasticity (storage or loss modulus of elasticity) in the normal direction z , because of increasing the contact stiffness, leads to a decrease in the area of contact. However, increasing the storage modulus in the loading direction has greater influence on the area of contact than an increase in the loss modulus. On the other hand, an increase in the loss/storage modulus changes the hysteresis friction coefficient in a different manner. Because of the fact that the hysteresis component of friction originates from the loss modulus, it increases by increasing the loss modulus. However, an increase in the storage modulus increases the contact stiffness, consequently the indentation depth decreases. The effect of reinforcement in loss/storage modulus on the hysteresis coefficient of friction is shown in Figure 3.3. Depending on the tribological conditions, hysteresis or area of contact might be the dominant contributor in friction. This analysis is required in a smart design of several engineering applications where a transversely isotropic viscoelastic material is used.

3.4 Summary

In order to model the contact and friction of a transversely isotropic viscoelastic solid in contact with a rigid rough surface, the theory of contact mechanics developed by Persson was extended. The sensitivity of the contact and friction to an increase in the elasticity modulus in one direction was examined and the model was validated experimentally.

Tribologically Modified Surface Layers*

Contribution from shearing a thin modified layer is an important component in the overall friction of elastomers and should be studied. The existence of a tribo-modified surface layer on elastomers is proven experimentally by AFM nanoindentations. A degradation in mechanical properties is seen on the elastomer sections that have been subjected to frictional energy. A physical model is presented which explains the formation rate of the modified surface layer as a function of mechanical loading of the elastomer and the wear rate. Moreover, the importance of wear on the existence of the modified surface layer and consequently on friction is investigated.

Although the shearing of the modified surface layer is an important component of friction, the properties of such a layer have not been studied well. The existence of a modified surface layer, which controls the friction by shearing due to the counter surface, is still doubtful and therefore should be investigated. Formation of a modified surface layer due to mechanical degradation is explained and modeled. Wear of the modified surface layer is as important as the formation in determining the existence of such a layer. An increase in the frictional energy might result in an increase in wear which might consequently remove the modified layer completely.

4.1 Existence of the modified surface layer

In most tribological contacts, the composition and tribological properties of the surfaces in contact change when compared with the original interface. This has been observed for various materials and under various tribological conditions [63]. Such differences are reported for elastomers [35, 69–72] likewise.

The existence of a tribologically modified surface layer on rubber samples was shown by SEM imaging [32]. However, not all rubber samples can be used for SEM imaging, because of the conductivity problems due to reinforcement fillers. To overcome this problem, samples should be covered with a thin layer of gold, which further increases doubts about the reliability of the images. In addition, no quantitative data about the properties of the modified surface layer (except the thickness of the layer) is obtained.

*Paper-C, Paper-D and Paper-E

To investigate the changes of the surface layers, in terms of modifications in mechanical properties, Atomic Force Microscopy (AFM) is used. AFM in the contact mode can be used as a depth-sensing instrument, measuring precisely the applied load as a function of the penetration depth. The stiffness of the sample can be calculated by applying a contact mechanics model to the load-penetration depth curve. This technique has been successfully applied to both polymers and rubbers [73–75]. The viscoelastic properties of the samples as a function of the frequency of the applied load can be obtained by performing measurements at various temperatures and/or indentation ratios [76, 77].

Figure 4.1. A typical cantilever deflection (force) plotted versus AFM piezo displacement, showing the loading and unloading curves.

A raw force-displacement curve is a plot of the voltage applied to the piezo versus the voltage output of the position sensitive diode (PSD) which monitors the cantilever deflection. The voltage output of the PSD translates the cantilever deflection via deflection sensitivity, which is a characteristic of the measurement device. If the cantilever’s spring constant is known, the cantilever deflection can be transformed to the cantilever force. A sample of a force-displacement curve is shown in Figure 4.1. During the loading phase, when the cantilever is sufficiently close to the rubber surface and shortly before contact, surface forces like van der Waals suddenly attract the cantilever tip. This is shown as the snap-on point. In the unloading curve, adhesion between the cantilever tip and the rubber keeps them in contact till the snap-off point, where the detachment force is sufficient to overcome adhesion. The loading part of the load-penetration depth is used to calculate the elasticity of the samples [78] in this study.

4.1.1 Controlled formation of the modified surface layer

To investigate the effect of the reinforcement filler, its content and input energy on the formation and degradation of a modified surface layer, four rubber samples filled with various contents of carbon black or silica were exposed to different levels of frictional energy, using a pin-on-disk setup. The rubber samples HC, LC, HS, LS (as introduced in Section 2.2), which correspond to high and low contents of carbon black and silica respectively, are used to examine the modified layer. The low content samples are filled with 70 phr of reinforcement fillers (carbon black or silica) and high content samples contain 100 phr of fillers, as presented in Table 1 of Paper A. Low severe tribological conditions are provided by tests performed with a sliding velocity of 5 mm/s and under a contact pressure of 0.4 MPa . The tests with high severity are performed by increasing the sliding velocity to 300 mm/s and the contact pressure to 1.2 MPa . A granite ball with a diameter of 30 mm and with arithmetic average roughness of 0.52 μm is used as a counter surface. The tests are kept running until the measured friction force becomes stable or, in other words, until the surface layer is generated and the running-in phase is passed.

4.1.2 AFM nanoindentations

To inspect the existence of a modified surface layer, a Nanosurf Easyscan 2 type of AFM is used. The cantilever is a contact mode silicon probe (SHOCONA) with a nominal spring constant of 0.10 N/m. A sample of the applied load versus measured penetration depth is shown in Figure 4.2.

Because of the fact that the tip-sample contact area, depth of penetration and consequently the calculated elastic modulus can be substantially affected by the surface roughness, a featureless, smooth region should be selected for indentation. The surface roughness in the selected area is checked using images taken before indentation. In addition, one should control whether plastic deformation occurs because of indentation. This is performed by images taken immediately after indentation. No evident residual imprint was detected after penetration, suggesting that only phenomena with a viscoelastic nature are active during indentation. Nanoindentation measurements are performed on rubber matrices, far from the filler particles and their surrounding interphase, both inside and outside the wear track.

To quantitatively characterize the modifications occurred in the wear track, in comparison with the bulk of the rubber, the contact model of a blunted pyramidal tip indenting an elastic half-space [79] is used. The effect of frequency on the modulus of elasticity is studied by varying the indentation rate. The results are demonstrated in Figures 4.3 and 4.4.

Figure 4.2. Sample of an AFM force indentation curve performed on a silica filled rubber sample. Indentations are performed inside and outside the wear track and on a silica particle. The applied load-penetration depth curve is steeper for materials with higher elastic modulus. Silica as a filler particle has a much higher modulus of elasticity.

The AFM nanoindentation results demonstrate the existence of a modified layer with degraded mechanical properties. The change in the Young's modulus is more observable when indenting at higher rates and is much more noticeable for stiffer samples (carbon black filled samples). The structure of fillers and their subsequent interaction with an elastomer matrix is very important in determining the elastomer stability against degradation. Another interesting result is the effect of tribological conditions on modifying the rubber surface. The loss in elastic modulus is more in systems exposed to severe conditions (by increasing velocity and normal contact pressure) for all indenting frequencies and for all the studied samples. This shows that modification of the surface layer is related to the tribological conditions. Furthermore, an increment in contact pressure and velocity might result in a higher wear rate. Therefore, the modified surface layer is a dynamic system where a competition between modification and wear of the surface layer occurs.

(a) High carbon black content (HC).

(b) Low carbon black content (LC).

Figure 4.3. Time dependence of elastic modulus for: (a) HC, (b) LC samples both inside and outside the wear track. The results for surface layer inside the wear track, modified with low and high tribological severity conditions, are shown by (L) and (H), respectively. The calculated elastic moduli are dependent on the indentation rate.

(a) High silica content (HS).

(b) Low silica content (LS).

Figure 4.4. Time dependence of elastic modulus for: (a) HS, (b) LS samples both inside and outside the wear track. The results for surface layer inside the wear track, modified with low and high tribological severity conditions, are shown by (L) and (H), respectively.

4.2 Formation of a tribologically modified surface layer

In the previous section, the existence of a modified surface layer was proven. The formation of the tribologically modified surface layers on elastomers has not been studied sufficiently. The formation process of such layers has been explained in some researches. However, no agreement between different studies was found on the determination of the driving phenomena as the source of the properties modification. Generally, rubber degradation is attributed to mechanical, thermal and chemical degradation mechanisms. In a study [71], the modifications of carbon black filled elastomers were related to tribo-chemical reactions and thermo-oxidative degradation of the rubber samples. However, in another study [69], similar experiments have been performed and it was shown that no thermo-oxidation processes occur in friction tests. In tribological contacts of several other materials, a modified surface layer is formed due to mechanical degradation in the course of sliding friction [80–82]. In high molecular weight polyethylenes, the wear rate severely changes due to the modification of the top layer [83]. The modification occurs because of orientation softening. Mechanical degradation in elastomers develops because of network evolution. In this study only mechanical degradation of elastomers is considered and modeled.

As the mechanical degradation in rubbers evolves as a result of network evolution, the filler-polymer interaction is a determining factor in the degradation process. The rubber network was briefly introduced in Chapter 2. It is assumed that the rubber network consists of three different networks, namely the pure rubber network, the polymer-filler network and the filler-cross-link network [84]. Each network has its own reference configuration and acts parallel to the other networks with no interaction in between. The elastic deformation of the bulk occurs in the pure rubber network which is assumed to be perfectly elastic. If small strains are applied to the rubber, the filler-cross-link network modifies. The modifications are due to the breakage and the recreation of aggregates. These modifications are at least partially recoverable due to the progressive rebirth of the bonds [85–87].

If the applied strain is higher than a threshold, the polymer-filler network also modifies. The threshold at which polymer-filler network modification occurs depends on several parameters such as filler type, filler size, rubber matrix component, filler content, cross-linking density, rubber-filler interaction, filler treatment, aggregation process, temperature and loading history [85]. In this study, mechanical degradation is assumed to be the result of polymer-filler network alteration; network alteration is due to chain

debonding from and chain sliding on the fillers. Chain debonding and chain sliding occurs only if the force applied to a single chain exceeds the effective interaction strength of polymer-filler bonds, indicated by F_c . The critical force F_c differs for each aggregate and depends on aggregate surface geometry, chain geometrical position with respect to the aggregate surface, etc. [84]. The degradation of the filler-rubber network of elastomers is a reversible phenomenon. However, healing is temperature dependent and at room temperature only a small recovery is observed [88]. It was observed that a carbon black filled rubber showed only partial recovery after a long stress release time of 4 weeks [89]. The stress softening in a silica filled elastomer could not be recovered after 6 months [90]. Therefore healing is neglected.

The rate of the chain debonding from and chain sliding on the filler particles at temperature T is assumed to be given by the standard expression of activated processes [91]:

$$\Omega = \frac{ak_B T}{\hbar} e^{-\frac{h-E}{k_B T}} \quad (4.1)$$

In Equation 4.1, a is the proportionality constant, k_B is the Boltzmann's constant, $\hbar$ is the reduced Planck's constant and h , E are the required energy to break a single bond and the stored elastic energy in each bond due to the applied strain respectively. To estimate the elastic energy stored in each bond, at first the subsurface energy field due to frictional sliding is required. The distributed elastic energy at each point in the bulk of the rubber can be calculated by:

$$W(x, y, z, t) = \int_{V_{total}} w(x, y, z, t) dV = \int_{V_{total}} \sigma(x, y, z, t) \frac{d\epsilon(x, y, z, t)}{dt} dV \quad (4.2)$$

The stress and strain rate distributions should be known to govern the energy field. The strain and stress fields are related by mechanical properties of the rubber. As explained in [92], the stresses in the bulk are related to the pressure and shear stress distribution at the interface using the influence coefficients. Consequently, to calculate the subsurface energy field, the normal pressure distribution at the contact area (and friction at the interface) should be governed. Therefore, to calculate the normal pressure distribution at the real area of contact, the contact model of Jackson and Streater is used [93]. This model is a non-statistical multi-scale model based on pioneering Archard's concept in which roughness consists of "protuberances on protuberances on protuberances"; this model assumes that asperities with smaller cross-sectional surface areas are located on top of the larger asperities.

The areal asperity density, η_i at each frequency f_i (reciprocal of the roughness wavelength, directly governed by FFT of the roughness data) is obtained by:

$$\eta_i = 2f_i^2 \quad (4.3)$$

At each frequency level, all the asperities carry an equal load such that the sum of the loads equals the total macroscopic load applied. Furthermore, the real area of contact at each frequency level should be smaller or equal to the contact area found at the previous level. In addition to the original assumptions of the model summarized above, another restriction arises from the nature of the viscoelastic materials. The frequency dependency of the complex elastic moduli of viscoelastic materials results in an increase in the elasticity by each increase in frequency level f_i . This increase in the elasticity decreases the contact area which induces the additional constraint; the contact area at each frequency level cannot be higher than the minimum value between the contact area at a previous level and the contact area calculated using mechanical properties at the considered frequency level. Furthermore, the exciting frequency applied by the roughness asperities is not only dependent on the sliding velocity and the wavelength of the roughness, but also on the angle ϕ between the sliding velocity and the wave vector. The induced rubber exciting frequency ω_i at each frequency level f_i follows the relation $\omega_i \sim v \cos \phi / f_i$. The roughness is assumed to be isotropic, therefore at each frequency level an averaged value of elasticity modulus $E(f_i)$ is used:

$$E(f_i) = \frac{1}{2\pi} \int_0^{2\pi} E(2\pi v \cos \phi / f_i) d\phi \quad (4.4)$$

Once the number of asperities at each level and consequently the carrying load by each asperity is determined, the contact area of each single asperity is calculated using an asperity model. The influence of neighboring asperities should be included in modeling the contact of soft materials, therefore, the contact model of a two dimensional wavy surface in contact with a flat [94] is used to calculate the contact area and pressure distribution at each level. The nominal contact area A_0 is the macroscopic area of contact and f_0 is the reciprocal of the wavelength corresponding to the length of the contact of the nominal contact area.

4.2.1 Application of the formation model to a friction test

The sliding contact between a carbon black filled elastomer and a rough granite sphere is studied. The elastomer matrix includes 30 parts per hundred rubber (phr) butadiene rubber (BR) and 70 phr solution

styrene-butadiene rubber (S-SBR). In addition, the rubber compound is reinforced by 70 phr of carbon black particles. The dynamic properties of the rubber sample were measured by Dynamical Mechanical Analysis in a Metravib DMA 2000 dynamic spectrometer in oscillatory shear mode at a constant strain amplitude of 0.1 % where the sample is fixed at both interfaces and sheared at different frequencies between 1 and 200 Hz . The whole procedure is repeated for different temperatures (the temperature is varied between -20 and $85^{\circ}C$). The obtained measurement data are shifted both horizontally (using Williams-Landel-Ferry [40] relation) and vertically (unrestrictedly) to obtain smooth master curves for a broad frequency range. The normalized shifted loss and storage shear moduli of elasticity as a function of frequency are presented in Figure 4.5.

Figure 4.5. Normalized shifted loss and storage shear moduli of elasticity as a function of frequency for a BR/SSBR elastomer reinforced with carbon black.

The prepared rubber disk is in sliding contact (pin-on-disk test) with a rough granite sphere which has a diameter of 30 mm . The sliding velocity is 5 mm/s and the nominal contact pressure is 0.2 MPa . The measured coefficient of friction in the running-in phase as a function of number of laps is shown in Figure 4.6.

The roughness of the granite sphere is measured by two different techniques, namely confocal microscopy and atomic force microscopy (AFM) in contact mode. The resulting frequency spectrum of the roughness is shown in Figure 4.7

Figure 4.6. Transient coefficient of friction.

Figure 4.7. Frequency spectrum of the granite surface. The roughness is measured using confocal microscopy and AFM in contact mode.

The mechanical properties of the rubber disk presented in Figure 4.5, the roughness data depicted in Figure 4.7 and the tribological conditions previously mentioned, together with the contact model of Jackson and Streater [93] in combination with formulations of contact mechanics of a wavy surface [94] are

used to calculate the contact area at each frequency level. The ratio of the real area of contact to the nominal contact area for each frequency is plotted against the magnification factor $\zeta = f_i/f_0$ and illustrated in Figure 4.8.

Figure 4.8. The ratio between contact area at each frequency to the nominal contact area as a function of magnification factor.

As Figure 4.8 illustrates, with an increase in frequency level, the real area of contact decreases up to a saturation limit. The contact is considered at the onset of saturation where the contact area does not change even if smaller asperities are considered. The fact that the contact area does not decrease after a specific frequency can be interpreted as follows; all the asperities smaller than the wavelength corresponding to the onset of saturation are in full contact with the elastomer.

The nominal contact area is assumed to consist of asperities with the wavelength corresponding to the frequency level at the onset of saturation, each carrying equal pressure such that the summation of the pressures is equal to the macroscopic contact pressure. Based on experimental measurements performed earlier, the shear stress is estimated by the adhesive component of friction arising in the sliding contact. Once the pressure and shear stress distributions at contact interface are known, the stress components at each point inside the bulk of the rubber are calculated using the method explained in [92]. After relating strains to stresses, the strain rates can be estimated using the equation given below (it is assumed that the sliding velocity is constant):

$$\dot{\epsilon} = \frac{\epsilon_{t+\Delta t} - \epsilon_t}{\Delta t} = v_s \frac{\epsilon_{x+\Delta x} - \epsilon_x}{\Delta x} \quad (4.5)$$

Figure 4.9. A rigid rough surface is shown schematically in sliding contact with a rubber half-space. The rough counter surface is assumed to be rough on several scales. Asperities at each level are considered to be a two dimensional wavy surface. Each asperity at a specific wavelength is assumed to be covered with smaller asperities on top. The sliding velocity is assumed to be constant, therefore the time derivative of strain is related to the spatial derivative of strain which is calculated by the difference between the strains at each point and another point with distance $\Delta x = v_s \cdot \Delta t$. The normal stress in z direction inside the bulk of the viscoelastic material in x - z plane and at a fixed y value is shown schematically.

The rubber degrades in the direction where the highest energy is applied [95]. Considering the loading conditions in this problem (normal pressure in z direction and friction applied in x direction), shear in the x - z induces the highest energy in the bulk. Therefore the subsurface energy distribution induced by shear in x - z plane is used as a measure for the applied energy to the rubber bulk. For the tribological conditions mentioned above, the calculated subsurface energy density due to shear in x - z plane as a function of depth of the bulk is shown in Figure 4.10 via line E_1 . In the same figure, line E_2 corresponds to a nominal contact pressure of 1 MPa with the same other tribological conditions. For both conditions, a heat partition factor [96] of 0.4 is used.

Figure 4.10. Distributed energy density due to shear in x - z plane as a function of the distance from top surface in a single contact.

The frictional work is dissipated in several ways. One can think of frictional heating, irreversible deformations like fracture or making/breaking of adhesive bonds in one or both bodies in contact, the formation of modified surface layers and wear as the most important mechanisms of energy dissipation. Among them, heat generation, modification of the surface layer and wear are the most important ones in elastomeric contacts. The frictional heating results in an increase in the rubber temperature and therefore changes the tribological behavior of the rubber by altering the mechanical properties. The effect of the flash temperature on the friction was previously studied [64] and can be added to the model presented, however, the heat generation due to friction can be neglected because of low sliding velocities used in this study. On the other hand, wear, modification of the top rubber layer due to frictional energy and their effects on each other should be analyzed together. The wear rate not only determines if the modified surface layer exists, but also regulates the rate of the modification. The importance of wear on the existence of the modified surface layer is demonstrated in the next section. In this part, the effect of wear on the formation rate is discussed.

The averaged specific wear rate during the whole measurement (see Figure 4.6) is $9.47 \times 10^{-3} \text{ mm}^3/\text{Nm}$. The average thickness of the worn layer per contact is determined experimentally. At each rotation of the disk $0.08 \text{ }\mu\text{m}$ of the top rubber layer is worn. In other words, at each contact, a layer with thickness of $0.08 \text{ }\mu\text{m}$ of the rubber disk will not find the opportunity to be modified at all. This worn thickness is shown by the red vertical line in Figure 4.10 for loading conditions corresponding to E_1 . Because of wear, the

highest available energy which can modify the rubber is decreased. A higher wear rate brings about a higher removal of the material per contact (the red line in Figure 4.10 shifts to the right) and therefore the available energy for modification decreases. A decrease in the applied energy to each chain results in a decrease in the formation rate. In addition, if the removed material thickness is even higher than the thickness at which a sudden decrease in the energy field is seen, no meaningful difference in the mechanical properties can be detected. For the energy field E_1 depicted in Figure 4.10, in the first $2.8 \mu\text{m}$ of the rubber, the distributed energy decreases drastically. The aforementioned thickness is approximately in the order of the thickness of the modified surface layer previously reported [32].

To calculate the rate of the degradation, the energy exerted on a single polymer chain should be estimated. The energy exerted on a single polymer chain not only depends on the distribution of the subsurface energy field (shown in Figure 4.10) but also on the number of cross-links. On the one hand, a lower cross-link density results in a higher elastic energy applied to a chain. On the other hand, a higher cross-link density decreases the threshold at which irreversible degradation occurs. Therefore an optimized cross-linking depends on the required application of the rubber component. In this study, the cross-link density is assumed to be in the order of $\sim 10^{22} / \text{cm}^3$. Once the applied energy to a chain is calculated, using $h \approx 2.5 \times 10^{-19}$, the degradation rate is governed to be $\Omega \approx 1/4 \text{ s}^{-1}$. This is also in agreement with Figure 4.6, where the measured friction gets stable only after approximately 210 laps which corresponds to approximately 5 s of contact of the nominal contact area. The governed time is in agreement with the calculated formation rate. A slight difference between the formation rate and the required time to degrade rubber is attributed to several other complex phenomena such as healing that are not considered in this model for the sake of simplicity, but are the subject of future studies.

4.3 Wear of the modified surface layer

Although the existence of a tribo-modified surface layer is shown for four rubber samples, gaining a quantitative insight into the changes of the modified surface layer is only possible by a detailed study of several tribo systems. Accordingly, in this section, the importance of wear on the existence of the modified surface layer is shown by examining two other rubber composites. The existence of a modified surface layer which can change the friction level is dependent on both the formation of the modified layer and the breakdown (wear) of it.

Two styrene butadiene rubber-based elastomers are subjected to frictional

energy. Sample (1) is unreinforced vulcanized SBR rubber and sample (2) is reinforced with 3 parts per hundred rubber (phr) fibers. Table 1 of Paper E in Part II of this thesis presents the rubber formulation of prepared samples, with the amounts of components indicated by weight parts of component per hundred weight parts of the rubber. The elasticity moduli of both samples in the form of master curves are presented in Figure 4.11. The mechanical properties of the two samples are not very different. However, sample (2) is expected to have much higher resistance against wear due to the reinforcement.

The friction between both rubber samples and a granite sphere with a diameter of 30 mm and a root mean square roughness of 2.1 μm is measured using a pin-on-disk setup. The sliding velocity is 5 mm/s and the contact pressure is 0.175 MPa. The total coefficient of friction and the contribution of hysteresis, both measured experimentally, and the running-in distances are shown in Figure 4.12. The run-in distance (the distance after which the coefficient of friction is stabilized to a steady-state value, see Figure 4.12) for sample (2) is much longer in comparison with sample (1). Moreover, the experimental results show a lower friction coefficient for sample (2).

The calculated hysteresis component of friction as a function of sliding velocity is shown in Figure 4.13 for both samples. Due to similar mechanical properties, the hysteresis component of friction is not that different.

Furthermore, the real area of contact is calculated for a sliding velocity of 5 mm/s and depicted in Figure 4.14. The small difference between real area of contact cannot explain the large difference in total measured friction (see Figure 4.12). As a conclusion, the frictional shear stress τ_f between the rubber and the granite surface (see Equation 1.1) should be the source of the difference in the measured total friction.

The existence of a tribo-modified surface layer on both samples is investigated by AFM nanoindentations. As Figure 4.15 presents, the mechanical properties of the wear track of sample (1) are not that different from the bulk of the material. In contrast, the existence of a degraded surface layer on the wear track of sample (2) is proven.

In the studied tribo systems, with similar tribological conditions, the coefficient of friction of sample (1) and therefore the frictional work generated are higher in comparison with the contact between sample (2) and the granite sphere. As explained in Section 4.2.1, the generated frictional energy is dissipated through three main mechanisms in elastomeric contacts. Heat generation, wear and formation of the modified layer are the most important ways. Because of low sliding velocities, heat generation is neglected. As expected, the resistance of the reinforced sample against wear is much higher than the unreinforced rubber; the specific wear rates are $k_1 = 1.83 \times 10^{-1} \text{ mm}^3/\text{Nm}$ and $k_2 = 3.87 \times 10^{-3} \text{ mm}^3/\text{Nm}$ for the samples (1) and (2), respectively.

(a)

(b)

Figure 4.11. Shifted storage (a) and loss (b) moduli of elasticity as a function of frequency.

Figure 4.12. Total and hysteresis component of friction (measured by pin-on-disk test rig) and the run-in distance for samples (1) and (2) before the measured friction is stabilized. Sample (1) is SBR and sample (2) is fiber reinforced SBR.

Figure 4.13. Hysteresis coefficient of friction as a function of sliding velocity. Sample (1) is SBR and sample (2) is fiber reinforced SBR.

Figure 4.14. Variation of real area of contact over nominal contact area as a function of magnification for sliding velocity of $v = 5 \text{ mm/s}$.

4.4 Balance between formation and wear of the modified surface layer

As aforementioned, the existence of a tribo-modified surface layer is dependent on the competition between formation and wear of such a layer. Formation and wear of the layer work in opposition to each other. The balance of the modified surface layer writes:

$$\frac{d\delta_{total}}{dt} = Q_f - Q_w \quad (4.6)$$

where δ_{total} is the thickness of the modified surface layer, Q_f is the formation rate of the modified surface layer and the Q_w is the wear depth rate. Under steady-state conditions, $d\delta_{total}/dt = 0$ or, $Q_f = Q_w$. According to Archard's formulation [97], the wear rate is directly proportional to the applied pressure σ_0 multiplied by the sliding speed v :

$$Q_w = k\sigma_0 v \quad (4.7)$$

In Equation 4.7, the proportionality constant k depends on the normal pressure σ_0 . Equation 4.6 can be presented as a balance in thickness:

$$\delta_{total} = \delta_f - \delta_w \quad (4.8)$$

(a) Sample (1)

(b) Sample (2)

Figure 4.15. Time dependence of elastic modulus for: (a) sample (1), (b) sample (2), both inside and outside the wear track, measured by AFM nanoindentations.

where, $\delta_w = k(\sigma_0)\sigma_0 s$, with s as the sliding distance. Obviously, the existence of a tribo-modified surface layer depends on the relation between δ_w and δ_f . As illustrated in Figure 4.16, the rubber is exposed to wear as soon as it comes

into contact with a counter surface. However, in order to generate a thin modified surface layer, a sufficient amount of energy should be exerted on the rubber surface. The thickness of the formed modified surface layer is non zero only when the energy input rate is higher than a minimum value required to modify the surface. This energy level E^* depends on the rubber compound, reinforcement fillers, interaction between fillers and the rubber matrix, cross-links, etc. The minimum energy level is related to the critical force F_c required for chain debonding from and chain sliding on the fillers mentioned in Section 4.2. The thickness of the formed modified surface layer and the layer thickness worn away both increase by an increase in energy input.

Figure 4.16. The thickness of the formation and wear layers, δ_f and δ_w is shown schematically as a function of the applied frictional energy.

Considering Equation 4.8 and Figure 4.16, the difference between the thicknesses of the formed modified surface layer and the worn layer is depicted schematically in Figure 4.17. Three different conditions are deduced; if the wear rate is higher than the formation rate, the whole modified layer is worn, and therefore, no modified surface layer is present (this condition is demonstrated by a green line (I) in Figure 4.17). However, if $\delta_f > \delta_w$, the modified surface layer exists. Under this condition, an increase in energy input rate (which increases both δ_f and δ_w) may result in two conditions; the first one is that with an increase in energy input, the thickness of the layer worn away increases more than the thickness of the formed modified surface layer, and therefore, the total modified surface layer thickness will decrease

and for high energy input will not be present (blue line II). The second situation is when both thicknesses increase proportionally such that the modified surface layer exists for higher energy input rates (black line III).

Figure 4.17. The existence of a modified surface layer as a function of energy input rate and wear rate is illustrated schematically: I. when the wear rate is higher than the formation rate and consequently the modified layer does not exist, II. when for low energy input rates, wear and formation rates stay in balance and a degraded layer exists but with an increase in the energy rate, the wear rate increases more than the formation rate and therefore the modified surface layer vanishes and III. when the modification and wear rates remain in balance even with an increase in energy input rate such that the modified surface layer exists. If the energy input rate is less than a critical value E^* which is the least required energy rate for modification, no layer is formed.

The difference between the measured total friction between samples (1) and (2) as shown in Section 4.3, Figure 4.13 can be explained by the remarkably different wear rates; because of the high wear rate of sample (1) in contact with the granite sphere, the tribo system does not find the opportunity to form a modified surface layer. This is why no significant difference is seen in mechanical properties of the wear track and outside the wear track. As a result, the running-in distance of sample (1) is very short. However, the wear and formation rate of the modified layer are in the same order for the second tribo system and therefore a competition occurs between generation and wear of the modified layer in the run-in phase. When the formation and wear rate

of the modified layer are in balance, the measured friction stabilizes (note the difference in run-in distances, presented in Figure 4.12). The existence of the modified surface layer has a huge effect in determining the total friction. Therefore, the measured friction of sample (2), with degraded mechanical properties on the top layer, is much lower than the friction of the first sample, both in contact with the granite rough surface. This illustrates the importance of the formation, wear and consequently the existence of the modified layer on the tribological behavior of elastomeric contacts.

4.5 Summary

The existence of a modified surface layer on elastomers due to frictional energy is shown using AFM nanoindentations. The degradation in mechanical properties is dependent on the tribological loading. An intensified loading (via an increase in contact pressure and sliding velocity) results in more degradation in mechanical properties. Therefore, the degradation is considered to occur as a result of mechanical loading. The process of mechanical degradation in elastomers is explained by considering the rubber network. The rubber network is divided into three different networks (namely pure rubber, filler-polymer and the filler-cross-link network) that work parallel to each other, without any interaction in between and with their own reference configuration. The mechanical degradation is taken to occur in the filler-polymer network. The stored energy in the bulk of the rubber as a function of the mechanical loading was calculated. The effect of the wear in decreasing the available energy for modification was explained and considered. Moreover, the rate of the degradation as a function of the stored elastic energy in each elastomer chain and rubber properties was presented. The explained model for the mechanical degradation of the elastomer is used to estimate the modification rate in a tribological test. The effect of wear in determining the existence of a tribologically modified surface layer is emphasized by comparing two rubber samples with severely different resistances against wear. Finally, based on the formation and wear, the existence of a modified surface layer is discussed as a function of the energy input rate.

Conclusions and Recommendations

In this thesis, the contact and friction of rubber is studied both theoretically and experimentally. The importance of a tribo-modified surface layer on friction is emphasized and its formation, removal and importance on friction is studied. In the following sections, the main results of this study are summarized. Finally, some recommendations for future research are given.

5.1 Conclusions

Contact and Friction Modeling of Rubber as a Soft Viscoelastic Solid

- Carbon black filled rubbers are elastically stiffer than silica filled rubbers among the studied compounds. Moreover, the elasticity increases as a function of the filler content.
- The wear debris from carbon black and silica reinforced compounds is remarkably different in its tendency to adhere together and form a smear film (carbon black) or to stay apart and form a dust-like powder (silica).
- The main friction components in elastomeric contacts were studied as a function of the tribological conditions. It was concluded that shearing of a modified surface layer by a rigid counter surface can play an important role in the total friction.

Contact Mechanics and Friction for Transversely Isotropic Viscoelastic Materials

- The contact and friction model of Persson was extended in such a way that it can model the contact and friction of a transversely isotropic viscoelastic material in contact with a rigid rough surface. The results were validated.

Tribologically Modified Surface Layers

- The existence of a tribologically modified surface layer on top of rubber sections that were subjected to frictional energy was shown using AFM nanoindentations.

- The modification was detected in the form of degradation in mechanical properties.
- The mechanical properties of the degraded layer modifies as a function of the tribological conditions; a higher exerted frictional energy results in additional degradation.
- Mechanical degradation is taken as the origin of modification. The degradation occurs due to chain debonding from and chain sliding on the fillers and in the polymer-filler network.
- A model is presented that estimates both the formation rate and the thickness of the modified layer as a function of frictional energy input and wear rates.
- The influence of wear on the existence of the modified surface layer is studied and emphasized; it was concluded that wear might even completely remove the modified layer if the wear rate is higher than the formation rate.

5.2 Discussion

Silica particles are relatively hydrophilic in comparison to carbon black particles which are less hydrophilic. Because of closer polarity to the polymer, carbon black has a stronger interaction with a hydrocarbon polymer than silica particles. A chemical coupling agent is used to improve the poor silica-polymer interaction. Therefore, silica particles make chemical bonding to the polymer while carbon black particles are physically connected to the polymer. It has been shown that only a small portion of silica surface is covered by the coupling agent and the majority of the surface is in physical contact with the polymer [35]. The penetration of water (or other liquids) through the graft layer and adsorption onto the silica surface might affect the degradation.

In the presented work, mechanical degradation is assumed as the main source of modification. The importance of other sorts of degradation such as chemical, thermal and oxidation on the change of mechanical properties is not clear.

5.3 Recommendations for future research

- The developed formation model was obtained for dry conditions and should be extended to consider degradation under wet conditions.

- At higher sliding velocities, the generated frictional heat increases the rubber temperature locally. The increased temperature results in a change in mechanical properties of the rubber. Therefore the induced mechanical energy in the bulk of the rubber is different and consequently the formation rate changes. Several studies have considered the effect of flash temperature. The presented formation model can be extended by coupling the current model to those studies.
- To investigate whether, besides mechanical degradation, any significant change in the material's composition occurs. A test can be done; the modified surface layer should be cut in very thin layers, using a microtome, and the material composition of each cut layer should be measured and compared using Thermal Gravimetric Analysis (TGA).
- The existence of a modified surface layer was shown and the rate of the degradation was modeled in this study. The effect of the degradation level and rate of change of the shear stress τ_f (see Equation 1.1) should be studied.

Bibliography

- [1] K.A. Grosch. The relation between the friction and visco-elastic properties of rubber. *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, 274(1356):21–39, 1963.
- [2] B.N.J. Persson. Theory of rubber friction and contact mechanics. *Journal of Chemical Physics*, 115(8):3840–3861, 2001.
- [3] B.N.J. Persson and M. Scaraggi. On the transition from boundary lubrication to hydrodynamic lubrication in soft contacts. *Journal of Physics Condensed Matter*, 21(18):185002, 2009.
- [4] G. Bóдай and T.J. Goda. Friction force measurement at windscreen wiper/glass contact. *Tribology Letters*, 45(3):515–523, 2012.
- [5] B. Lorenz and B.N.J. Persson. Leak rate of seals: Comparison of theory with experiment. *EPL*, 86(4):44006, 2009.
- [6] J. M. Pardillo Mayora and R. J. Piña. An assessment of the skid resistance effect on traffic safety under wet-pavement conditions. *Accident Analysis & Prevention*, 41(4):881 – 886, 2009.
- [7] M. Mofidi, B. Prakash, B.N.J. Persson, and O. Albohr. Rubber friction on (apparently) smooth lubricated surfaces. *Journal of Physics Condensed Matter*, 20(8):085223, 2008.
- [8] Y. Fujii. Method for measuring transient friction coefficients for rubber wiper blades on glass surface. *Tribology International*, 41(1):17–23, 2008.
- [9] B.N.J. Persson. Rubber friction and tire dynamics. *Journal of Physics Condensed Matter*, 23(1):015003, 2011.
- [10] W. Brostow, D. Pietkiewicz, and S.R. Wisner. Polymer tribology in safety medical devices: Retractable syringes. *Advances in Polymer Technology*, 26(1):56–64, 2007.
- [11] G. Heinrich and M. Klüppel. Rubber friction, tread deformation and tire traction. *Wear*, 265(7-8):1052–1060, 2008.
- [12] V.A. Yastrebov, G. Anciaux, and J.-F. Molinari. From infinitesimal to full contact between rough surfaces: Evolution of the contact area. *International Journal of Solids and Structures*, 52:83–102, 2015.

- [13] W.B. Dapp, N. Prodanov, and M.H. Müser. Systematic analysis of Persson’s contact mechanics theory of randomly rough elastic surfaces. *Journal of Physics Condensed Matter*, 26(35):355002, 2014.
- [14] V. Dorsch, A. Becker, and L. Vossen. Enhanced rubber friction model for finite element simulations of rolling tyres. *Plastics, Rubber and Composites*, 31(10):458–464, 2002.
- [15] K. Hofstetter, J. Eberhardsteiner, and H.A. Mang. A thermo-mechanical formulation describing the frictional behavior of rubber. *PAMM*, 2(1): 238–239, 2003.
- [16] P. Wriggers. *Computational contact mechanics*. 2006.
- [17] T. Huemer, W.N. Liu, J. Eberhardsteiner, and H.A. Mang. A 3D finite element formulation describing the frictional behavior of rubber on ice and concrete surfaces. *Engineering Computations*, 18(3/4):417–436, 2001.
- [18] K.A. Grosch. Visco-elastic properties and the friction of solids: Relation between the friction and visco-elastic properties of rubber. *Nature*, 197 (4870):858–859, 1963.
- [19] A. Le Gal and M. Klüppel. Investigation and modelling of rubber stationary friction on rough surfaces. *Journal of Physics Condensed Matter*, 20(1), 2008.
- [20] P. Wriggers and J. Reinelt. Multi-scale approach for frictional contact of elastomers on rough rigid surfaces. *Computer Methods in Applied Mechanics and Engineering*, 198(21-26):1996 – 2008, 2009.
- [21] L. Busse, I. Boubakri, and M. Klüppel. Friction master curves for rubber on dry and wet granite experiments and simulations. *Kautschuk Gummi Kunststoffe*, 64(5):35–39, 2011.
- [22] G. Carbone and L. Mangialardi. Adhesion and friction of an elastic half-space in contact with a slightly wavy rigid surface. *Journal of the Mechanics and Physics of Solids*, 52(6):1267 – 1287, 2004.
- [23] L. Busse, A. Le Gal, and M. Klüppel. Modelling of dry and wet friction of silica filled elastomers on self-affine road surfaces. *Lecture Notes in Applied and Computational Mechanics*, 51:1–26, 2010.
- [24] X-D. Pan. Wet sliding friction of elastomer compounds on a rough surface under varied lubrication conditions. *Wear*, 262(5-6):707 – 717, 2007.

- [25] B. Lorenz, B.N.J. Persson, S. Dieluweit, and T. Tada. Rubber friction: Comparison of theory with experiment. *The European Physical Journal E*, 34(129):129, 2011.
- [26] C. Myant, H.A. Spikes, and J.R. Stokes. Influence of load and elastic properties on the rolling and sliding friction of lubricated compliant contacts. *Tribology International*, 43(1-2):55 – 63, 2010.
- [27] M. Scaraggi and B.N.J. Persson. Theory of viscoelastic lubrication. *Tribology International*, 72:118 – 130, 2014.
- [28] S. Vincent, A. Sarthou, J-P. Caltagirone, F. Sonilhac, P. Février, C. Mignot, and G. Pianet. Augmented lagrangian and penalty methods for the simulation of two-phase flows interacting with moving solids. application to hydroplaning flows interacting with real tire tread patterns. *Journal of Computational Physics*, 230(4):956 – 983, 2011.
- [29] L.D. Poulikakos, M. Sedighi Gilani, D. Derome, I. Jerjen, and P. Vontobel. Time resolved analysis of water drainage in porous asphalt concrete using neutron radiography. *Applied Radiation and Isotopes*, 77:5 – 13, 2013.
- [30] S. Torbruegge and B. Wies. Characterization of pavement texture by means of height difference correlation and relation to wet skid resistance. *Journal of Traffic and Transportation Engineering (English Edition)*, 2(2):59 – 67, 2015.
- [31] X-D. Pan. Significance of tuning bulk viscoelasticity via polymer molecular design on wet sliding friction of elastomer compounds. *Tribology Letters*, 20(3-4):209–219, 2005.
- [32] N.V. Rodriguez, M.A. Masen, and D.J. Schipper. Tribologically modified surfaces on elastomeric materials. *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology*, 227(5): 398–405, 2013.
- [33] R. Rauline. Rubber compound and tires based on such a compound, September 2, 1992. EP Patent App. EP19,920,102,313.
- [34] Y-X. Wang, J-H. Ma, L-Q. Zhang, and Y-P. Wu. Revisiting the correlations between wet skid resistance and viscoelasticity of rubber composites via comparing carbon black and silica fillers. *Polymer Testing*, 30(5):557 – 562, 2011.
- [35] M-J. Wang and Y. Kutsovsky. Effect of fillers on wet skid resistance of tires. part i: Water lubrication vs. filler-elastomer interactions. *Rubber Chemistry and Technology*, 81(4):552–575, 2008.

- [36] Y-X. Wang, Y-P. Wu, W-J. Li, and L-Q. Zhang. Influence of filler type on wet skid resistance of SSBR/BR composites: Effects from roughness and micro-hardness of rubber surface. *Applied Surface Science*, 257(6): 2058 – 2065, 2011.
- [37] X-D. Pan. Contribution of fine filler particles to energy dissipation during wet sliding of elastomer compounds on a rough surface. *Journal of Physics D: Applied Physics*, 40(15):4657, 2007.
- [38] R. Dargazany, V.N. Khiêm, and M. Itskov. A generalized network decomposition model for the quasi-static inelastic behavior of filled elastomers. *International Journal of Plasticity*, 63:94 – 109, 2014.
- [39] L. Mullins. Softening of rubber by deformation. *Rubber Chemistry and Technology*, 42(1):339–362, 1969.
- [40] M. L. Williams, L.F. Robert, and J.D. Ferry. The temperature dependence of relaxation mechanisms in amorphous polymers and other glass-forming liquids. *Journal of the American Chemical Society*, 77(14):3701–3707, 1955.
- [41] B. Lorenz, W. Pyckhout-Hintzen, and B.N.J. Persson. Master curve of viscoelastic solid: Using causality to determine the optimal shifting procedure, and to test the accuracy of measured data. *Polymer*, 55(2): 565 – 571, 2014.
- [42] J.A. Greenwood and J.B.P. Williamson. Contact of nominally flat surfaces. *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, 295(1442):300–319, 1966.
- [43] A.W. Bush, R.D. Gibson, and T.R. Thomas. The elastic contact of a rough surface. *Wear*, 35(1):87–111, 1975.
- [44] J.I. McCool. Comparison of models for the contact of rough surfaces. *Wear*, 107(1):37–60, 1986.
- [45] G. Carbone and F. Bottiglione. Asperity contact theories: Do they predict linearity between contact area and load? *Journal of the Mechanics and Physics of Solids*, 56(8):2555–2572, 2008.
- [46] J.A. Greenwood. A simplified elliptic model of rough surface contact. *Wear*, 261(2):191–200, 2006.
- [47] M. Paggi and M. Ciavarella. The coefficient of proportionality between real contact area and load, with new asperity models. *Wear*, 268(7-8): 1020 – 1029, 2010.

- [48] L. Afferrante, G. Carbone, and G. Demelio. Interacting and coalescing hertzian asperities: A new multiasperity contact model. *Wear*, 278-279: 28 – 33, 2012.
- [49] J.A. Greenwood and J.J. Wu. Surface roughness and contact: An apology. *Meccanica*, 36(6):617–630, 2001.
- [50] W. Manners and J.A. Greenwood. Some observations on Persson’s diffusion theory of elastic contact. *Wear*, 261(5-6):600 – 610, 2006.
- [51] B.N.J. Persson. On the elastic energy and stress correlation in the contact between elastic solids with randomly rough surfaces. *Journal of Physics Condensed Matter*, 20(31):312001, 2008.
- [52] G. Carbone and F. Bottiglione. Contact mechanics of rough surfaces: a comparison between theories. *Meccanica*, 46(3):557–565, 2011.
- [53] G. Carbone, B. Lorenz, B.N.J. Persson, and A. Wohlers. Contact mechanics and rubber friction for randomly rough surfaces with anisotropic statistical properties. *The European Physical Journal E*, 29 (3):275–284, 2009.
- [54] G. Machado, G. Chagnon, and D. Favier. Induced anisotropy by the mullins effect in filled silicone rubber. *Mechanics of Materials*, 50:70 –80, 2012.
- [55] B.N.J. Persson, O. Albohr, U. Tartaglino, A.I. Volokitin, and E. Tosatti. On the nature of surface roughness with application to contact mechanics, sealing, rubber friction and adhesion. *Journal of Physics Condensed Matter*, 17(1):R1–R62, 2005.
- [56] B.N.J. Persson. On the fractal dimension of rough surfaces. *NanoScience and Technology*, 31:235–248, 2015.
- [57] A. Schallamach. A theory of dynamic rubber friction. *Wear*, 6(5):375 – 382, 1963.
- [58] B.N.J. Persson and A.I. Volokitin. Rubber friction on smooth surfaces. *The European Physical Journal E*, 21(1):69–80, 2006.
- [59] S. Momozono, K. Nakamura, and K. Kyogoku. Theoretical model for adhesive friction between elastomers and rough solid surfaces. *The Journal of Chemical Physics*, 132(11):114105, 2010.
- [60] B.N.J. Persson, O. Albohr, G. Heinrich, and H. Ueba. Crack propagation in rubber-like materials. *Journal of Physics: Condensed Matter*, 17(44): R1071, 2005.

- [61] S. Momozono, H. Takeuchi, Y. Iguchi, K. Nakamura, and K. Kyogoku. Dissipation characteristics of adhesive kinetic friction on amorphous polymer surfaces. *Tribology International*, 48:122 – 127, 2012.
- [62] B. Lorenz, B.N.J. Persson, G. Fortunato, M. Giustiniano, and F. Baldoni. Rubber friction for tire tread compound on road surfaces. *Journal of Physics Condensed Matter*, 25(9), 2013.
- [63] S. Jacobson and S. Hogmark. Surface modifications in tribological contacts. *Wear*, 266(34):370 – 378, 2009.
- [64] B.N.J. Persson. Rubber friction: Role of the flash temperature. *Journal of Physics Condensed Matter*, 18(32):7789–7823, 2006.
- [65] J. Wang, P. Agrawal, L. Alexander, and R. Rajamani. An experimental study with alternate measurement systems for estimation of tire-road friction coefficient. *Proceedings of the American Control Conference*, 6: 4957–4962, 4-6 June 2003.
- [66] K.B. Singh, M.A. Arat, and S. Taheri. An intelligent tire based tire-road friction estimation technique and adaptive wheel slip controller for antilock brake system. *Journal of Dynamic Systems, Measurement and Control, Transactions of the ASME*, 135(3), 2013.
- [67] S.R. Rickaby and N.H. Scott. Transversely isotropic cyclic stress-softening model for the mullins effect. *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, 468(2148):4041–4057, 2012.
- [68] H. Hai-Chang. On the equilibrium of a transversely isotropic elastic half space. *Science china mathematics*, (4):463, 1954.
- [69] L. Martínez, R. Nevshupa, D. Felhös, J.L. de Segovia, and E. Román. Influence of friction on the surface characteristics of EPDM elastomers with different carbon black contents. *Tribology International*, 44(9):996 – 1003, 2011.
- [70] J-M. Degrange, M. Thomine, P. Kapsa, J.M. Pelletier, L. Chazeau, G. Vigier, G. Dudragne, and L. Guerbé. Influence of viscoelasticity on the tribological behaviour of carbon black filled nitrile rubber (nbr) for lip seal application. *Wear*, 259(1-6):684 – 692, 2005.
- [71] J. Karger-Kocsis, A. Mousa, Z. Major, and N. Békési. Dry friction and sliding wear of epdm rubbers against steel as a function of carbon black content. *Wear*, 264(3-4):359 – 367, 2008.

- [72] M.-J. Wang and Y. Kutsovsky. Effect of fillers on wet skid resistance of tires. part ii: Experimental observations on effect of filler-elastomer interactions on water lubrication. *Rubber Chemistry and Technology*, 81(4):576–599, 2008.
- [73] D. Tranchida, S. Piccarolo, and S. Maria. Nanoscale mechanical characterization of polymers by afm nanoindentations: a critical approach to the elastic characterization. *Macromolecules*, 39(13):4547–4556, 2006.
- [74] C. Reynaud, F. Sommer, C. Quet, N. El Bounia, and T.M. Duc. Quantitative determination of Young’s modulus on a biphasic polymer system using atomic force microscopy. *Surface and Interface Analysis*, 30(1):185–189, 2000.
- [75] R. Ferencz, J. Sanchez, B. Blümich, and W. Herrmann. AFM nanoindentation to determine Young’s modulus for different EPDM elastomers. *Polymer Testing*, 31(3):425 – 432, 2012.
- [76] D. Tranchida, Z. Kiflie, S. Acierno, and S. Piccarolo. Nanoscale mechanical characterization of polymers by atomic force microscopy (AFM) nanoindentations: viscoelastic characterization of a model material. *Measurement Science and Technology*, 20(9):095702, 2009.
- [77] V. Tsukruk, V. Gorbunov, Z. Huang, and S.A. Chizhik. Dynamic microprobing of viscoelastic polymer properties. *Polymer International*, 49(5):441–444, 2000.
- [78] D. Tranchida and S. Piccarolo. On the use of the nanoindentation unloading curve to measure the Young’s modulus of polymers on a nanometer scale. *Macromolecular Rapid Communications*, 26(22):1800–1804, 2005.
- [79] F. Rico, P. Roca-Cusachs, N. Gavara, R. Farré, M. Rotger, and D. Navajas. Probing mechanical properties of living cells by atomic force microscopy with blunted pyramidal cantilever tips. *Phys. Rev. E*, 72:021914, 2005.
- [80] V. Panin, A. Kolubaev, S. Tarasov, and V. Popov. Subsurface layer formation during sliding friction. *Wear*, 249(10-11):860–867, 2001.
- [81] J. Shang, W. Ma, and J. Lu. Formation of laminar structure under unlubricated friction of Cu-SiO₂ composite. *Tribology Letters*, 48(2):249–254, 2012.
- [82] S. Tarasov, V. Rubtsov, and A. Kolubaev. Subsurface shear instability and nanostructuring of metals in sliding. *Wear*, 268(1-2):59 – 66, 2010.

- [83] R.K. Lee, L.A. Korduba, and A. Wang. An improved theoretical model of orientation softening and cross-shear wear of ultra high molecular weight polyethylene. *Wear*, 271(9-10):2230 – 2233, 2011.
- [84] R. Dargazany and M. Itskov. A network evolution model for the anisotropic mullins effect in carbon black filled rubbers. *International Journal of Solids and Structures*, 46(16):2967–2977, 2009.
- [85] S. Merabia, P. Sotta, and D.R. Long. A microscopic model for the reinforcement and the nonlinear behavior of filled elastomers and thermoplastic elastomers (payne and mullins effects). *Macromolecules*, 41(21):8252–8266, 2008.
- [86] L. Chazeau, J. D. Brown, L. C. Yanyo, and S. S. Sternstein. Modulus recovery kinetics and other insights into the payne effect for filled elastomers. *Polymer Composites*, 21(2):202–222, 2000.
- [87] Z. Zhu, T. Thompson, S-Q Wang, E.D. von Meerwall, and A. Halasa. Investigating linear and nonlinear viscoelastic behavior using model silica-particle-filled polybutadiene. *Macromolecules*, 38(21):8816–8824, 2005.
- [88] L. Mullins. Effect of stretching on the properties of rubber. *Rubber Chemistry and Technology*, 21(2):281–300, 1948.
- [89] Z. Rigbi. Reinforcement of rubber by carbon black. *Advances in Polymer Science*, 36:21–68, 1980.
- [90] D.E. Hanson, M. Hawley, R. Houlton, K. Chitanvis, P. Rae, E.B. Orler, and D.A. Wroblewski. Stress softening experiments in silica-filled polydimethylsiloxane provide insight into a mechanism for the Mullins effect. *Polymer*, 46(24):10989 –10995, 2005.
- [91] W.G. Knauss. *Rupture phenomena in viscoelastic materials*. PhD thesis, California Institute of Technology, 1963.
- [92] S. Liu and Q. Wang. Studying contact stress fields caused by surface tractions with a discrete convolution and fast fourier transform algorithm. *Journal of Tribology*, 124(1):36–45, 2002.
- [93] R.L. Jackson and J.L. Streater. A multi-scale model for contact between rough surfaces. *Wear*, 261(11-12):1337–1347, 2006.
- [94] K.L. Johnson, J.A. Greenwood, and J.G. Higginson. The contact of elastic regular wavy surfaces. *International Journal of Mechanical Sciences*, 27(6):383–396, 1985.

- [95] Y. Merkel, M. Brieu, J. Diani, and J. Caillard. A mullins softening criterion for general loading conditions. *Journal of the Mechanics and Physics of Solids*, 60(7):1257 – 1264, 2012.
- [96] J. Bos. *Friction heating of tribological contacts*. PhD thesis, University of Twente, The Netherlands, 1995.
- [97] J.F. Archard. Contact and rubbing of flat surfaces. *Journal of Applied Physics*, 24(8):981–988, 1953.

Part II

The effect of a tribo-modified surface layer on friction in elastomer contacts

Part II

Paper-A: M. Mokhtari, D.J. Schipper and T.V. Tolpekina. On the Friction of Carbon Black- and Silica-Reinforced BR and S-SBR Elastomers. *Tribology Letters* (2014) 54:297-308.

Paper-B: M. Mokhtari, D.J. Schipper, N. Vleugels, J.W.M. Noordermeer. Transversely isotropic viscoelastic materials: Contact mechanics and friction. *Submitted to Tribology International* (8-2015).

Paper-C: M. Mokhtari, D.J. Schipper. Existence of a tribo-modified surface layer of BR/S-SBR elastomers reinforced with silica or carbon black. *Tribology International* (2014), *Article in press*.

Paper-D: M. Mokhtari, M.B. de Rooij, D.J. Schipper and R. Bosman. Formation of a tribo-modified surface layer on elastomers. *Submitted to Tribology Letters* (8-2015).

Paper-E: M. Mokhtari, D.J. Schipper, N. Vleugels, J.W.M. Noordermeer. Existence of a tribo-modified surface layer on SBR elastomers: balance between formation and wear of the modified layer. *Tribology Letters* (2015) 58:22.

On the Friction of Carbon Black- and Silica-Reinforced
BR and S-SBR Elastomers

M. Mokhtari, D.J. Schipper and T.V. Tolpekina
Tribology Letters (2014) 54:297-308

Tribol Lett (2014) 54:297–308
DOI 10.1007/s11249-014-0354-z

ORIGINAL PAPER

On the Friction of Carbon Black- and Silica-Reinforced BR
and S-SBR Elastomers

Milad Mokhtari · Dirk J. Schipper ·
Tetyana V. Tolpekina

Received: 24 December 2013 / Accepted: 8 April 2014 / Published online: 23 April 2014
© Springer Science+Business Media New York 2014

Abstract Friction of carbon black- and silica-reinforced elastomers is studied experimentally and theoretically, using Persson's model. The effect of reinforcement fillers on elasticity was determined by dynamical mechanical analysis. Carbon black-filled samples have a higher Young's modulus than the silica-filled compounds. Silica-filled rubbers have a higher $\tan \delta$ at lower temperatures and a lower loss tangent at higher temperatures, which is a rough indication for higher wet grip and lower rolling resistance, respectively. Friction tests on a ball-on-disk test rig were performed to study the effect of the reinforcement fillers and their amount on the friction between rubber samples (disks) and relatively smooth or rough granite surfaces (balls). The results were discussed and compared with the friction model presented by Persson. It was shown theoretically and experimentally that hysteresis does not play a significant role in the friction of rubber samples in contact with smooth granite and that it plays a minor role in contact with a rough granite sphere. Therefore, the hysteresis contribution of friction can be neglected in the contact of rubbers with just smooth spheres. Moreover, a higher friction coefficient is seen in samples with a higher content of fillers. Silica-filled compounds show a slightly higher coefficient of friction compared with the carbon black-filled compounds. The effect of attached wear debris to the granite surfaces on the friction level has been

studied. The results are supported by SEM and confocal microscopic images of the wear debris itself and wear debris attached to the granite spheres, respectively.

Keywords Friction · Elastomer · Hysteresis · Real area of contact · Interfacial layer

List of symbols

F_f	Total friction force (N)
F_{ad}	Hysteresis contribution of friction force induced by viscoelastic losses (N)
$\tau_f(v)$	Frictional shear stress as a function of velocity (Pa)
$A(v)$	Real area of contact as a function of velocity (m^2)
μ	Total coefficient of friction
F_N	Nominal normal load (N)
q_0	Nominal contact pressure (Pa)
A_0	Nominal area of contact (m^2)
μ_{ad}	Viscoelastic or hysteresis coefficient of friction
$P(q)$	Real to the nominal area of contact ratio as a function of wave vector
ω	Frequency of the applied load to the rubber (rad/s)
λ	Length scale of the roughness under study (m)
$\vec{q}$	Roughness wave vector (1/m)
q	Amplitude of the roughness wave vector (1/m)
q_1	Lower wave vector cutoff corresponding to the longest wave length of roughness (1/m)
q_1	Higher wave vector cutoff corresponding to the shortest wave length of roughness (1/m)
$C(q)$	Power spectral density of the roughness (m^2)
$A(q)$	Apparent contact area when the surface is smooth on all wave vectors $> q$ (m^2)
ϕ	Angle between the velocity vector and the wave vector $\vec{q}$ (rad)
E	Modulus of elasticity (Pa)
$G(\omega)$	The shear modulus (Pa)

M. Mokhtari (✉) · D. J. Schipper
Surface Technology and Tribology, Faculty of Engineering
Technology, University of Twente, P.O. Box 317,
7500 AE Enschede, The Netherlands
e-mail: m.mokhtari@utwente.nl; mokhtari@utwente.nl

T. V. Tolpekina
Apollo Tyres Global R&D B.V., Colsonweg 2,
7521 PT Enschede, The Netherlands

Notation

F_f	Total friction force	(N)
F_{hys}	Hysteresis contribution of friction force	(N)
F_N	Nominal normal load	(N)
$A(v)$	Real area of contact as a function of velocity	(m ²)
A_0	Nominal area of contact	(m ²)
$A(q)$	Apparent contact area when the surface is smooth on wave vectors $> q$	(m ²)
$P(q)$	Real to the nominal area of contact ratio	(-)
$C(q)$	Power spectral density of the roughness	(m ⁴)
$\vec{q}$	Roughness wave vector	(1/m)
q	Amplitude of the roughness wave vector	(1/m)
q_0	Lower wave vector cutoff related to the longest wave length	(1/m)
q_1	Higher wave vector cutoff related to the shortest wave length	(1/m)
E	Modulus of elasticity	(Pa)
$G(\omega)$	Shear modulus of elasticity	(Pa)
$G(v)$	Energy/area to break the interfacial rubber-substrate bond	(J/m ²)
a	Crack-tip radius	(m)
a_T	Temperature-frequency viscoelastic horizontal shift factor	(-)
T_g	Glass transition temperature	(°C)

ω	Frequency of the applied load to the rubber	(rad/s)
λ	Length scale of the roughness under study	(m)
ϕ	Angle between the velocity vector and the wave vector $\vec{q}$	(rad)
σ_0	Nominal contact pressure	(Pa)
μ_f	Total coefficient of friction	$(-)$
μ_{hys}	Viscoelastic or hysteresis coefficient of friction	$(-)$
$\tau_f(v)$	Frictional shear stress as a function of velocity	(Pa)
τ_c	Frictional stress related to energy dissipation at a crack opening	(Pa)
τ_s	Frictional stress related to shearing a thin confined film	(Pa)
ζ	Magnification factor	$(-)$
ν	Poisson's ratio	$(-)$

On the Friction of Carbon Black- and Silica-Reinforced BR and S-SBR Elastomers

M. Mokhtari, D.J. Schipper and T.V. Tolpekina*

Surface Technology and Tribology, Faculty of Engineering Technology, University of Twente,
P.O. Box 217, 7500 AE Enschede, The Netherlands

*Apollo Tyres Global R&D B.V., Colosseum 2, 7521 PT Enschede, The Netherlands

Abstract

Friction of carbon black- and silica-reinforced elastomers is studied experimentally and theoretically, using Persson's model. The effect of reinforcement fillers on elasticity was determined by dynamical mechanical analysis. Carbon black-filled samples have a higher Young's modulus than the silica-filled compounds. Silica filled rubbers have a higher $\tan(\delta)$ at lower temperatures and a lower loss tangent at higher temperatures, which is a rough indication for higher wet grip and lower rolling resistance, respectively. Friction tests on a ball-on-disk test rig were performed to study the effect of the reinforcement fillers and their amount on the friction between rubber samples (disks) and relatively smooth or rough granite surfaces (balls). The results were discussed and compared with the friction model presented by Persson. It was shown theoretically and experimentally that hysteresis does not play a significant role in the friction of rubber samples in contact with smooth granite and that it plays a minor role in contact with a rough granite sphere. Therefore, the hysteresis contribution of friction can be neglected in the contact of rubbers with just smooth spheres. Moreover, a higher friction coefficient is seen in samples with a higher content of fillers. Silica-filled compounds show a slightly higher coefficient of friction compared with the carbon black-filled compounds. The effect of attached wear debris to the granite surfaces on the friction level has been studied. The results are supported by SEM and confocal microscopic images of the wear debris itself and wear debris attached to the granite spheres, respectively.

1 Introduction

The interaction between tire and road determines whether sufficient traction is present under wet and dry conditions [1–3] as well as the amount of noise radiation [4], energy losses [5], vibration

[6] and rubber particles production [7]. Providing adequate grip between tire and road while simultaneously minimizing the undesirable effects of the tire-road interaction has been the subject of several researches in the past decades [8–10]. Solving the aforementioned problem seems

impossible unless the main mechanisms responsible for the tire-road interaction are well understood. Friction of polymers against solid surfaces is one of the most important mechanisms engaged in the tire-road interaction. Rubber seals, wiper blades, conveyor belts and syringes are some practical applications that require sufficient knowledge on rubber friction. Although great interest has been kindled by studying the tribological behavior of rubber sliding contacts in the past 50 years [11–13], the friction problem is not yet fully understood.

Several parameters such as contact pressure, (sliding) velocity, temperature and surface roughness, as well as morphology of the rubber compounds, play a role in the friction of polymers in contact with solid surfaces and, as a consequence, modeling rubber friction is not a simple task. The friction of polymers in contact with a solid surface differs from friction of other solids and simple friction models, such as the Coulomb’s friction law, are not adequate to describe friction under different conditions. Historically, the friction force between rubber and a rough surface was considered as a summing up of two main contributions, commonly described as the adhesion and hysteresis components [14]. The intermolecular attractive forces between the contacting bodies are considered as the mechanism responsible for the adhesion [15]. On the other hand, cyclic deformation of the rubber, caused by exerted oscillating forces of asperities of a rough surface, dissipates energy and generates the hysteresis component of friction [16]. There has been an ongoing debate among researchers on the question

of which component plays the major role in the overall friction. In the early works of Persson [17], the hysteresis was assumed to be the main contributor of rubber friction, while Le Gal and others [1] found that adhesion plays a dominant role. In a recent paper of Lorenz et al. [18], some other contributors to rubber friction are considered: energy dissipation due to crack opening and energy dissipation in shearing a thin viscous film [3]. Pan emphasizes the significance of interfacial interactions in determining the wet sliding friction of elastomer compounds in his research [19]. Moreover, a contribution to rubber friction as a result of wear processes is also mentioned and not well studied yet [3, 18].

The problem gets even more complicated by adding different fillers to the rubber compound. The effect of different fillers in rubber friction is of interest from a scientific point of view as well as for industrial applications, especially the tire industry. Silica and carbon black have been used as the main reinforcing agents in rubber compounds. It has been reported that substitution and/or addition of silica to carbon black-filled rubbers may modify the wet grip behavior as well as the rolling resistance of tires [19, 20]; however, much less is known about the mechanism responsible for this.

This paper studies the effect on friction of carbon black and silica, as reinforcement fillers, using a mixture of butadiene rubber (BR) and solution styrene-butadiene rubber (S-SBR) against rock (granite) based on a combined experimental-theoretical approach and tries to find the main contributor in friction.

The outline of this paper is as follows: In Sect. 2, the basic equations developed by Persson are presented, which are used to calculate the friction of rubber in contact with a solid rough surface. Section 3 starts with the materials used in the experiments and discusses DMA measurements performed to determine the mechanical characteristics of the rubber samples. Then, the results of the friction tests are discussed. Section 4 contains the numerical results based on the equations presented in Sect. 2. In Sect. 5, the results of Sect. 4 are used to explain the results of Sect. 3 and different aspects of the results are discussed. Finally, in Sect. 6, the main conclusions are given.

2 Rubber friction

The model developed by Persson is used to calculate the friction. Friction is modeled by incorporating the contributions of the roughness-induced viscoelastic deformation of the rubber as well as the contribution from the area of contact [3, 18]:

$$F_f = F_{hys} + \tau_f(v)A(v) \quad \text{or} \quad \mu_f = \frac{F_f}{F_N} = \frac{F_{hys}}{\sigma_0 A_0} + \frac{\tau_f(v)A(v)}{\sigma_0 A_0} \quad (1)$$

where σ_0 and A_0 are the nominal contact pressure and contact area, respectively. F_{hys} is the friction force related to the hysteresis losses in the bulk of the material that originates from the viscoelastic nature of the rubbers, $A(v)$ is the real area of contact as a function of velocity, $\tau_f(v)$ is the frictional stress due to the contribution from the area of

contact and F_f is the total friction force in contact between the rubber and a rigid surface. Rubber friction contributors are shown schematically in Fig. 1.

2.1 Hysteresis Component of Friction

The hysteresis component of the friction is originated from the oscillating forces that the surface asperities exert onto the rubber surface. These forces lead to cyclic deformations and energy dissipation due to internal frictional damping. The asperities of a rigid solid, with a sinusoidal rough surface with period l , exert a fluctuating force with a characteristic frequency $\omega = v/l$ to a rubber solid if the relative velocity between the rubber block and the rigid surface is equal to v . Surfaces are rough with roughness on many different length scales λ [21]; therefore, the contribution to rubber friction from the viscoelastic deformation (and consequently hysteresis losses) of the rubber surface exerted by the substrate asperities depends on the frequency-dependent viscoelastic modulus $E(\omega)$ (see Sect. 3.2 which deals with characterizing and determining the elasticity modulus over a range of frequencies). The asperities and the distribution of length scales λ in the roughness of the counter surface determine the distribution of frequency components in the Fourier decomposition of the surface stresses acting on the sliding rubber. In the model of Persson, the power spectral density of the roughness, $C(q)$, is considered as a function which contains all the necessary information regarding oscillating exerted forces from asperities. The definition and calculation method of

Figure 1: Sphere in sliding contact with rubber is shown schematically. All the surfaces are rough and many length scales are involved in the roughness and consequently, the friction [16]. The contribution from the area of contact in total friction is shown by the *green color* in nominal contact area, while the real area of contact is a function of magnification. The real area of contact decreases with an increase in magnification. Two magnifications are shown in the figure. Evidently, the contribution from the area of contact is just applied to the real area of contact and not to noncontact areas.

the power spectral density of a rough surface can be found in [21] where q is the amplitude of the wave vector related to the wavelength λ by $q = 2\pi/\lambda$. Friction is also a function of (flash) temperature as a consequence of heat generated as a result of loss of energy in the contact. In this research, low velocity in the contact of rubber with the rigid surface is considered, so the influence of flash temperature on friction is neglected.

The real area of contact is much smaller than the apparent area of contact A_0 . As an example, the real area of contact between the tire and the road is typically only $\sim 1\%$ of the nominal footprint contact area [16]. The real area of contact is important because it plays a role in determining the friction. Persson defines the real area of contact as a function of length scale λ , where the surface would be smooth on all length

scales shorter than λ . The basic equations of the hysteresis coefficient of friction as well as the real area of contact are summarized below [16, 18]:

$$\mu_{hys} \approx \frac{1}{2} \int_{q_0}^{q_1} dq \, q^3 C(q) P(q) \times \int_0^{2\pi} d\phi \, \cos \phi \, \text{Im} \left[\frac{E(qv \cos \phi)}{(1 - \nu^2)\sigma_0} \right] \quad (2)$$

where the function $P(q) = A(q)/A_0$ is given by

$$P(q) = \frac{2}{\pi} \int_0^\infty dx \, \frac{\sin x}{x} \exp \left[-x^2 G(q) \right] \quad (3)$$

where

$$G(q) = \frac{1}{8} \int_{q_0}^q dq \, q^3 C(q) \int_0^{2\pi} d\phi \left| \frac{E(qv \cos \phi)}{(1 - \nu^2)\sigma_0} \right|^2 \quad (4)$$

$A(q)$ is the apparent area of contact if the surface were smooth for all wave

vectors larger than q , A_0 is the nominal contact area at the shortest wave vector q_0 and x is an integration variable. It should be noted that it is assumed that rough surfaces are isotropic, so just the amplitude of the wave vector $|\vec{q}| = q = 2\pi/\lambda$ is important and not its direction where λ is the considered wavelength of the roughness. The theory is presented in the general form and is valid for all surfaces; however, the formulations can become simpler if the surface is self-fractal for $q_0 < q < q_1$ where the limitations are defined by the shortest and longest wavelengths of the roughness studied. ϕ is the angle between the velocity vector and the wave vector $\vec{q}$, σ_0 the nominal contact pressure and ν the Poisson's ratio. For an extended definition of the parameters, see [16, 17].

2.2 Contributions from Real Area of Contact

Two different physical phenomena are responsible for the contribution of the real area of contact to the overall friction, $\tau_f(v) = \tau_c(v) + \tau_s(v)$ where τ_c and τ_s are the effective frictional stresses with regard to energy dissipation at a crack opening and shearing a thin confined film, respectively.

Dissipation of energy at the crack openings results in the effective frictional stress τ_c acting at the real area of contact. The energy per unit area required to break the interfacial rubber-substrate bonds is called $G(v, T) = G_0[1 + f(v, T)]$ which is a function of crack-tip velocity v and the temperature T . G_0 is the energy to break the interfacial rubber-substrate bonds at extremely low crack velocities. If one

assumes that the contact area consists of N regions of average size l (i.e., $A = Nl^2$), then the following balance of energy is satisfied during a sliding distance of dx :

$$\begin{aligned} \tau_c A dx &= G(v) N l dx \quad \text{or} \\ \tau_c &= \frac{G(v)}{l} = \frac{G(v)}{G_0} \frac{G_0}{l} \end{aligned} \quad (5)$$

The dissipated energy as a result of crack propagation in high velocities for a viscoelastic solid is caused by hysteresis losses. The perturbing frequency is related to the distance r from the crack tip. The crack-tip radius a is recognized as the smallest possible r . Hence, the highest possible frequency will be v/a (see [22] for more details). It is shown in [22] that,

$$\frac{G(v)}{G_0} = \left[1 - \frac{2}{\pi} E_0 \int_0^{2\pi v/a} d\omega \frac{F(\omega)}{\omega} \operatorname{Im} \frac{1}{E(\omega)} \right]^{-1} \quad (6)$$

where $E_0 = E(\omega = 0)$, a is the crack-tip radius and $F(\omega) = \left[1 - \left(\frac{\omega a}{2\pi v} \right)^2 \right]^{1/2}$. The crack-tip radius cannot be smaller than an atomic diameter; therefore, in references [18, 22], $a_0 = 1 \text{ nm}$ is proposed and used. Because of difficulties in calculating the integral in Eq. 6 (originated from broad frequency range that extends over many decades), a simpler method is proposed [18, 22].

The second physical phenomenon dealing with the real area of contact contribution in the overall friction is due to the force of shearing a thin fluid-like film formed by segments of rubber molecules [3, 18]. Persson has suggested using,

$$\tau_s = \tau_0 (a T v)^\alpha \quad (7)$$

where a_T is the temperature-frequency viscoelastic shift factors and τ_0 is basically a fitting parameter. One can find more about the origin of the formulas in [18].

It is mentioned in [3, 18] that wear can also play a role in the friction of rubbers against solid surfaces; however, it was not further developed. Some simple models do exist that have considered the contribution and the effect of wear in the total friction [23] and, specifically, the friction of polymers [24]. In this research, in Sect. 5, the role of wear on the total friction is studied based on an experimental approach.

3 Experimental

3.1 Materials

The rubber samples employed in this study include 30 parts per hundred rubber (phr) butadiene rubber (BR) and 70 phr solution styrene-butadiene rubber (S-SBR). The samples are mixed with two different filler systems, carbon black (N375) and silica. The compounds are prepared by varying the amount of fillers, namely 100, 85 and 70 phr of carbon black or silica. For silica-filled compounds, depending on the amount of silica, the amount of processing oil needed to functionalize and disperse the silica particles was varied. Bifunctional organosilanes, such as bis(triethoxysilylpropyl)-tetrasulphide (TESPT), are used (depending on the silica content) to chemically modify the silica surfaces to enhance the compatibility of hydrocarbon rubbers and precipitated silica by modifying the surface of the silica. An overview of the different

rubber compounds prepared with the corresponding amounts (phr) of the components is given in Table 1.

In this paper, we refer to the samples as HC, MC, LC, HS, MS, LS which correspond to high, medium and low contents of carbon black (C) and silica (S), respectively.

3.2 Viscoelasticity of Compounds

The glass transition temperature of the samples is determined using dynamical mechanical analysis (DMA) in temperature sweep mode at a fixed frequency of 10 Hz under dynamic and static strains of 0.1 and 1 %, respectively. Then, the shear modulus $G(\omega)$ is measured in oscillatory shear mode at a constant strain amplitude of 0.1 % where the sample is fixed at both interfaces and sheared at different frequencies between 1 and 200 Hz . The whole procedure is repeated then for different temperatures (the temperature is varied between -20 and 85 $^{\circ}C$). The measured glass transition temperature and the selected reference temperature $T_{ref} = 27$ $^{\circ}C$ are used to shift the measured shear modulus $G(\omega)$ against frequency ω both horizontally and vertically; Based on the time-temperature superposition principle, the effect of changing the temperature and applying a multiplication factor a_T to the time scale is similar; therefore, the measured shear modulus in a limited frequency range ($1 < f < 200$ Hz) can be used to estimate the modulus at high frequencies [25]. Williams-Landel-Ferry (WLF) equation presented below is applied for the horizontal shifting:

Table 1: Different rubber compounds prepared with the amounts of components indicated in phr where HC:high carbon black content, MC: medium carbon black content, LC:low carbon black content, HS:high silica content, MS:medium silica content and LS:low silica content.

Compound	HC	MC	LC	HS	MS	LS
Description	phr	phr	phr	phr	phr	phr
BR, high cis	30	30	30	30	30	30
SSBR	70	70	70	70	70	70
N375	100	85	70	-	-	-
Silica	-	-	-	100	85	70
TESPT	-	-	-	7.8	6.63	5.5
Processing Oil	31	17	4	31	21	17
Sulphur	1.3	1.3	1.3	1.3	1.3	1.3
TBBS	1.3	1.3	1.3	1.3	1.3	1.3
DPG	2	2	2	2	2	2
ZnO	3	3	3	3	3	3
Stearic Acid	2	2	2	2	2	2
PVI	0.2	0.2	0.2	-	-	-
Anti-aging chemicals	6	6	6	6	6	6
Zinc salt of fatty acids	3	3	3	3	3	3

$\log f_h = \frac{-C_1(T - T_{ref})}{C_2 + T - T_{ref}}$, where C_1 and C_2 are two constants that depend on the elastomer as well as the selected reference temperature. Construction of broad frequency scale master curves from the limited measured modulus is only feasible for amorphous, unfilled rubbers [26] where the rubber behaves linearly. A necessary condition for using the shift factors of the unfilled systems for a filled compound is that the filler does not influence the location of the glass transition [27, 28]. This is the case for all six studied samples (see Figs. 2, 3).

Figure 2: Loss tangent as a function of temperature for six different filled compounds.

Figure 3: Young's storage (a) and loss (b) modulus of elasticity as a function of temperature for different samples.

Considering the fact that all the samples are filled with different fillers and filled rubbers show nonlinear viscoelastic behavior, only horizontal shifting cannot provide a continuous broad master curve; therefore, a vertical shifting should be also employed to shift the measured data along the vertical axis. The reasons of failure of the WLF equation for filled samples are mentioned in Ref. [27]. Vertical shifting is performed in some other researches [1, 28].

In tire application, deformations can be of the order of 100 %; therefore, the measurements should be performed at high strains; however, the rubber has a nonlinear behavior at high strains where the WLF relation is not valid; therefore, our measurements were performed at lower strains. The authors are aware of the effect of the strain softening in rubbers where the elasticity modulus might decrease at higher strains. A new procedure for

shifting is proposed by Lorenz et al. [29]. However, it is not possible at this moment to conduct direct measurements for high strains that correspond to the tire application and high frequencies at the same time. Therefore, there is no direct validation which method is the best for making master curves.

The measured loss tangent, which is the ratio between the loss and storage modulus of the samples as a function of temperature, is plotted in Fig. 2 as shown; the peak of loss tangent is higher for silica-filled compounds compared with the carbon black-filled samples. The phase angle is inversely dependent on the filler content. This trend is discussed in [22]. Moreover, the peak occurs at slightly higher temperatures for silica-filled compounds. Also, the temperature at which the peak value of the $\tan(\delta)$ occurs decreases with increasing filler content.

On the other hand, at higher temperatures ($T > 30\text{ }^{\circ}\text{C}$), silica-filled compounds show lower $\tan(\delta)$. This result is consistent with the results of other researchers where it has been generally accepted that replacement of carbon black by silica results in a decline of the rolling resistance due to a decrease of $\tan(\delta)$ at higher temperatures, while it simultaneously leads to a comparable $\tan(\delta)$ at lower temperatures, providing a comparable wet grip [30].

The effect of the filler and its content on the Young's modulus of elasticity is shown in Fig. 3. It can be concluded that the carbon black-filled samples generally possess a higher elasticity than the silica-filled compounds. In addition, the modulus of elasticity is dependent on the filler content.

The calculated master curve for the modulus of elasticity as a function of frequency is shown in Fig. 4 (just for one sample) for the MS rubber.

Figure 4: Shifted loss and storage shear modulus of elasticity as a function of frequency for 85 phr silica-filled rubber.

3.3 Friction tests

The friction tests are performed by a ball-on-disk setup schematically shown in Fig. 5 and under controlled environmental conditions. The temperature was kept constant at $27\text{ }^{\circ}\text{C}$ and the relative humidity at 50 %. The counter surfaces against the rubber samples are granite balls with a diameter of 30 mm. The sliding velocity was kept constant at 5 mm/s as well as the contact pressure, i.e., 0.4 MPa. A sample of the measured signal is shown in Fig. 5. The coefficient of friction is considered as the mean value when the signal is stabilized; in other words, the running-in friction is neglected.

The granite spheres are prepared with two different roughnesses, namely smooth and rough, i.e., with arithmetic average roughness of 0.52 and 2.28 μm , respectively. The power spectral densities of the spheres are shown in Fig. 6.

As is shown in the figure, the granite surfaces are self-fractal and the polished surface is much smoother than the rough one. The granite surfaces used in the present study are smoother than the road roughness but they are comparable with the stones present in the asphalt (that are even polished after some time of usage). Therefore, this study can provide information about the contribution of hysteresis and area of real contact on that roughness level.

The results of the friction measurements are shown in Fig. 7.

In the figure, the average and the standard deviation of the measured friction coefficient is shown. From these measurements, one can conclude that silica-filled compounds have a higher level

Figure 5: (a) Ball-on-disk setup used for friction measurements. (b) A sample of measured coefficient of friction versus time. The running-in phase is neglected and the stabilized part is used in determining the friction coefficient. The friction signal repeats itself.

of friction (except for low filled samples in contact with rough granite where the difference is not sensible) and also, an increase in filler content (for silica-filled rubbers) increases the coefficient of friction as well. Further, smooth surfaces in contact with the rubber samples do produce higher friction forces than rough surfaces. These results are consistent with the numerical calculations of the model results presented below, but to understand the rubber friction in the studied system in more detail, and in order to estimate the contribution of the hysteresis component of the friction in the total friction, a simple measurement was performed. The rubber surface was wetted by a thin layer of oil (Ondina 927 with a dynamic viscosity of 78 *mPas* at 20 °C) such that the lubricated tribosystem remains in the boundary lubrication regime, i.e., no

hydrodynamic effects. It was seen that for the smooth ball, the coefficient of friction decreases drastically (as an example, for 85 phr silica-filled rubber from 1.55 to 0.05), showing the limited role of deformation or hysteresis in the overall friction (see Eq. 1). Therefore, the hysteresis component of friction can be neglected when a smooth surface is in contact with rubber. On the other hand, when the relatively rough surface was in contact with the rubbers, although the coefficient of friction dropped to lower values as well (e.g., from 1.3 for low silica-filled compound to 0.5), but because of this value, the effect of hysteresis contribution on friction cannot be neglected. This result is consistent with [3].

Figure 6: Power spectral density of roughness for relatively smooth and rough granite spheres.

Figure 7: Coefficient of friction for carbon black- and silica-filled compounds with different filler contents where 1 and 2 indicate the relative rough and smooth counter surfaces roughness condition, respectively.

4 Numerical Results

Based on Eq. 3 and using the measured roughness, the real area of contact is calculated, for a sliding velocity of $v = 5$

mm/s as a function of the magnification, $\zeta = q/q_0$, for the different samples in contact with the relatively smooth and rough spheres. The results are presented in Fig. 8. The shortest wave vector, $q_0 = 2\pi/L$, depends on the longest wave length (L) in contact. This can be determined by the apparent area of contact. For this purpose, the Hertz contact model is used to calculate the diameter of the contact area for the different samples. The linear size of the contact regions, l , plays a crucial role in calculating the shear stress corresponding to the energy dissipation in crack openings (see Eq. 5). This value was found to be in relation to the large wave vector cut-off q_1 [18]. As shown in Fig. 8 and Eqs. 2 and 3, the large cut-off wave vector is the determining factor as well in calculating the real area of contact and the hysteresis component of the overall friction. Therefore, the large cut-off wave vector has an effect on the whole analysis. It has been suggested that the size of the road contamination particles (dust or sand particles) could be one of the determining factors in relation to the large cut-off wave vector q_1 [21]. However, for clean surfaces, Persson introduced a yield condition, which is related to an intrinsic property of the rubber, to determine the cut-off wave vector q_1 . It is assumed that the local stress and temperature in the asperity contact regions for a length scale $\lambda_1 = 2\pi/q_1$ are sufficiently high to break the rubber bonds, so a thin confined layer of rubber with thickness $\approx 1/q_1$ is formed at the rubber surface that is in contact with the counter surface asperities. This process to determine q_1 is closely related to the wear of the rubber samples. However, to determine the optimum cut-off, values

Figure 8: Variation of real area of contact over nominal contact area as a function of magnification for sliding velocity of $v = 5 \text{ mm/s}$ for rubbers in contact with (a) smooth and (b) rough granite surfaces.

of other parameters have to be known in advance, and these values are found in such a way that the numerical results fit properly with the experiments [31]. On the other hand, one can initially fit the experiments with the numerical results to find the optimum value for q_1 . The latter procedure is also used to validate Persson's theory [3]. Different values for q_1 are used for different rubber-granite tribosystems to fit with the experiments. The short wavelengths are of the order of $\lambda_1 \approx 0.5 \text{ } \mu\text{m}$ for rough granite spheres in contact with HC sample (λ_1 increases with a decrease in filler content, it is lower for contact of a rough sphere in comparison with contact of a smooth granite sphere with the same rubber and is higher for contact between a silica-filled than carbon black-filled rubber and similar sphere) and of the order of $\lambda_1 \approx 8 \text{ } \mu\text{m}$ for smooth granite spheres in contact

with LS rubber (see also Fig. 11 and the difference in the size of the carbon black- and silica-reinforced rubber debris). The short wavelengths selected for all other tribosystems vary between these two values and increases as explained above. These values are of the order of the short wavelengths used or measured in the different rubber systems with rough and smooth surfaces such as concrete, sandpaper or asphalt roads [1, 18, 22, 32].

Figure 8 shows that, as expected, the area of real contact decreases with an increase in the Young's modulus of elasticity (as a result of an increase in the filler content).

Another interesting result illustrated by Fig. 8 is that the real area of contact for all rubber samples increases approximately 3-5 times when a smooth ball is in contact with rubber compared to the rough one. The calculated viscous coefficient of

friction, based on Eq. 2 for both surfaces in contact with the rubber samples, is shown in Fig. 9 as a function of the sliding velocity.

Figure 9: Hysteresis coefficient of friction as a function of sliding velocity for carbon black- and silica-filled samples in contact with relatively smooth and rough spheres.

The ratio $G(v)/G_0$ (see Eq. 5) is calculated and plotted against velocity v in Fig. 10. In the calculations, the value suggested in [18, 22] for the crack-tip radius for low velocities $a_0 = 1 \text{ nm}$ is used. It has been reported that the measured value for G at extremely low crack velocities is of the order $\approx 0.1 \text{ J/m}^2$ [18]. G_0 values are selected in the same order for the samples used in this research. For “high” crack velocities, $G(v) \approx G_0 E_\infty/E_0$ [1, 22, 33]. The ratio of the dynamic modulus in the glassy state to that in the rubbery state, E_∞/E_0 , is higher for silica-filled compounds and is related inversely to the filler content (for both silica and carbon black-filled samples). Figure 10 shows that $G(v)$ increases with an increase in E_∞/E_0 . In short, for $v = 5 \text{ mm/s}$, the carbon

black-filled samples show lower energy dissipation (at crack openings) than silica-filled samples and the dissipated energy increases with a decrease in filler content. As a conclusion, the dissipated energy in the crack openings is inversely related to the modulus of elasticity.

Figure 10: Crack propagation energy enhancement factor $G(v)/G_0$ as a function of the crack-tip velocity for different samples.

The contribution of energy dissipation at crack openings to the overall friction coefficient is $\frac{\tau_c(v)A(v)}{\sigma_0 A_0}$ (see Eq. 1). The effective frictional stress with regard to energy dissipation at a crack opening, τ_c , is governed by Eq. 5. As shown in Fig. 10, $1.1 < \log_{10} G/G_0 < 1.2$ (which does not differ severely for different samples), it was mentioned earlier that $0.5 < l < 8 \text{ } \mu\text{m}$. However, the real area of contact changes drastically for different tribosystems. Substituting the given numbers for each system reveals that dissipation of energy at crack openings for contact of rubbers with rough spheres (and especially carbon black-filled rubbers where $A(v)/A_0$ is much smaller) is

negligible while this phenomenon plays a minor role in total friction for contact of smooth balls with rubbers (especially silica-filled samples which have much higher real contact areas). Moreover, for systems which hysteresis is negligible, dissipation of energy in crack openings plays a minor role in total friction and vice versa. None of these two phenomena can describe the measured friction coefficients. Therefore, shearing of a thin interfacial layer is the main contributor in friction of studied rubber disks and granite balls.

The frictional shear stress τ_0 in Eq. 7 is selected such that the numerical results are in agreement with the measurements. These values are of the order of a few *MPa* to 22 *MPa* and with a power $\alpha = 0.05$ in Eq. 7 which are in the range of values found elsewhere [1, 3, 18].

5 Discussion

It is seen that for the samples with a higher modulus of elasticity (higher filler content), the viscous coefficient of friction is just slightly higher. This can be explained by Eq. 2, where the competition between $P(q)$ and the imaginary part of the elastic modulus determines the viscous friction. Although a higher filler content decreases the real area of contact, as is illustrated in Fig. 8, the loss modulus also increases (Fig. 3). It can be observed from Fig. 7 that an increase in the filler content (or modulus of elasticity) results in an increase in the total measured coefficient of friction and stays approximately in the same range for silica and carbon black-filled samples. This increase is the superposition of a slight increase in

the viscous coefficient of friction and a decrease in the real area of contact (the contact area decreases 3 to 5 times). This can only be valid if τ_f , presented in Eq. 1, also increases as the filler content increases.

Although dissipation of energy at the crack openings plays a role in the overall friction, it is not the main contributor. When rubbers are in contact with rough surfaces, the real area of contact is much smaller; however, it plays a minor role in contact with smooth counter surfaces. Moreover, for smooth surfaces and when no debris is attached to the counter surface, adhesional interaction might also increase the area of real contact contribution. For rough surfaces, the hysteresis component of friction together with friction induced by shearing a thin interfacial layer explains the levels of the measured friction, while for the smooth surfaces, shearing of a thin interfacial layer plays the dominant role and the energy dissipation at crack openings just slightly contributes to the overall friction. The strain softening effect might result in higher areas of real contact which brings about lower values for τ_0 than the calculated shear stresses. This shows the importance of studying the origin of τ_0 and not considering it just as a fitting parameter which has not been performed yet. Therefore, a more detailed theoretical-experimental approach is required to acquire sufficient knowledge on the properties of the interfacial rubber surface layer.

Studying the wear debris of the different rubber samples shows that the wear debris of carbon black-filled rubbers was more sticky and could easily attach

Figure 11: Scanning electron microscopic pictures of rubber wear particles: (a) wear particle from 85 phr carbon black-filled rubber and (b) wear particle from 85 phr silica-filled rubber.

to the granite ball, while the wear debris of the silica-reinforced samples was more “dusty-like”. Scanning electron microscopic pictures of the debris are shown in Fig. 11 where the carbon black reinforced debris has the tendency to attach together and form a smear film, while the silica-filled debris stays apart from each other. It was observed that when the experiment runs for a long period of time, rubber wear particles stick to the granite surface and the tribosystem under study changes. The stabilized measured coefficient of friction when the spheres are contaminated with debris is shown in Fig. 12.

Fresh smooth and rough spheres cleaned by isopropanol as well as wear debris attached spheres (wear debris resulting from the contact of MC sample and spheres) are shown in Fig. 13. The images are made by the laser scanning microscope VK 9700 Keyence on an area of $200 \times 286 \mu m$. The debris attached to the rough sphere of MS is shown in Fig. 14.

The difference between Figs. 13-(c) and 14 can be explained by Fig. 11. As discussed before, the silica-filled compound’s debris shows a tendency to leave the contact area, while carbon black-filled compound’s debris mainly sticks to the sphere.

Figure 12: Coefficient of friction for carbon black- and silica-filled compounds with different filler contents in contact with contaminated granite surfaces where 1 and 2 indicate the relative rough and smooth counter surfaces roughness condition, respectively.

Figure 13: Confocal microscopic pictures of cleaned rough (a), smooth (b) and debris attached to the rough (c) and smooth (d) granite spheres in contact with MC.

It can be illustrated from Fig. 13 that the wear debris fills the valleys of the sphere, so the contact is between a combination of rubber-rubber as well as rubber-granite at the asperities (depending on the initial roughness and the compound used, the contact is divided in different ratios of rubber-rubber to rubber-granite contact). A simple comparison between Figs. 7 and 12 shows an increase in the coefficient of friction when the contact region is partially influenced (by the attached wear debris) in all studied tribosystems. The increment in the friction coefficient is dependent on the filler content and filler itself; therefore, the increase in friction for high filler contents is more recognized than for low filled samples. The highest increase in friction

level is seen for the HC sample. This is because the carbon black-reinforced rubber debris has a greater tendency to stick to the granite and changes the tribosystem than the silica-filled rubbers. Similar observations have been made in [24, 34, 35]. This situation also occurs in the contact between tire and road. The increase in the friction coefficient can be explained by the modified roughness of the contact as well as modified shearing layers where shearing occurs between a combination of rubber-rubber and rubber-granite in comparison with shear between rubber and granite. In all contacts, the roughness of the granite sphere becomes less because wear debris fills the valleys between the asperities, thus the real area of contact increases; this is seen in Fig. 12.

This is more proof of the importance of the real area of contact.

Figure 14: Confocal microscopic picture of a polluted rough granite sphere in contact with MS.

6 Conclusions

A theoretical-experimental approach is used to study the effect of carbon black and silica as reinforcement fillers on friction. DMA measurements showed that carbon black-filled samples have a higher Young's modulus than the silica-filled compounds, and the filler content and the modulus of elasticity are related. Silica-filled rubbers have a higher $\tan(\delta)$ at lower temperatures and a lower loss tangent at higher temperatures than carbon black-filled compounds, which is a rough indication of higher wet grip and lower rolling resistance for the tire-road contact, respectively.

A ball-on-disk setup was used to conduct friction measurements of six different rubber samples in contact with smooth and rough granite spheres. It was shown theoretically and experimentally that hysteresis has a negligible effect on the coefficient of friction for the smooth counter surface and does play a minor role in the rough surface for the systems studied.

The real area of contact decreases with an increase in elastic modulus as a result of an increase in filler content. On the other hand, the hysteresis increases just slightly with an increase in filler content. Therefore, the real area of contact plays a major role on friction of the studied systems as well as on the interfacial surface layer. In conclusion, because the real area of contact is higher when a smooth sphere is in contact with rubber, and based on the fact that the real area of contact plays the major role in the total friction of granite spheres and rubbers, the coefficient of friction is higher when a smooth sphere is in contact with the rubber samples compared to a rough ball.

Silica-filled samples generally show a higher coefficient of friction than carbon black-filled ones. The coefficient of friction increases with increased filler content for silica-filled rubbers.

The role of wear debris on friction was studied experimentally. It was shown that wear debris attached to the spheres in contact with the rubber samples shows higher friction coefficients. This difference is because of the modified roughness of the balls, as shown in Figs. 13 and 14, and shear stress when rubber is rubbed against rubber or when rubber is rubbed against granite. This research shows the necessity of studying in more detail the nature of shearing a thin surface layer (with modified properties) as the main contributor to the total friction.

Acknowledgements

This project is carried out in the framework of the innovation program "GO Gebundelde Innovatiekracht" and funded by the "European

Regional Development Fund”, “Regio Twente” and “Provincie Overijssel”. The project partners Apollo Tyres Global R&D B.V., University of Twente (Tire-Road Consortium), Reef Infra, Stemmer Imaging B.V. and the Provincie Gelderland are gratefully acknowledged.

7 References

- [1] A. Le Gal, X. Yang, and M. Klüppel. Evaluation of sliding friction and contact mechanics of elastomers based on dynamic-mechanical analysis. *Journal of Chemical Physics*, 123(1), 2005.
- [2] X. Claeys, J. Yi, L. Alvarez, R. Horowitz, C. Canudas De Wit, and L. Richard. Tire friction modeling under wet road conditions. In *American Control Conference*, volume 3, pages 1794–1799, 25–27 June 2001.
- [3] B. Lorenz, B.N.J. Persson, G. Fortunato, M. Giustiniano, and F. Baldoni. Rubber friction for tire tread compound on road surfaces. *Journal of Physics Condensed Matter*, 25(9), 2013.
- [4] D.J. O’Boy and A.P. Dowling. Tyre/road interaction noise-numerical noise prediction of a patterned tyre on a rough road surface. *Journal of Sound and Vibration*, 323(1-2): 270–291, 2009.
- [5] R. Brancati, S. Strano, and F. Timpone. An analytical model of dissipated viscous and hysteretic energy due to interaction forces in a pneumatic tire: Theory and experiments. *Mechanical Systems and Signal Processing*, 25(7):2785–2795, 2011.
- [6] E. Rustighi, S.J. Elliott, S. Finnveden, K. Gulyás, T. Mócsai, and M. Danti. Linear stochastic evaluation of tyre vibration due to tyre/road excitation. *Journal of Sound and Vibration*, 310(4-5):1112–1127, 2008.
- [7] S. Amemiya, Y. Tsuritaa, T. Masudaa, A. Asawaa, K. Tanakaa, T. Katoha, M. Mohrib, and T. Yamashinab. Investigation of environmental problems caused by studded tires of automobiles using PIXE. *Nuclear Inst. and Methods in Physics Research, B*, 3(1-3):516–521, 1984.
- [8] R. Bond, G.F. Morton, and L.H. Krol. A tailor-made polymer for tyre applications. *Polymer*, 25(1):132–140, 1984.
- [9] K.A. Grosch. The rolling resistance, wear and traction properties of tread compounds. *Rubber Chemistry and Technology*, 69(3): 495–568, 1996.
- [10] A.R. Williams. Tyre to road interaction: A case for application of research. *Tribology International*, 17(5):235–241, 1984.
- [11] J.M. Golden. A molecular theory of adhesive rubber friction. *Journal of Physics A: General Physics*, 8(6):966–979, 1975.
- [12] C.J. Rand and A.J. Crosby. Insight into the periodicity of schallamach waves in soft material friction. *Applied Physics Letters*, 89(26):261907, 2006.
- [13] D. Tabor. The mechanism of rolling friction. II. the elastic range. *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, 229(1177):198–220, 1955.
- [14] D.F. Moore. *The friction and lubrication of elastomers*. Pergamon Press, 1972.
- [15] P. Wriggers and J. Reinelt. Multi-scale approach for frictional contact of elastomers on rough rigid surfaces. *Computer Methods in Applied Mechanics and Engineering*, 198(21-26):1996–2008, 2009.
- [16] B.N.J. Persson. Theory of rubber friction and contact mechanics. *Journal of Chemical Physics*, 115(8):3840–3861, 2001.
- [17] B.N.J. Persson. On the theory of rubber friction. *Surface Science*, 401(3):445–454, 1998.
- [18] B. Lorenz, B.N.J. Persson, S. Dieluweit, and T. Tada. Rubber friction: Comparison of theory with experiment. *The European Physical Journal E*, 34(129):129, 2011.

- [19] X-D. Pan. Wet sliding friction of elastomer compounds on a rough surface under varied lubrication conditions. *Wear*, 262(5-6):707 – 717, 2007.
- [20] R. Rauline. Rubber compound and tires based on such a compound (to compagnie generale des etablissements Michelin), EU 0501227 (1992).
- [21] B.N.J. Persson, O. Albohr, U. Tartaglino, A.I. Volokitin, and E. Tosatti. On the nature of surface roughness with application to contact mechanics, sealing, rubber friction and adhesion. *Journal of Physics Condensed Matter*, 17(1):R1–R62, 2005.
- [22] B.N.J. Persson, O. Albohr, G. Heinrich, and H. Ueba. Crack propagation in rubber-like materials. *Journal of Physics: Condensed Matter*, 17(44):R1071, 2005.
- [23] P.J. Blau. Embedding wear models into friction models. *Tribology Letters*, 34(1):75–79, 2009.
- [24] L. Boissonnet, B. Duffau, and P. Montmitonnet. A wear particle-based model of friction in a polymer-metal high pressure contact. *Wear*, 286-287:55–65, 2012.
- [25] M.L. Williams, L.F. Robert, and J.D. Ferry. The temperature dependence of relaxation mechanisms in amorphous polymers and other glass-forming liquids. *Journal of the American Chemical Society*, 77(14):3701–3707, 1955.
- [26] J.D. Ferry. *Viscoelastic properties of polymers*. Wiley, 1980.
- [27] J. Fritzsche and M. Klüppel. Structural dynamics and interfacial properties of filler-reinforced elastomers. *Journal of Physics: Condensed Matter*, 23(3):035104, 2011.
- [28] M. Klüppel. Evaluation of viscoelastic master curves of filled elastomers and applications to fracture mechanics. *Journal of Physics: Condensed Matter*, 21(3):035104, 2009.
- [29] B. Lorenz, W. Pyckhout-Hintzen, and B.N.J. Persson. Master curve of viscoelastic solid: Using causality to determine the optimal shifting procedure, and to test the accuracy of measured data. *Polymer*, 55(2):565 – 571, 2014.
- [30] P. Cochet, L. Barriquand, Y. Bomal, and S. Touzet. Precipitated silica in tire tread. Paper presented at the ACS, Rubber Division, Cleveland, OH, 17-20 Oct 1995.
- [31] B.N.J. Persson. Rubber friction: Role of the flash temperature. *Journal of Physics Condensed Matter*, 18(32):7789–7823, 2006.
- [32] N.V. Rodriguez, M.A. Masen, and D.J. Schipper. Tribologically modified surfaces on elastomeric materials. *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology*, 227(5): 398–405, 2013.
- [33] S. Momozono, K. Nakamura, and K. Kyogoku. Theoretical model for adhesive friction between elastomers and rough solid surfaces. *The Journal of Chemical Physics*, 132(11):114105, 2010.
- [34] S. Bahadur. The development of transfer layers and their role in polymer tribology. *Wear*, 245(1-2):92–99, 2000.
- [35] Y.J. Mergler, R.P. Schaake, and A.J. Huis in’t Veld. Material transfer of POM in sliding contact. *Wear*, 256(3-4):294–301, 2004.

Paper B

Transversely isotropic viscoelastic materials: Contact mechanics and friction

M. Mokhtari, D.J. Schipper, N. Vleugels, J.W.M. Noordermeer

Submitted to the Journal of Tribology International

Transversely isotropic viscoelastic materials: Contact mechanics and friction

M. Mokhtari, D.J. Schipper, N. Vleugels*, J.W.M. Noordermeer*

Surface Technology and Tribology, Faculty of Engineering Technology, University of Twente,
P.O. Box 217, 7500 AE Enschede, The Netherlands

*Elastomer Technology and Engineering, Faculty of Engineering Technology, University of
Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

Abstract

Transversely isotropic materials are a unique group of materials whose properties are the same along two of the three principal axes. Various natural and artificial materials behave effectively as transversely isotropic elastic solids therefore this specific case of anisotropy has several engineering and industrial applications. Various components can be classified as transversely isotropic materials including crystals, rocks, piezoelectrics, biological tissues such as muscles, skin, cartilage tissue or brainstem and fibrous composites. In this study, the theory of contact mechanics developed by Persson is extended in such a way that it can model the contact and friction of a transversely isotropic viscoelastic solid in contact with a rigid rough surface. Numerical results show that anisotropy should be taken into account when dealing with transversely isotropic solids. The experimental results validate the theory.

1 Introduction

The interaction between two contacting solids which is the main subject of tribology plays a major role in a large number of physical phenomena and engineering applications such as friction, lubrication and wear. The analysis of the stresses, contact stiffness, surface deformations and contact areas generated by the contact between bodies with rough surfaces needs to be accurately accounted for in a smart design of various engineering components including but not limited to tires,

seals, bio-inspired adhesives, coatings, piezoelectric materials, electrical contacts and syringes. The mechanics of isotropic elastic materials is a quite developed research field. The contact problems for anisotropic solids were studied in many papers [1–4]. Transversely isotropic materials are a unique group of materials whose properties are the same along two of the principal axes. Several materials can be classified as transversely isotropic materials including crystals, rocks, piezoelectric materials, some biological tissues such as muscles, skin, cartilage tissue or brainstem and

fibrous composites. Researchers have been investigating the mechanics of transversely isotropic materials for many years [1, 3, 5–8] simply because many natural and artificial materials behave effectively as transversely isotropic elastic solids. Viscoelasticity which makes the contact problem even more complex, is crucial in modelling rubber-like materials and biological tissues and should not be ignored.

Several approaches dealing with the contact of real random rough surfaces have been introduced. Greenwood and Williamson (GW) proposed asperity-based models [9], in which the roughness is reduced to a set of identical asperities distributed according to a Gaussian or exponential height distribution. The GW model has attracted several researchers for a long time. Every asperity is incorporated with a Hertzian punch in this model. Little is gained by proposed modified versions of the GW contact model, treating the asperities as ellipsoids, or by introducing a distribution of asperity sizes [10]. Random process theory is used in other modified versions of the GW model to make the asperity curvature depending on their heights. In another attempt, fractal theory is used to recognize the multiscale nature of real surfaces [11]. Although the achieved results through multi-asperity contact models are of practical interest, neglecting the interactions between neighboring microcontacts is the main disadvantage of such models. In the study of soft materials like rubbers or soft biological tissues, the effect of the asperities on each other cannot be neglected because these flexible materials

can deform much easier and therefore the problem of neglecting interactions between neighboring asperities is heavier especially when approaching full contact, i.e. when the contact spot separation is of comparable size with the spot size itself. The interaction between the asperities can be added to the current asperity models [12, 13], however, these approaches remain quite approximate [14]. On the other hand, a new model was proposed by Persson [15] that does not pre-exclude any scale of roughness from the analysis. In his model, the exact solution for the case of full contact is firstly obtained and further analysis is extended to the partial contact by imposing a boundary condition which is an approximate solution. Even though Manners and Greenwood [16] raise some concerns about the boundary conditions applied in Persson’s theory, the behavior of elastically soft materials (with the ability to bend and fill out the roughness on at least small wave lengths) is more analogous to Persson’s analysis, than the asperity contact models (where it is assumed that contact occurs on segregated islands, far from each other, which are named asperities and do not have any influence on each other because of the far distances in between). Persson introduced a correction of the expression used for the elastic energy in the asperity contact regions [17]. A comparison between numerical results and Persson’s contact model has led to a suitable value for the correction factor [18]. Multi asperity contact models and Persson’s approach have been comparatively analyzed [19].

The theory of contact mechanics and friction of Persson has been extended to model the contact and friction

Figure 1: A granite semi-sphere in sliding contact with a transversely isotropic viscoelastic half space is shown schematically. The contributions to friction from (i) shearing of a thin modified surface layer (τ_f) and (ii) hysteresis in the bulk of the rubber are demonstrated.

between surfaces with anisotropic surface roughness [20]. The main purpose of this study is to extend Persson’s theory in such a way that it can model the contact and friction of a transversely isotropic viscoelastic solid in contact with a rigid rough surface. This is of importance in modelling the contact of soft biological tissues such as, muscles, skin and brainstem. Mechanical properties of the novel composites can be controlled and tuned by morphology, distribution and alignment processes to achieve the desired characteristics [21]. Moreover, fiber reinforced composites can (depending on the direction of the fibers in the composite) show transversely isotropic characteristics. They have a wide range of industrial applications such as tires, transmission belts and seals. In Sect. 2, the theory is explained. In the next section, both the real area of contact and the viscoelastic contribution to the overall friction of a transversely isotropic material are calculated and the results are compared with the results for an isotropic material. The measured dynamic mechanical properties (in different directions) of a prepared unidirectional fiber reinforced

rubber sample as well as the measured friction between two rough granite surfaces and the rubber sample are presented in Sect. 4. The experimental results are compared with the numerical results of the theory in Sect. 5 and the conclusions are summarized in the last section.

2 Friction between a Transversely Isotropic Viscoelastic Solid and a Rough Rigid Surface

The friction contributors in the contact between a viscoelastic solid and a rigid rough surface are commonly described by two main contributors i.e. the adhesion component and the hysteresis component [22]. Hysteresis component of friction is generated by (cyclic) deformation of the rubber which dissipates energy via the internal damping in the bulk of the material [15]. Adhesion is characterized by the attractive forces between the contacting bodies [23]. Energy dissipation due to crack opening [24] and energy dissipation in shearing of a thin viscous film [25] are other contributors to friction

of elastomers. Pan [26] has shown the significant role of interfacial interactions, in addition to the bulk viscoelastic hysteresis, in determining the wet sliding friction of elastomer compounds. The friction force contributions mentioned before are summarized in terms of two main forces (see Fig. 1): (1) the contributions related to the viscoelastic deformations; and (2) the contributions related to the real area of contact as defined in Eq. 1. One contributor cannot be indicated as the main contributor to the friction as a generalized rule [27], but depending on the tribological conditions, hysteresis or the real area of contact can play a dominant role in determining the overall friction.

$$F_f = F_{hys} + \tau_f A_{real} \quad (1)$$

where F_f , F_{hys} are the forces concerning the total friction and the contribution from the hysteresis losses respectively and the product $\tau_f A_{real}$ represents the force in the real area of contact where τ_f , A_{real} are the frictional shear stress and real area of contact. In some tribological systems, the shear stress between the two contacting bodies changes according to the tribological conditions and the frictional energy input [28].

2.1 Contact Mechanics between a Transversely Isotropic Viscoelastic Solid and a Rough Rigid Surface

Consider a rough rigid surface sliding at a constant velocity v on a transversely isotropic viscoelastic half space (whose surface is parallel to the planes of

isotropy). Take a rectangular coordinate system $(\mathbf{x}, z) = (x, y, z)$. By the application of a concentrated load $F(\mathbf{x}, 0) = F_0$ on the free surface of the transversely isotropic viscoelastic solid, the displacement at any point on the surface, $u_z(\mathbf{x}, 0)$, can be calculated by the equation below [29], substituting $z = 0$:

$$u_z(\mathbf{x}, z) = - \sum_{i=1,2} \frac{\alpha - \gamma s_i^2}{s_i^2} \frac{\partial \varphi_i}{\partial z} \quad (2)$$

In the above equation,

$$\begin{aligned} \varphi_{1,2}(\mathbf{x}, z) = & \frac{-s_{1,2}[\alpha + (1 - \gamma)s_2^2]}{s_2 k_2 [\alpha + (1 - \gamma)s_1^2] - s_1 k_1 [\alpha + (1 - \gamma)s_{2,1}^2]} \\ & \times \frac{F}{2\pi B_{66}} \log(\sqrt{x^2 + y^2 + s_1^2 z^2} - s_{1,2} z). \end{aligned}$$

The constants α , γ , k_1 are determined by

$$\begin{cases} \alpha = \frac{B_{11}}{B_{13}}, \gamma = \frac{B_{44}}{B_{13}}, \\ k_i = \frac{1 - \gamma - \beta(\alpha - \gamma s_i^2)}{\gamma s_0^2} \\ \text{where } \beta = \frac{B_{33}}{B_{13}}, s_0^2 = \frac{B_{66}}{B_{44}} \end{cases}$$

and are related to the 5 elastic constants. In addition,

$$s_{1,2}^2 = \frac{A \pm \sqrt{A^2 - 4B_{11}B_{33}B_{44}^2}}{2B_{33}B_{44}},$$

$$A = B_{44}^2 + B_{11}B_{33} - B_{13}^2.$$

If the generalized Hook's law for a transversely isotropic solid, with symmetry plane x - y is written:

$$\begin{bmatrix} \sigma_x \\ \sigma_y \\ \sigma_z \\ \tau_{yz} \\ \tau_{zx} \\ \tau_{xy} \end{bmatrix} = \begin{bmatrix} A_{11} & A_{12} & A_{13} & 0 & 0 & 0 \\ A_{12} & A_{11} & A_{13} & 0 & 0 & 0 \\ A_{13} & A_{13} & A_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & A_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & A_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & A_{66} \end{bmatrix} \times \begin{bmatrix} \frac{\partial u_x}{\partial x} \\ \frac{\partial u_y}{\partial y} \\ \frac{\partial u_z}{\partial z} \\ \frac{\partial u_z}{\partial y} + \frac{\partial u_y}{\partial z} \\ \frac{\partial u_z}{\partial x} + \frac{\partial u_x}{\partial z} \\ \frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x} \end{bmatrix} \quad (3)$$

then the following relations hold:

$$\begin{cases} A_{11} = \frac{1 - \nu_{pz}\nu_{zp}}{E_p E_z \Delta}, & A_{12} = \frac{\nu_p + \nu_{pz}\nu_{zp}}{E_p E_z \Delta} \\ A_{13} = \frac{\nu_{zp} + \nu_p \nu_{zp}}{E_p E_z \Delta}, & A_{33} = \frac{1 - \nu_p^2}{E_p E_z \Delta} \\ A_{44} = G_{zp}, & A_{66} = \frac{E_p}{2(1 + \nu_p)} \\ \Delta = \frac{(1 + \nu_p)(1 - \nu_p - 2\nu_{pz}\nu_{zp})}{E_p^2 E_z} \end{cases}$$

and the B_{ij} constants are related to the 5 elastic constants by the following relations:

$$\begin{cases} B_{11} = A_{11}, & B_{33} = A_{33}, \\ B_{44} = A_{44}, & B_{66} = A_{66}, \\ B_{12} = A_{12} + A_{66}, & B_{13} = A_{13} + A_{44} \end{cases}$$

The Hook's law in stiffness form presented above is determined by 5

independent elastic constants $E_p, E_z, G_{zp}, \nu_p, \nu_{pz}$. In the above formulations, the Young's modulus and Poisson's ratio in the x - y symmetry plane are given by E_p, ν_p , the Young's modulus and Poisson's ratio in the z direction are E_z, ν_{pz} and the shear modulus in the z direction is G_{zp} . The Poisson's ratios must satisfy $\frac{\nu_{pz}}{E_p} = \frac{\nu_{zp}}{E_z}$.

The displacement at the interface, as a function of the elastic constants can be governed using Eq. 2, substituting $z = 0$:

$$u_z(\mathbf{x}, 0) = \frac{DF_0}{2\pi|\mathbf{x}|} \quad (4)$$

where D is a function of 5 independent elastic constants of a transversely isotropic solid as defined below,

$$\begin{aligned} D &= \left[2\alpha^2 + \alpha(1 - 2\gamma) \right. \\ &\quad \times \left(\frac{B_{44}^2 + B_{11}B_{33} - B_{13}^2}{B_{33}B_{44}} \right) \\ &\quad \left. - 2\gamma(1 - \gamma) \frac{B_{11}}{B_{33}} \right] \cdot \left(\frac{1}{B_{66}} \right) \\ &\quad \times \frac{1}{s_2 k_2 [\alpha + (1 - \gamma)s_1^2] - s_1 k_1 [\alpha + (1 - \gamma)s_2^2]}. \end{aligned}$$

The displacement field is symmetric and depends on the distance from the location of the applied point load and elastic properties of the infinite half-space. With the assumption of constant sliding velocity, the normal stress and displacements repeat themselves in time domain or in other words, $\sigma_z(x, t) = \sigma_z(x - vt)$ and $u_z(\mathbf{x}, t) = u_z(\mathbf{x} - vt)$. The Fourier transforms of the normal stress σ_z and the normal displacement u_z (shown simply as σ, u from now on, because only a normal force is applied on the free surface of the transversely isotropic viscoelastic

solid) are related by the response function M :

$$M(\mathbf{q}, \omega) \sigma(\mathbf{q}, \omega) = u(\mathbf{q}, \omega) \quad (5)$$

The response function M can be easily calculated by taking the Fourier transform of Eq. 4 and substituting in Eq. 5.

$$M(\mathbf{q}, \omega) = \frac{2D}{|\mathbf{q}|} \quad (6)$$

When the transversely isotropic half-space is viscoelastic, the independent elastic constants are dependent on the excitation frequency ω , therefore in this case, D depends on the frequency of the applied load which is related to the sliding velocity and the wave vector of the roughness, $\omega = \mathbf{q} \cdot \mathbf{v}$. Consider the contact at a length scale $= L/\zeta$, where L is the diameter of the macroscopic contact area and ζ is the magnification factor. It is assumed that rough surfaces are isotropic, so just the amplitude of the wave vector $|\vec{q}| = q = 2\pi/\lambda$ is important and not its direction. The probability distribution of the normal stress σ , in the contact area at a fixed magnification factor ζ namely called as $P(\sigma, \zeta)$ can be written as:

$$P(\sigma, \zeta) = \langle \delta(\sigma - \sigma_1(\mathbf{x}, \zeta)) \rangle \quad (7)$$

where $\sigma_1(\mathbf{x}, \zeta)$ is the stress which occurs in a contact area on the length scale λ . It can be shown that the stress probability distribution $P(\sigma, \zeta)$ satisfies the diffusion equation below [15]:

$$\frac{\partial P(\sigma, \zeta)}{\partial \zeta} = f(\zeta) \frac{\partial^2 P(\sigma, \zeta)}{\partial \sigma^2} \quad (8)$$

It can be shown that the diffusivity function $f(\zeta)$ which has a general form $\frac{1}{2} \frac{\langle (\Delta \sigma)^2 \rangle}{\Delta \zeta}$ is related to the transformation matrix [15]:

$$f(\zeta) = \frac{1}{2} \frac{\langle (\Delta \sigma)^2 \rangle}{\Delta \zeta} = \frac{1}{2} q q_L \quad (9)$$

$$\times \int_0^{2\pi} d\theta |M^{-1}(\mathbf{q}, \mathbf{q} \cdot \mathbf{v})|^2 C(\mathbf{q})$$

where $C(\mathbf{q})$ is the spectral density of the roughness and is defined by [30]:

$$C(\mathbf{q}) = \frac{1}{(2\pi)^2} \int d^2x \langle h(\mathbf{x}) h(0) \rangle e^{-i(\mathbf{q} \cdot \mathbf{x})} \quad (10)$$

If one defines $g(\zeta) = f(\zeta)/\sigma_0^2$ for simplicity, where $\sigma_0 = F_0/A_0$ is the nominal stress applied to the transversely isotropic viscoelastic solid at length scale L (or at nominal contact area A_0) and considering isotropy in the surface roughness, then it has been shown that

$$P(\zeta) = \frac{2}{\pi} \int_0^\infty dx \frac{\sin x}{x} \quad (11)$$

$$\times \exp[-x^2 \int_1^\zeta d\zeta' g(\zeta')]$$

$$G(q) = \int_1^\zeta d\zeta' g(\zeta') = \frac{1}{2} \int_{q_L}^q q dq C(q)$$

$$\times \int_0^{2\pi} d\theta \frac{|M^{-1}(q, q \cdot v)|^2}{\sigma_0^2} \quad (12)$$

where θ is the angle between the velocity vector and the wave vector $\vec{q}$. One can show that the frictional stress at the surface can be governed by:

3 Numerical Results

$$\begin{aligned} \sigma_{hys} = & -i \int dq q^2 C(q) \\ & \times \int_0^{2\pi} d\theta \cos \theta M^{-1}(q, q.v) \end{aligned} \quad (13)$$

The friction coefficient, per definition is defined as $\mu_{hys} = F_{hys}/F_0 = \sigma_{hys}A(q)/\sigma_0A_0 = \sigma_{hys}P(q)/\sigma_0$ and can be calculated from,

$$\begin{aligned} \mu_{hys} = & \frac{-i}{\sigma_0} \int dq q^2 C(q) P(q) \\ & \times \int_0^{2\pi} d\theta \cos \theta M^{-1}(q, q.v) \end{aligned} \quad (14)$$

where the relative fraction of the contact area $P(q) = A(q)/A_0$ (the ratio between the contact area at wave-vector q , where the rough surface is assumed to be smooth for all wave-vectors higher than q and the nominal contact area at wave-vector q_L , or wave-length L) is,

$$P(q) = \frac{2}{\pi} \int_0^\infty dx \frac{\sin x}{x} \exp[-x^2 G(q)] \quad (15)$$

$$\begin{aligned} G(q) = & \frac{1}{2} \int_{q_L}^q q dq C(q) \\ & \times \int_0^{2\pi} d\theta \frac{|M^{-1}(q, q.v)|^2}{\sigma_0^2} \end{aligned} \quad (16)$$

The ratio of the real area of contact to the apparent area of contact and the hysteresis contribution to the overall friction in sliding contact between a transversely isotropic viscoelastic solid and a rough rigid counter surface can be then calculated by replacing Eq. 6 into Eqs. 14 to 16.

The effect of the anisotropy on the contact area and the hysteresis contribution of a viscoelastic material on the overall friction is examined by the presented contact and friction model. The dynamical mechanical properties of a rubber compound are used for this goal. The normalized modulus of elasticity of an isotropic viscoelastic rubber compound together with a surface roughness power spectra are depicted in Fig. 2.

To study the sensitivity of the presented model to an increase in loss or storage modulus and investigate the importance of anisotropy in the form of transversely isotropy on the contact and friction of a viscoelastic solid, the following sensitivity analysis is performed; the presented isotropic material is virtually reinforced (reinforcement is performed by increasing both the storage and loss modulus independently, by a factor of 2.5, for the whole frequency range, in the direction of indentation) while all the other mechanical properties (such as Poisson's ratio) are kept constant. One should note that the mechanical properties in a linear viscoelastic solid obey Kramers-Kronig relation [31]. In the linear regime, loss and storage moduli cannot change independently, however, in this section a sensitivity analysis is performed to study the effect of different parameters on contact independently. In other words, for the isotropic solid, $E_x = E_y = E_z = E' + i E''$. The elastic moduli for the first transversely isotropic solid are governed by $(E_x)_{R1} = (E_y)_{R1} = E' + i E''$, $(E_z)_{R1} = 2.5E' + i E''$.

Figure 2: Normalized modulus of elasticity of an isotropic viscoelastic material (tire tread) (a) and the power spectral density of a rigid surface roughness in contact with the rubber (b).

The mechanical properties of the second transversely isotropic solid are determined by the following relations, $(E_x)_{R2} = (E_y)_{R2} = E' + i E''$, $(E_z)_{R2} = E' + 2.5i E''$. The dynamic mechanical properties and the surface roughness power spectral density presented in Fig. 2 are used to calculate the hysteresis coefficient of friction as a function of sliding velocity for the isotropic viscoelastic solid and the two transversely isotropic materials. The calculated hysteresis coefficient of friction is illustrated in Fig. 3.

The real area of contact can also play a significant role in determining the overall friction [32]. The real area of contact decreases with an increase in the sliding velocity, therefore the ratio between the real area of contact to the apparent contact area is shown for a sliding velocity of 5 mm/s to study the effect of transversely isotropy. The results

are demonstrated in Fig. 4.

Figure 3: Hysteresis coefficient of friction as a function of velocity for an isotropic viscoelastic solid and two transversely isotropic viscoelastic solids.

Figure 4: Variation of real area of contact over nominal contact area as a function of magnification for sliding velocity of 5 mm/s for an isotropic viscoelastic solid and two transversely isotropic viscoelastic solids.

The numerical results show that anisotropy in the class of transversely isotropy has a significant effect on both, the hysteresis coefficient of friction and the real area of contact and should not be neglected. Additionally, the presented contact and friction model will be validated by experimental results in the next section.

4 Materials and Experimental Methods

4.1 Materials

A transversely isotropic elastomer composite is prepared to validate the contact and friction model presented above. The rubber matrix used in this study is based on a blend of a 37.5 wt% oil-extended solution-polymerized styrene-

butadiene rubber (S-SBR) and high-cis-polybutadiene (BR) with a rubber ratio of 70/30 phr (excluding the extender oil in the S-SBR). An overview of the rubber compound prepared with the corresponding amounts of the components is given in Table 1. The rubber sample is prepared based on a common “Green Tire”, silica-reinforced passenger car tire tread [33]. The rubber sample is filled with 80 parts per hundred rubber (phr) of highly dispersible silica 1165 MP and reinforced with 20 phr of poly (p-phenylene terephthalamide) (PPTA) fibers. In order to provide sufficient connection between silica particles and polymer compound, bis (tri-ethoxy-silyl propyl) tetrasulfide (TESPT) as a coupling agent is used according to the commonly accepted optimum level for a silica reinforced elastomer [34].

Orientation of the fibers in fiber reinforced composites has a significant role on the mechanical behavior of the composite materials [35]. Fibers in a reinforced elastomer are oriented during processing and consequent fabrication which is dependent on the nature of the flow, i.e. convergent, divergent, and elongational or shear. Unidirectional orientation can be governed by shear flow [36]. Although, not all the fibers can orient to the desired direction, usually a high degree of fiber orientation is achieved by repetitive passing through a two-roll mill in a milling process. The fibers are prone to damage during milling. Therefore the poly (p-phenylene terephthalamide) (PPTA) fibers were selected to withstand the shear forces during the orientation process in the mill. Moreover, the fibers were selected to be sufficiently thin

Table 1: Rubber formulation of prepared sample with the amounts of components indicated in weight parts of component per hundred weight parts of the rubber (phr).

Compound	Content (phr)	Supplier
S-SBR	96.3	Buna VSL 5025-2 HM Lanxess, Leverkusen, Germany
BR	30	Kumho KBR Seoul, S-Korea
Silica (1165 MP)	80	Rhodia Silices, Lyon, France
TESPT	7	Evonik GmbH, Essen, Germany
TDAE	6.7	Hansen & Rosenthal, Hamburg, Germany
Stearic acid	2.5	Sigma Aldrich, St. Louis, United states
6PPD	2	Flexsys Brussels, Belgium
TMQ	2	Flexsys Brussels, Belgium
PPTA	20	Teijin BV, Arnhem, the Netherlands
Sulfur	1.4	Sigma Aldrich, St. Louis, United state
TBBS	1.7	Flexsys Brussels, Belgium
ZnO	2.5	Sigma Aldrich, St. Louis, United states
DPG	2	Flexsys Brussels, Belgium

and closely spaced, so that the material appears homogeneous on the length scales which matter for friction. To improve the adhesion between the fibers and the rubber matrix, fibers were coated chemically. The unidirectional orientation of the fibers results in different mechanical properties in the direction parallel to the fibers than in the transverse plane, therefore the prepared rubber composite can be assumed to be transversely isotropic viscoelastic.

Reinforced rubbers behave nonlinearly at relatively high strains. Mechanical properties of the rubbers at higher strains is a complex problem and is still subject of several studies. The tensile test performed on the prepared sample shows that the mechanical behaviour can be assumed to be linear up to 30% of strain. Above this limit the bonding between the fiber and

matrix is affected and as a consequence the integrity of the material is lost. Up to this limit, the material behaviour is linear.

Figure 5: Tensile test performed on the fiber reinforced rubber shows that the material behaves linearly up to 30% of strain.

4.2 Viscoelasticity of Compounds

To characterize the fiber orientation, the mechanical properties of the elastomeric composite are measured [37]. The time/temperature dependent mechanical properties of the prepared sample are measured along different axes. A Metravib DMA 2000 dynamic spectrometer is used to measure the dynamic properties. Frequency-dependent elasticity modulus measurements in tension mode is performed at different temperatures between -30 and 50°C , each varying the frequency between 1 and 200 Hz . The reference temperature $T_{ref} = 27^\circ\text{C}$ is selected to shift the measured elastic modulus $E(\omega)$ versus frequency ω both horizontally and vertically. The elastomer has similar properties in the plane perpendicular to the fiber orientation (along x and y axes) but different properties in the direction parallel to the fiber orientation (z direction) as shown in Fig. 6.

The master curves of the normalized elasticity moduli as a function of frequency are shown in Fig. 7 just for two of the directions, simply because the properties along x and y axes are similar (as the definition of a transversely isotropic material). The normalized storage (loss) modulus is obtained as the ratio of the modulus at a given frequency and the value of the minimum storage (loss) modulus when the loading direction is perpendicular to the fiber orientation. The modulus of elasticity is higher when the load is applied in the same direction as the fiber orientation. This is the case because the fibers contribute in carrying

the load when the load is applied in the same direction as the fiber's orientation. The difference between the measured loss moduli of elasticity (when the load is applied in two different directions regarding the fiber orientation) is less in comparison with the difference between the storage moduli since the viscoelastic losses are mainly due to the rubber matrix which is the same in both cases. However, the contribution of the fibers to the storage modulus is much more when the applied force is in the same direction as the fiber orientation. This observation is more distinct for higher frequencies.

Figure 6: Uniaxial fiber reinforced rubbers with fibers oriented parallel (left) and perpendicular (right) to the loading direction. The angle between the loading direction and the fibers orientation is shown.

4.3 Friction tests

In order to validate the presented contact and friction model, the hysteresis contribution to the overall friction between rubber and two rough rigid surfaces is measured by a ball-on-disk setup. The contribution from the hysteresis component of friction is decoupled from

Figure 7: Shifted and normalized storage (a) and loss (b) moduli of elasticity as a function of frequency when the angle between loading and fiber orientation are 0 and 90 degrees.

the total friction by a simple experiment; the rubber surface is wetted by a very thin layer of oil (Ondina 927 with a dynamic viscosity of 78 *mPas* at 20°C) such that the lubricated tribo-system remains in the boundary lubrication regime.

Two granite spheres with a diameter of 30 *mm* but with different micro roughness are prepared, namely smooth and rough. Two different scanning techniques are used to measure the roughness; confocal microscopy and atomic force microscopy (AFM) in the contact mode. The confocal microscope measurements as well as the calculated power spectral density of the roughness of the granite balls are shown in Fig. 8 for both the rough and smooth granite surfaces. The confocal microscopy and atomic force microscopy measurements provide consistent measurements. As illustrated, the granite surface is self-fractal. The

slope of the power spectrum in the self-affine fractal region for rough and smooth granites correspond to the Hurst exponent $H = 0.85$ and $H = 0.88$ or fractal dimension $D_f = 3 - H = 2.12$ and $D_f = 2.15$ respectively that is very typical for most surfaces [38].

The arithmetic average roughness of the smooth and rough surfaces is measured to be 0.73 and 6.47 μm respectively, on an area of $286 \times 200 \mu\text{m}$. Friction is measured with sliding velocities of 5, 50, 200 and 400 *mm/s* and the nominal contact pressure is 1.5 *MPa*. All the measurements are performed under controlled environmental conditions: The temperature is kept constant at 27°C and the relative humidity at 50%. The hysteresis component of friction in contact with the smooth and rough granite counter surfaces was measured under the operational conditions mentioned and at steady state situation.

Figure 8: The roughness is measured using two techniques: confocal microscope and AFM in contact mode. The smooth (a) and rough (b) counter surfaces measured by confocal microscope in the wave vector range $1.58 \times 10^4 \text{ m}^{-1} \leq q \leq 9.77 \times 10^5 \text{ m}^{-1}$ are shown. The power spectral density of the roughness (c) is calculated from both confocal microscope and AFM measurements (in the range $9.77 \times 10^5 \text{ m}^{-1} \leq q \leq 7.07 \times 10^8 \text{ m}^{-1}$).

Figure 9: Hysteresis coefficient of friction as a function of velocity for the transversely isotropic viscoelastic rubber disk in contact with a relatively rough and smooth granite sphere.

Figure 10: Hysteresis coefficient of friction as a function of velocity for the transversely isotropic viscoelastic rubber disk in contact with a relatively rough and smooth granite sphere.

The mechanical properties of the rubber measured in the indentation direction and the transverse plane (presented in Sect. 4.2) together with the presented model are used to calculate the hysteresis component of friction and the real area of contact. The results are shown in Fig. 9 and Fig. 10. The experimental

results are rather in agreement with the presented model.

The hysteresis component of friction is higher in the contact between the rougher granite ball and the rubber. This matches with the experimental measurements. On the other hand, the real area of contact is higher when a smoother granite sphere is in contact which confirms the importance of the real area of contact component in the overall friction in contact of smoother surfaces.

5 Discussion

It was shown in Sect. 3 that any increase in the elasticity in the normal direction leads to a decrease in the area of contact (see Fig. 4). This is the case, simply because the contact stiffness is increased. Obviously, increasing the storage modulus in the loading direction has greater influence on the area of contact. On the other hand, an increment in the loss/storage modulus changes the hysteresis friction coefficient in a different manner. Evidently, the hysteresis component of friction originates from the loss modulus. Therefore, the hysteresis friction is increased by an increment in the loss modulus. However, an increase in the storage modulus increases the contact stiffness, consequently the indentation depth decreases. A lower strain brings about a lower hysteresis. This different effect of reinforcement in loss/storage modulus on the hysteresis coefficient of friction is shown in Fig. 3. Depending on the tribological conditions, hysteresis or area of contact might be the dominant contributor in the friction. This

analysis is required in a smart design of several engineering applications where a transversely isotropic viscoelastic material is used.

Considering Eqs. 6, 14-16 and the definition of the D function, one can conclude that the ratio of the real area of contact to the nominal contact area P scales with the absolute value of D . The hysteresis component of friction scales with the ratio between the imaginary part of D and its amplitude. The sensitivity of the hysteresis coefficient of friction and the contact area to a virtual increase of the both loss and storage moduli in the indentation direction was discussed. The effect of a mutual increase of the elasticity (equal increase in both loss and storage moduli) in the both indentation direction and in the plane of isotropy in comparison with an isotropic material are discussed here; increasing both the loss and the storage moduli in the indentation direction (unlike an individual increase in storage or loss moduli that decreases and increases the hysteresis component of friction respectively) does not change the hysteresis contribution severely. However, it reduces the real area of contact. The hysteresis component of friction is more sensitive to the frequency variation of the complex elastic modulus in this case. On the other hand, increasing both the loss and the storage moduli in the plane of isotropy equally, increases the hysteresis coefficient and decreases the area of contact.

A difference between the numerical results of the contact model and the experiments is seen in Fig. 9. This difference can be explained by the Poisson's ratio in different directions. The viscoelastic

anisotropic rubber studied experimentally has a low anisotropy, therefore, in the numerical calculations, the Poisson's ratio was assumed to be the same in all directions and similar to isotropic rubbers ($\nu = 0.45$). However, the exact Poisson's ratio might be different at different directions (as mentioned in Sect. 2.1) which can be accurately measured by novel methods [39]. Not precise determination of the Poisson's ratio might result in a disagreement between the model and the experiments for a material with high anisotropy. Therefore accurate characterization of the mechanical properties should be considered when dealing with transversely isotropic materials with significant different properties in the different directions.

6 Summary and Conclusions

Many artificial and natural materials such as fibrous composites behave as transversely isotropic solids. Transversely isotropic materials are a unique group of materials whose properties are the same along two of the principal axes. This type of anisotropy may have advantages in engineering and industrial applications. Therefore, studying the tribological behavior of this group of materials is of interest.

In modelling the contact between two rough surfaces, multi-asperity contact models have attained accepted results which are of practical worth, however, the main disadvantage of such models is neglecting the interactions between

neighboring microcontacts. The effect of the asperities on each other cannot be neglected when considering soft materials like rubbers or soft biological tissues, as these flexible materials can deform much easier and therefore the problem of neglecting interactions between asperities is doubtful especially when approaching full contact. The advantage of the contact model presented by Persson [15] is that it does not pre-exclude any scale of roughness from the analysis. This study extends the contact and friction model of Persson for transversely isotropic viscoelastic solids.

It was shown that anisotropy in mechanical properties (in the form of transversely isotropy) can significantly change contact and friction. This is established by comparing the numerical results governed for an isotropic solid using Persson's contact model and transversely isotropic solids, using the presented model. Moreover, the extended model has been validated using friction measurements. A unidirectional fiber reinforced rubber disk with similar properties in two principle axes and different mechanical properties along the third principle axis is prepared. The friction results governed by pin-on-disk apparatus, using two different rough surfaces validate the model.

7 References

- [1] J.R. Willis. Hertzian contact of anisotropic bodies. *Journal of the Mechanics and Physics of Solids*, 14(3):163–176, 1966.
- [2] J.R. Willis. Boussinesq problems for an anisotropic half-space. *Journal of the Mechanics and Physics of Solids*, 15(5):331–339, 1967.
- [3] F.M. Borodich. Hertz contact problems for an anisotropic physically nonlinear elastic medium. *Strength of Materials*, 21(12):1668–1676, 1989.
- [4] F.M. Borodich. The Hertz frictional contact between nonlinear elastic anisotropic bodies (the similarity approach). *International Journal of Solids and Structures*, 30(11):1513–1526, 1993.
- [5] A. Delafargue and F.-J. Ulm. Explicit approximations of the indentation modulus of elastically orthotropic solids for conical indenters. *International Journal of Solids and Structures*, 41(26):7351–7360, 2004.
- [6] I.I. Argatov. Depth-sensing indentation of a transversely isotropic elastic layer: Second-order asymptotic models for canonical indenters. *International Journal of Solids and Structures*, 48(25-26):3444–3452, 2011.
- [7] A.E. Green and W. Zerna. Theoretical elasticity. *Dover, New York*, 1968.
- [8] H.D. Conway, K.A. Farnham, and T.C. Ku. The indentation of a transversely isotropic half space by a rigid sphere. *Journal of Applied Mechanics*, 34(2):491–492, 1967.
- [9] J.A. Greenwood and J.B.P. Williamson. Contact of nominally flat surfaces. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, 295(1442):300–319, 1966.
- [10] J.A. Greenwood and J.J. Wu. Surface roughness and contact: An apology. *Meccanica*, 36(6):617–630, 2001.
- [11] J.A. Greenwood. A simplified elliptic model of rough surface contact. *Wear*, 261(2):191–200, 2006.
- [12] M. Paggi and M. Ciavarella. The coefficient of proportionality κ between real contact area and load, with new asperity models. *Wear*, 268(7-8):1020–1029, 2010.
- [13] L. Afferrante, G. Carbone, and G. Demelio. Interacting and coalescing hertzian asperities: A new multiasperity contact model. *Wear*, 278-279(0):28–33, 2012.

- [14] V.A. Yastrebov, G. Anciaux, and J-F. Molinari. From infinitesimal to full contact between rough surfaces: Evolution of the contact area. *International Journal of Solids and Structures*, 52:83–102.
- [15] B.N.J. Persson. Theory of rubber friction and contact mechanics. *Journal of Chemical Physics*, 115(8):3840–3861, 2001.
- [16] W. Manners and J.A. Greenwood. Some observations on persson's diffusion theory of elastic contact. *Wear*, 261(5-6):600–610, 2006.
- [17] B.N.J. Persson. On the elastic energy and stress correlation in the contact between elastic solids with randomly rough surfaces. *Journal of Physics Condensed Matter*, 20(31), 2008.
- [18] A. Almqvist, C. Campañá, N. Prodanov, and B.N.J. Persson. Interfacial separation between elastic solids with randomly rough surfaces: Comparison between theory and numerical techniques. *Journal of the Mechanics and Physics of Solids*, 59(11): 2355–2369, 2011.
- [19] G. Carbone and F. Bottiglione. Contact mechanics of rough surfaces: a comparison between theories. *Meccanica*, 46(3):557–565, 2011.
- [20] G. Carbone, B. Lorenz, B.N.J. Persson, and A. Wohlers. Contact mechanics and rubber friction for randomly rough surfaces with anisotropic statistical properties. *The European Physical Journal E*, 29(3):275–284, 2009.
- [21] M.H. Malakooti, H-S. Hwang, and H.A. Sodano. Morphology-controlled zno nanowire arrays for tailored hybrid composites with high damping. *ACS Applied Materials & Interfaces*, 7(1):332–339, 2015.
- [22] D.F. Moore. *The friction and lubrication of elastomers*. Pergamon Press, Oxford, New York, 1972.
- [23] P. Wriggers and J. Reinelt. Multi-scale approach for frictional contact of elastomers on rough rigid surfaces. *Computer Methods in Applied Mechanics and Engineering*, 198(21-26):1996–2008, 2009.
- [24] B. Lorenz, B.N.J. Persson, S. Dieluweit, and T. Tada. Rubber friction: Comparison of theory with experiment. *European Physical Journal E*, 34(129):11129, 2011.
- [25] B. Lorenz, B.N.J. Persson, G. Fortunato, M. Giustiniano, and F. Baldoni. Rubber friction for tire tread compound on road surfaces. *Journal of Physics Condensed Matter*, 25(9):095007, 2013.
- [26] X-D. Pan. Wet sliding friction of elastomer compounds on a rough surface under varied lubrication conditions. *Wear*, 262(5-6):707–717, 2007.
- [27] M. Mokhtari, D.J. Schipper, and T.V. Tolpekina. On the friction of carbon black- and silica-reinforced br and s-sbr elastomers. *Tribology Letters*, 54(3):297–308, 2014.
- [28] M. Mokhtari, D.J. Schipper, N. Vleugels, and J.W.M. Noordermeer. Existence of a tribo-modified surface layer on sbr elastomers: Balance between formation and wear of the modified layer. *Tribology Lett*, 58(2):1–13, 2015.
- [29] H. Hai-chang. On the equilibrium of a transversely isotropic elastic half space. *Science china mathematics*, (4):463–479, 1954.
- [30] B.N.J. Persson, O. Albohr, U. Tartaglino, A.I. Volokitin, and E. Tosatti. On the nature of surface roughness with application to contact mechanics, sealing, rubber friction and adhesion. *Journal of Physics Condensed Matter*, 17(1):R1–R62, 2005.
- [31] B. Lorenz, W. Pyckhout-Hintzen, and B.N.J. Persson. Master curve of viscoelastic solid: Using causality to determine the optimal shifting procedure, and to test the accuracy of measured data. *Polymer*, 55(2):565–571, 2014.
- [32] M. Mokhtari and D.J. Schipper. Existence of a tribo-modified surface layer of br/s-sbr

- elastomers reinforced with silica or carbon black. *Tribology International (Article in press)*, (2014).
- [33] R. Rauline. Rubber compound and tires based on such a compound (to compagnie generale des etablissements Michelin), EU 0501227 (1992).
 - [34] L. Guy, S. Daudey, P. Cochet, and Y. Bomal. New insights in the dynamic properties of precipitated silica filled rubber using a new high surface silica. *KGK Kautschuk Gummi Kunststoffe*, 62(7-8):383–391, 2009.
 - [35] H.W. Wang, H.W. Zhou, L.L. Gui, H.W. Ji, and X.C. Zhang. Analysis of effect of fiber orientation on Young’s modulus for unidirectional fiber reinforced composites. *Composites Part B: Engineering*, 56(0):733–739, 2014.
 - [36] V.G. Geethamma, K. Thomas Mathew, R. Lakshminarayanan, and S. Thomas. Composite of short coir fibres and natural rubber: effect of chemical modification, loading and orientation of fibre. *Polymer*, 39(6-7):1483–1491, 1998.
 - [37] M. Ashida. *Composites of polychloroprene rubber with short fibres of poly(ethylene terephthalate) and nylon*, chapter 5, pages 116–143. Woodhead Publishing, 1996.
 - [38] B.N.J. Persson. On the fractal dimension of rough surfaces. *Tribology Letters*, 54(1):99–106, 2014.
 - [39] R.H. Pritchard, P. Lava, D. Debruyne, and E.M. Terentjev. Precise determination of the poisson ratio in soft materials with 2d digital image correlation. *Soft Matter*, 9(26):6037–6045, 2013.

Existence of a tribo-modified surface layer of BR/S-SBR elastomers reinforced with silica or carbon black

M. Mokhtari, D.J. Schipper

Tribology International(2014), Article in press

ARTICLE IN PRESS

Tribology International 4 (2014) 100–109

Contents lists available at ScienceDirect

Tribology International

journal homepage: www.elsevier.com/locate/triboint

Existence of a tribo-modified surface layer of BR/S-SBR elastomers reinforced with silica or carbon black

Milad Mokhtari^{a,*}, Dirk J. Schipper

University of Twente, Faculty of Engineering Technology, Surface Technology and Tribology, P.O. Box 217, 7500 AE, Enschede, The Netherlands

ARTICLE INFO

Article history:

Received 10 July 2014

Received in revised form 13 September 2014

Accepted 16 September 2014

Keywords:

Friction-modified surface layer

AFM nano-indentation

Mechanical properties

Rubber friction

ABSTRACT

The existence of a modified surface layer on top of a rubber disk, in contact with a rigid counter-surface, is still a point of discussion. In this study, we show that a modified surface layer with different mechanical properties exists. Modification of the reinforced elastomers is discussed and the subsequent effect of existence of such a layer on the friction is emphasized. The elasticity modulus both inside and outside the wear track is determined by atomic force microscope nano-indentations and compared with the macro-scale mechanical properties measured using dynamical mechanical analysis. The elastic modulus inside the wear track is lower than the bulk. Internalizing the tribological conditions by means of increasing normal pressure and sliding velocity will result in a greater loss of mechanical properties.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Rubber friction has interested many researchers because of its huge practical importance. Various industrial applications, such as tires, rubber seals, wiper blades, conveyor belts and syringes, require detailed knowledge about rubber friction [1–6]. Although great interest has been kindled by studying the tribological behavior of rubber sliding contacts over the last 50 years, the friction problem is not yet fully understood. This is because several parameters, such as contact pressure, (sliding) velocity, temperature, surface roughness and morphology of the rubber compounds, all play a role in the friction of elastomers in contact with solid surfaces.

Historically, the friction force between rubber and a rough surface was considered the sum of two main contributors, commonly described as the adhesion and the hysteresis components [7]. Because of the complex nature of the rubber friction problem and the various factors that affect the friction, contradictory results have been reported among different researchers. There has been an ongoing debate among researchers as to which component makes the major contribution to the overall friction. Adhesion is related to the intermolecular attractive forces between the contacting bodies [8]. Dissipation of energy in the bulk of the material because of cyclic deformation of the rubber, which has been caused by exerted oscillating forces of asperities of a rough surface, generates the hysteresis component of friction [9]. In the early works of Persson [10], hysteresis was regarded as the major contributor to rubber friction; however, this was not in agreement with results of other researchers. Le Gal and others [11] found that adhesion plays the dominant role. In a recent paper published by Lorenz et al. [12], some other contributors to rubber friction are considered: energy dissipation due to crack opening and energy dissipation in shearing of a thin viscous film [13]. Fan [14] emphasizes the significance of interfacial interactions in determining the wet sliding friction of elastomer compounds in his research. One can summarize all the friction force contributions in terms of two main forces: (1) the contribution of the viscoelastic deformation of the rubber; and (2) the contribution from the area of contact defined as:

$$F_f = F_{\text{vis}} + \tau_f A_{\text{real}} \quad (1)$$

where F_{vis} are the forces concerning the total friction and the contribution from the hysteresis losses, respectively; $\tau_f A_{\text{real}}$ are the frictional shear stress and real area of contact, both depending on the velocity, temperature, sliding history, nominal normal stress, and so on.

1.1. Modified surface layer

Many researchers have shown changes in both the mechanical properties and the chemical compositions of the rubber surface, which is in contact with the counter-surface in comparison with the bulk or with the non-contact parts of the rubber surface [15–21]. These changes are of importance in modelling the rubber friction. In various friction models [11–13], the values for τ_f – the frictional shear stress due to shearing a thin modified layer (see Fig. 1) – are selected (calculated) so that the theoretical model results and

* Corresponding author.
E-mail address: m.mokhtari@utwente.nl (M. Mokhtari).

<http://dx.doi.org/10.1016/j.triboint.2014.09.021>
0301-4796/2014 Elsevier Ltd. All rights reserved.

Please cite this article as: Mokhtari M, Schipper DJ. Existence of a tribo-modified surface layer of BR/S-SBR elastomers reinforced with silica or carbon black. Tribology International (2014). <http://dx.doi.org/10.1016/j.triboint.2014.09.021>

Existence of a tribo-modified surface layer of BR/S-SBR elastomers reinforced with silica or carbon black

M. Mokhtari and D.J. Schipper

Surface Technology and Tribology, Faculty of Engineering Technology, University of Twente,
P.O. Box 217, 7500 AE Enschede, The Netherlands

Abstract

The existence of a modified surface layer on top of a rubber disk, in contact with a rigid counter-surface, is still a point of discussion. In this study, we show that a modified surface layer with different mechanical properties exists. Modification of the reinforced elastomers is discussed and the subsequent effect of existence of such a layer on the friction is emphasized. The elasticity modulus both inside and outside the wear track is determined by atomic force microscope nano-indentations and compared with the macroscale mechanical properties measured using dynamical mechanical analysis. The elastic modulus inside the wear track is lower than the bulk. Intensifying the tribological conditions by means of increasing normal pressure and sliding velocity will result in a greater loss of mechanical properties.

1 Introduction

Rubber friction has interested many researchers because of its huge practical importance. Various industrial applications, such as tires, rubber seals, wiper blades, conveyor belts and syringes, require detailed knowledge about rubber friction [1–6]. Although great interest has been kindled by studying the tribological behavior of rubber sliding contacts over the last 50 years, the friction problem is not yet fully understood. This is because several parameters, such as contact pressure, (sliding) velocity, temperature, surface roughness and morphology of the rubber compounds, all play a role in the friction of elastomers in contact with solid

surfaces.

Historically, the friction force between rubber and a rough surface was considered the sum of two main contributors, commonly described as the adhesion and the hysteresis components [7]. Because of the complex nature of the rubber friction problem and the various factors that affect the friction, contradictory results have been reported among different researches. There has been an ongoing debate among researchers as to which component makes the major contribution to the overall friction. Adhesion is related to the intermolecular attractive forces between the contacting bodies [8]. Dissipation of energy in the bulk of the material because

of cyclic deformation of the rubber, which has been caused by exerted oscillating forces of asperities of a rough surface, generates the hysteresis component of friction [2]. In the early works of Persson [9], hysteresis was regarded as the major contributor to rubber friction; however, this was not in agreement with results of other researchers; Le Gal and others [10] found that adhesion plays the dominant role. In a recent paper published by Lorenz et al. [11], some other contributors to rubber friction are considered: energy dissipation due to crack opening and energy dissipation in shearing of a thin viscous film [12]. Pan [13] emphasizes the significance of interfacial interactions in determining the wet sliding friction of elastomer compounds in his research.

Figure 1: A granite semi-sphere in sliding contact with rubber is shown schematically. The contributions to friction from (i) shearing of a thin modified surface layer (τ_f) and (ii) hysteresis in the bulk of the rubber are demonstrated.

One can summarize all the friction force contributions in terms of two main forces: (1) the contribution of the viscoelastic deformation of the rubber and (2) the contribution from the area of

contact defined as:

$$F_f = F_{vis} + \tau_f A_{real} \quad (1)$$

where F_f , F_{vis} are the forces concerning the total friction and the contribution from the hysteresis losses respectively; τ_f , A_{real} are the frictional shear stress and real area of contact, both depending on the velocity, temperature, sliding history, nominal normal stress, etc.

1.1 Modified Surface Layer

Many researchers have shown changes in both the mechanical properties and the chemical compositions of the rubber surface, which is in contact with the counter-surface in comparison with the bulk or with the non-contact parts of the rubber surface [14–20]. These changes are of importance in modelling the rubber friction. In various friction models [10–12], the values for τ_f — the frictional shear stress due to shearing a thin modified layer (see Fig. 1) — are selected (calculated) so that the theoretical model results and experiments fit. Moreover, in some cases [11], the selection of these constants has been supported by molecular dynamic simulations [21]. However, no model has yet been presented that can predict the changes in the modified rubber layer properties. Moreover, there is no agreement between the different studies about the determination of the driving phenomena for this change in properties. Kocsis et al. [16] attributed fibril formation and smearing of the overall rubber surface, shown in their work, to tribo-chemical reactions and thermo-oxidative degradation of the rubbers studied. On the other hand, Martínez

et al. [14] performed similar experiments and showed that no thermo-oxidation processes occur because of friction tests. Persson [22] believes that the formation of a modified surface layer is a mechanical-chemical process involving the breaking of chemical bonds followed by the formation of new bonds. The resulting thermal and stress-induced degradation ends up with a thin layer of modified rubber at the surface. This process is activated thermally. Using the standard expression to describe activated processes and substituting some rough estimations for the activation energy for bond breaking and the stress necessary for bond breaking at zero temperature, a friction coefficient is acquired, which is in a good agreement with experimental results. However, hysteresis has been considered the main contributor to friction [22] even though it now appears that, depending on the tribological conditions, the role of shearing of a very thin confined rubber smear film can be very important [12, 23]. The shearing of confined films has also been simulated by molecular dynamics [21].

Nakazono et al. [17] showed that the mechanical properties of tire treads do change substantially after running at a speed of 100–150 *km/h* for ~ 1 *h*. This change was ascribed to the thermal and mechanical deterioration of the materials. It was, however, revealed in [17] (and references therein) that SBR vulcanizates are essentially immune from thermal and mechanical aging. It has been suggested [17] that another factor, such as an interaction between the rubber matrix and the added carbon black, should be considered to fully explain the change in mechanical properties of passenger car

tires after the road-running.

Wang and Kutsovsky [19, 20] studied the effect of silica and carbon black on the wet skid resistance of filled rubbers and showed the different effects of carbon black and silica in combination with water on the top skin of the worn surfaces. They showed that in silica-filled compounds, the top skin of the worn surface contains bare silica surface but carbon black aggregates remain covered by rubber in carbon black-filled samples. This claim was supported by atomic force microscope (AFM) investigations and measurements of the surface energies of the fillers and adsorption energies of various chemicals, analyzing the properties of filled vulcanizates.

The authors believe that gaining a quantitative insight into the changes of the modified surface layer is only possible by a detailed study of several tribo-systems (various types of rubber) under a range of sliding conditions (such as velocity, temperature and humidity).

1.2 Nanoscale Mechanical Characterization

The existence of a modified rubber layer, modified due to the interaction between the rubber and counter-surface, has been shown previously using scanning electron microscopy (SEM) imaging [18]. Even though the SEM technique can immediately provide helpful confirmation of the existence of the modified surface layer and its thickness, still, not all the rubber samples can be studied by SEM because of conductivity problems. Therefore, covering some samples with a thin layer of gold is inevitable,

which further increases doubts about the reliability of the images. Furthermore, no quantitative data (except about the thickness of the layer) is obtained about the properties of the modified surface layer.

The AFM is a probe-based microscope that allows the user to study the structure and morphology of surfaces under either ambient or aqueous conditions. Furthermore, it can be used to measure surface stiffness and adhesive properties, as the cantilever probe assembly can be considered a spring.

The AFM in tapping mode provides both height and phase contrast measurements of the surface. The proportionality of the phase shift between the driving force, and the actual tip oscillation with Young's modulus of the sample, has been reported [24]. Qualitative comparison between hard and soft samples is possible with tapping mode phase contrast images; however, quantitative information cannot be obtained.

On the other hand, AFM can be used as a depth-sensing instrument. It can record the load applied on the tip, that is, through cantilever deflection, and the relative displacement between the sample and the tip, that is, the penetration. A plot of the voltage applied to the piezo versus the voltage output of the position sensitive diode (PSD), monitoring cantilever deflection, is termed a raw force-displacement curve. After measuring some experimental quantities and performed some calibrations (see Sect. 2.4), a more commonly used load-penetration depth curve is obtained. The load-penetration depth curve can be used together with a

contact mechanics model to calculate the stiffness of the sample.

This technique has been successfully applied to both polymers and rubbers [25–27]. The viscoelastic properties of the samples can be obtained by performing measurements at various temperatures and/or indentation ratios [28, 29].

2 Materials and Methods

2.1 Materials

Four rubber samples, including 30 parts per hundred rubber (phr) butadiene rubber (BR) and 70 phr solution styrene-BR (S-SBR) are prepared. The samples are reinforced with two filler systems: carbon black (N375) and silica. An overview of the various rubber compounds prepared with the corresponding amounts (phr) of the components is presented in Table 1. The compounds are prepared by varying the amount of fillers, namely 100 and 70 phr of carbon black or silica. For silica-filled compounds, depending on the amount of silica, the amount of processing oil needed to functionalize and disperse the silica particles is varied. Bifunctional organosilanes, such as bis(triethoxysilylpropyl)-tetrasulphide (TESPT), are used (depending on the silica content) to chemically modify the silica surfaces to improve the compatibility of hydrocarbon rubbers and precipitated silica by modifying the surface of the silica. In this article, we refer to the samples as HC, LC, HS, LS, which correspond to high and low contents of carbon black (C) and silica (S).

Table 1: Various rubber compounds prepared with the amounts of components indicated in phr where HC: high carbon black content, LC: low carbon black content, HS: high silica content and LS: low silica content.

Compound	HC	LC	HS	LS
Description	phr	phr	phr	phr
BR, high cis	30	30	30	30
SSBR	70	70	70	70
N375	100	70	-	-
Silica	-	-	100	70
TESPT	-	-	7.8	5.5
Processing Oil	31	4	31	17
Sulphur	1.3	1.3	1.3	1.3
TBBS	1.3	1.3	1.3	1.3
DPG	2	2	2	2
ZnO	3	3	3	3
Stearic Acid	2	2	2	2
PVI	0.2	0.2	-	-
Anti-aging chemicals	6	6	6	6
Zinc salt of fatty acids	3	3	3	3

Figure 2: The Young's storage (a) and loss moduli (b) of elasticity as a function of temperature for different samples.

2.2 Viscoelasticity of Compounds

Viscoelastic properties of the samples at macroscale is measured using dynamical mechanical analysis (DMA). To determine the glass transition temperature of the samples, DMA in temperature sweep mode, under dynamic and static strains of 0.1 and 1%, respectively, at a fixed frequency of 10 Hz is used. The measured storage and loss modulus of elasticity of the four samples are shown in Fig. 2. Carbon black-filled samples are stiffer than silica-filled samples, and the modulus of elasticity increases with an increase in filler content.

The shear modulus $G(\omega)$ is measured in oscillatory shear mode at a constant strain amplitude of 0.1%, where the sample is fixed at both interfaces and sheared at a range of frequencies between 1 and 200 Hz . The whole procedure is then repeated for various temperatures between 20 and 85 $^{\circ}C$. The measured glass transition temperature and the selected reference temperature $T_{ref} = 27^{\circ}C$ are used to shift the measured shear modulus $G(\omega)$ versus frequency ω both horizontally and vertically. The calculated master curve for the modulus of elasticity as a function of frequency is shown in Fig. 3 for the LS rubber. The fact that no plateau is seen for the elastic modulus around room temperature suggests that (based on the time-temperature superposition principle) different mechanical behaviors should be expected when indenting at different loading rates, that is, different timescales. This is the case for the other three samples.

Figure 3: Shifted loss and storage shear modulus of elasticity as a function of frequency for one sample (low silica filled rubber).

2.3 Modified Surface Layer Generation

The friction tests are performed by a ball-on-disk setup shown schematically in Fig. 4 and under controlled environmental conditions. The tests are kept running until the measured friction force becomes stable or, in other words, until the surface layer is generated and the running-in phase is passed. The temperature was kept constant at 27 $^{\circ}C$ and the relative humidity at 50%. The counter surface against the rubber samples is a granite ball with a diameter of 30 mm with arithmetic average roughness of 0.52 μm . The effect of tribological conditions on mechanical properties of the rubber surface layer is studied by increasing both the sliding velocity and the normal contact pressure. Low severity tribological conditions is provided by tests performed with a sliding

velocity of 5 *mm/s* and under a contact pressure of 0.4 *MPa*. The tests with high severity are performed by increasing the sliding velocity to 300 *mm/s* and the contact pressure to 1.2 *MPa*.

2.4 AFM Nano-indentations

A Nanosurf Easyscan 2 type of AFM is used. The cantilever is a contact mode silicon probe (SHOCONA) with a nominal spring constant of 0.10 *N/m*. A low spring constant provides the opportunity to apply low loads and consequently low penetration depths. This implies very good resolution, which might be very useful for mapping mechanical properties of inhomogeneous materials, such as filled rubbers. Nano-indentations are performed with loads ranging from about 0.04 *nN* to 30 *nN* and indentation rates in the range $12 - 7.3 \times 10^9$ *nm/s*.

The voltage output from the PSD is translated into a cantilever deflection by deflection sensitivity, which is measured by indenting silicon at various indenter rates. The spring constant of the cantilever, which relates the cantilever deflection into the applied load, is measured according to the procedure proposed by Green [30]. The absolute roughness of the samples is in the order of a few *nm* on a $1 \mu\text{m} \times 1 \mu\text{m}$ scale. SEM micrographs are used to estimate both the cantilever dimensions and the tip shape.

Various contact mechanics models have been used for calculating the elastic modulus from AFM nano-indentation data. The models described by Oliver-Pharr [31], Hertz [32] and JKR/DMT [33, 34] are the three most frequently cited models in the literature. The

suitability of the Hertz contact model (or modified versions of it that consider adhesion) for describing force-penetration depth curves obtained by AFM nano-indentations is highly questionable. One basic assumption of this model is not satisfied: Hertz assumed that the radius of the contact is much smaller than the radius of the indenting sphere. However, this assumption is not valid when a sharp tip probe with a nominal radius of less than 10 *nm* is used. Moreover, it was discussed in [35] that the unloading part of the AFM nano-indentation curves cannot be used to extract information about the Young's modulus through, for example, the commonly used Oliver-Pharr analysis, therefore the loading part has been used to calculate the elasticity of the samples.

The cantilever tip has a pyramidal shape; however, the tip apex differs from ideal sharp pyramid and can be best modelled as a blunted pyramid. One can estimate the tip apex as a sphere and measure its radius using SEM imaging. For indentation depths lower than the apparent radius of curvature of the tip, simple contact models, such as Hertz [32] or Sneddon [36], for indenting a sphere into a flat surface can be used. On the other hand, for deeper indentations, they do fail to predict the force-penetration depth diagrams correctly. It has been shown in some researches [25, 28], penetrating into rubbers, that the load scales with penetration depth with an exponent of 1.5. We noted a slightly lower slope in our measurements. The difference can be explained by the shape of the cantilever tip; in the mentioned references, the cantilever tip was modelled as a paraboloid. A similar comparison is

Figure 4: (a) Ball-on-disk setup. (b) A typical cantilever deflection (force) plotted versus AFM piezo displacement, showing the loading and unloading curves. In the loading curve, when the cantilever is sufficiently close to the rubber surface and immediately before contact, van der Waals forces suddenly attract the cantilever tip. This is shown as snap-on point. In the unloading curve, adhesion between the cantilever tip and the rubber keeps them in contact till the snap-off point, where the detachment force is sufficient to overcome adhesion.

shown by Haugstad [37], between a load-penetration depth diagram for a sphere-ended cone indenting into a flat half-space material and a $3/2$ power curve for the classic Hertzian sphere. We used a contact model of blunted pyramidal tip indenting an elastic half-space [38] to quantitatively characterize the studied surfaces. A sample of a measured force/deflection-displacement curve is shown in Fig. 4.

3 Results

Images of the area to be indented are collected both before and after indentation. Images taken before indentation are used to check the surface roughness in the selected area. The surface roughness can substantially affect the

calculated elastic modulus by changing the tip-sample contact area and depth of penetration; therefore, a featureless, smooth region should be selected. Moreover, one should control whether plastic deformation occurs because of indentation. This is performed by images taken immediately after indentation. No evident residual imprint was detected after penetration, suggesting that only phenomena with viscoelastic nature are active during indentation.

The height maps obtained from both low and high portion-filled samples are shown in Fig. 5. Isolated particle morphologies are easily detectable. AFM nano-indentation results show a higher modulus of elasticity for isolated particles than for the rubber matrix, as seen elsewhere [39–41]. Moreover,

Figure 5: Height images obtained using the AFM Nanosurf Easyscan 2: (a) HC, (b) HS, (c) LC, (d) LS. An increase in the number of particles per area is easily detectable comparing (a) with (c) or b) with (d). Scan sizes: $6 \times 6 \mu\text{m}$.

the mechanical response of the isolated particles did not show any significant difference when changing the loading rate during indentation, suggesting that the isolated particles are not viscoelastic. In addition, an increase in the number of particles per area is seen as a result of an increase in the filler loading; therefore, the isolated particles are regarded as carbon black and silica filler particle units.

Nano-indentation measurements are performed on rubber matrixes, far from the filler particles and their surrounding interphase (as shown in references [40, 41], the interphase is stiffer than the rubber matrix itself) both inside and outside the wear track with various loading rates on all samples.

A sample of the experimental data is shown in Fig. 6 in the form of applied load versus penetration depth curves for two rubber samples both inside and outside the wear track and a silica filler particle. The difference in elasticity moduli of the rubbers and silica as filler particle is clearly seen.

Figure 6: AFM force indentation curves performed on the rubber samples, inside and outside the wear track. The applied load-penetration depth curve is steeper for higher elastic materials. Silica as filler particle has a much higher elasticity modulus.

Furthermore, the force-penetration depth curves are analyzed using the contact model for a blunted pyramid [38] to calculate the elastic moduli of the samples, both outside and inside the wear track for various indentation ratios as well as tribological conditions.

(a)

(b)

(c)

(d)

Figure 7: Time dependence of elastic modulus for: (a) HC, (b) LC, (c) HS, (d) LS samples both inside and outside the wear track. The results for surface layer inside the wear track, modified with low and high tribological severity conditions, are shown by (L) and (H), respectively. The calculated elastic moduli are dependent on indenter rate.

The results are presented in Fig. 7. As it is seen, the calculated elasticity moduli increase with indenter rate, similar to Fig. 3, where modulus of elasticity increases with an increase in frequency. However, a direct relation between the horizontal axes in Figs. 3 (frequency) and 7 (indentation rate) is not possible. These graphs show that the moduli outside the track are higher than inside the track. Furthermore, high severity in tribological conditions causes more loss in mechanical properties.

4 Discussion

The AFM nano-indentation results show the existence of a modified rubber layer with degraded mechanical properties. The change in the Young's modulus is more detectable when indenting at higher rates and is much more noticeable for stiffer samples (carbon black-filled samples). Structure of fillers and their subsequent interaction with an elastomer matrix is very important in determining elastomer stability against degradation. The influence of CB loading on thermal aging resistance of SBR has been studied by Mostafa et al. [42], where it was found that carbon black accelerates the oxygen uptake and acts as a catalyst for direct oxidation. The effect of silica on thermal oxidative degradation of SBR has been studied in [43]. It was shown that silica has an effect on improving thermal stability of the matrix as filler. It is known that carbon black makes mechanical bonds with the rubber matrix, while silica makes chemical bonds. Therefore, silica can generate a protective barrier over

the surface of rubber to protect the rubber matrix. This comparison between silica and carbon black can explain the different degradation levels of carbon black and silica-filled elastomers in sense of loss in elasticity modulus. The loss in physical properties associated with degradation processes is normally caused by either chain scission resulting in the reduction of chain length and average molecular weight, cross linking resulting in a three-dimensional structure and higher molecular weight or chemical alteration of the molecule by introduction of new chemical groups.

Another interesting result is the effect of tribological conditions on modifying the rubber surface layer. The loss in elastic modulus is more in systems exposed to severe conditions (by increasing velocity and normal contact pressure) for all indenting frequencies and for all the studied samples. This shows that modification of the surface layer is related to the tribological conditions. However, tests were performed under only two conditions, and the authors believe that further generalizations from the current results should be avoided. Increasing contact pressure and velocity might result in a higher wear rate too, which results in a dynamic system where a competition between modification and wear of the surface layer occurs. This is the subject of more research in the future.

The filler particles did not show a substantial change in their mechanical behavior. Therefore, only the rubber matrix and the interphase mechanical properties change. This is important for the mechanical properties of the modified layer on macroscale. As

discussed before, the modified top layer of the rubber in contact with the counter surface controls friction level. Loss of mechanical properties because of degradation causes a decrease in the friction level. This is in agreement with tire friction measurements, where the friction decreases after running-in.

5 Conclusions

Two main contributors, namely hysteresis, generated by viscoelastic losses in the bulk of the material, and shearing of the top rubber layer determine the friction between rubber and a solid rough surface. It has been shown elsewhere [23] that hysteresis is not the main contributor in rubber friction (rigid ball against rubber disc) unless the counter-surface in contact is rough. The shearing of the top layer plays a significant role in the friction; therefore, studying and modelling the top rubber layer is crucial. It is shown that the surface layer properties change because of exerted high stresses and/or high temperatures occurring in the contact area. However, existence of such a modified layer has been questioned in some researches. SEM pictures from the cross section of rubber samples could not only provide useful information about the existence of such a layer, but also the thickness of such a layer could be measured. However, SEM cannot be used for all sorts of rubbers because of charging effects. In addition, no quantitative information about the properties of the modified rubber layer can be gained. Therefore, AFM nano-indentation is used in this study to numerically investigate the

mechanical properties of the surface layer.

Four rubber samples are made from a combination of BR and S-SBR filled with various amounts of carbon black or silica. Pin-on-disk tests are used to generate a modified rubber layer. The measurements are stopped when the measured friction is stable, that is, when running-in phase is finished.

AFM nano-indentation is performed inside and outside the wear track at different indentation rates. The filler particles did not show any change in their mechanical properties inside and outside the wear track, while the rubber matrix at the surface degrades substantially. Generating the modified surface layer by higher energy input (higher velocity and contact pressure) resulted in more loss in elastic modulus of the samples.

This loss of properties is much more noticeable in carbon black-filled samples that possess a higher elastic modulus. The local change in the rubber at the surface does not affect the real area of contact or hysteresis part of friction. It can, however, change the frictional shear stress acting at the real area of contact substantially. Therefore, this layer with different mechanical properties should be modelled through studying several tribo-systems (various types of rubber and substrate surfaces) under a range of sliding conditions (such as velocity, temperature and humidity).

Acknowledgements

This project is carried out in the framework of the innovation program “GO Gebundelde Innovatiekracht” and funded by the “European Regional Development Fund”, “Regio Twente”

and “Provincie Overijssel”. The project partners Apollo Tyres Global R&D B.V., University of Twente (Tire-Road Consortium), Reef Infra, Stemmer Imaging B.V. and the Provincie Gelderland are gratefully acknowledged.

6 References

- [1] K.A. Grosch. The relation between the friction and visco-elastic properties of rubber. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, 274(1356):21–39, 1963.
- [2] B.N.J. Persson. Theory of rubber friction and contact mechanics. *Journal of Chemical Physics*, 115(8):3840–3861, 2001.
- [3] G. Heinrich, M. Klüppel, and T.A. Vilgis. Evaluation of self-affine surfaces and their implication for frictional dynamics as illustrated with a rouse material. *Computational and Theoretical Polymer Science*, 10(1-2):53–61, 2000.
- [4] B. Lorenz and B.N.J. Persson. Leak rate of seals: Comparison of theory with experiment. *EPL (Europhysics Letters)*, 86(4):44006, 2009.
- [5] B.N.J. Persson and M. Scaraggi. On the transition from boundary lubrication to hydrodynamic lubrication in Åsoft contacts. *Journal of Physics: Condensed Matter*, 21(18):185002, 2009.
- [6] G. Bóдай and T.J. Goda. Friction force measurement at windscreen wiper/glass contact. *Tribology Letters*, 45(3):515–523, 2012.
- [7] D.F. Moore. *The friction and lubrication of elastomers*. International series of monographs on materials science and technology; v. 9. Pergamon Press, Oxford, New York, 1972.
- [8] P. Wriggers and J. Reinelt. Multi-scale approach for frictional contact of elastomers on rough rigid surfaces. *Computer Methods in Applied Mechanics and Engineering*, 198(21-26):1996–2008, 2009.
- [9] B.N.J. Persson. On the theory of rubber friction. *Surface Science*, 401(3):445–454, 1998.
- [10] A. Le Gal, X. Yang, and M. Klüppel. Evaluation of sliding friction and contact mechanics of elastomers based on dynamic-mechanical analysis. *Journal of Chemical Physics*, 123(1):014704, 2005.
- [11] B. Lorenz, B.N.J. Persson, S. Dieluweit, and T. Tada. Rubber friction: Comparison of theory with experiment. *European Physical Journal E*, 34(129):11129, 2011.
- [12] B. Lorenz, B.N.J. Persson, G. Fortunato, M. Giustiniano, and F. Baldoni. Rubber friction for tire tread compound on road surfaces. *Journal of Physics: Condensed Matter*, 25(9):095007, 2013.
- [13] X-D. Pan. Wet sliding friction of elastomer compounds on a rough surface under varied lubrication conditions. *Wear*, 262(5-6):707–717, 2007.
- [14] L. Martínez, R. Nevshupa, D. Felhös, J. L. de Segovia, and E. Romín. Influence of friction on the surface characteristics of EPDM elastomers with different carbon black contents. *Tribology International*, 44(9):996–1003, 2011.
- [15] J.M. Degrange, M. Thomine, P. Kapsa, J.M. Pelletier, L. Chazeau, G. Vigier, G. Dudragne, and L. Guerbé. Influence of viscoelasticity on the tribological behaviour of carbon black filled nitrile rubber (NBR) for lip seal application. *Wear*, 259(1-6):684–692, 2005.
- [16] J. Karger-Kocsis, A. Mousa, Z. Major, and N. Békési. Dry friction and sliding wear of EPDM rubbers against steel as a function of carbon black content. *Wear*, 264(3-4):359–367, 2008.
- [17] T. Nakazono and A. Matsumoto. Mechanical aging behavior of styrene-butadiene rubbers evaluated by abrasion test. *Journal of*

- Applied Polymer Science*, 120(1):379–389, 2011.
- [18] N.V. Rodríguez, M.A. Masen, and D.J. Schipper. Tribologically modified surfaces on elastomeric materials. *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology*, 227(5): 398–405, 2012.
 - [19] M.-J. Wang and Y. Kutsovsky. Effect of fillers on wet skid resistance of tires. Part I: Water lubrication vs. filler-elastomer interactions. *Rubber Chemistry and Technology*, 81(4): 552–575, 2008.
 - [20] M.-J. Wang and Y. Kutsovsky. Effect of fillers on wet skid resistance of tires. Part II: Experimental observations on effect of filler-elastomer interactions on water lubrication. *Rubber Chemistry and Technology*, 81(4): 576–599, 2008.
 - [21] I.M. Sivebaek, V.N. Samoilov, and B.N.J. Persson. Effective viscosity of confined hydrocarbons. *Physical Review Letters*, 108 (3):036102, 2012. PRL.
 - [22] B.N.J. Persson. Rubber friction: Role of the flash temperature. *Journal of Physics Condensed Matter*, 18(32):7789–7823, 2006.
 - [23] M. Mokhtari, D.J. Schipper, and T.V. Tolpekina. On the friction of carbon black- and silica-reinforced BR and S-SBR elastomers. *Tribology Letters*, 54(3):297–308, 2014.
 - [24] R. García and R. Pérez. Dynamic atomic force microscopy methods. *Surface Science Reports*, 47(6-8):197–301, 2002.
 - [25] D. Tranchida, S. Piccarolo, and M. Soliman. Nanoscale mechanical characterization of polymers by AFM nanoindentations: Critical approach to the elastic characterization. *Macromolecules*, 39(13):4547–4556, 2006.
 - [26] C. Reynaud, F. Sommer, C. Quet, N. El Bounia, and T.M. Duc. Quantitative determination of Young’s modulus on a biphasic polymer system using atomic force microscopy. *Surface and Interface Analysis*, 30(1):185–189, 2000.
 - [27] R. Ferencz, J. Sanchez, B. Blümich, and W. Herrmann. AFM nanoindentation to determine Young’s modulus for different EPDM elastomers. *Polymer Testing*, 31(3): 425–432, 2012.
 - [28] D. Tranchida, Z. Kiflie, S. Acierno, and S. Piccarolo. Nanoscale mechanical characterization of polymers by atomic force microscopy (AFM) nanoindentations: Viscoelastic characterization of a model material. *Measurement Science and Technology*, 20(9):095702, 2009.
 - [29] V.V. Tsukruk, V.V. Gorbunov, Z. Huang, and S.A. Chizhik. Dynamic microprobing of viscoelastic polymer properties. *Polymer International*, 49(5):441–444, 2000.
 - [30] C.P. Green, H. Lioe, J.P. Cleveland, R. Proksch, P. Mulvaney, and J.E. Sader. Normal and torsional spring constants of atomic force microscope cantilevers. *Review of Scientific Instruments*, 75(6):1988–1996, 2004.
 - [31] W.C. Oliver and G.M. Pharr. Improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *Journal of Materials Research*, 7(6):1564–1580, 1992.
 - [32] Hertz. On the contact of elastic solids. *Reine Angew. Math.*, 92:156–171, 1881.
 - [33] K.L. Johnson, K. Kendall, and A.D. Roberts. Surface energy and the contact of elastic solids. *Proceedings of the Royal Society of London. A. Mathematical and Physical Sciences*, 324(1558):301–313, 1971.
 - [34] B.V. Derjaguin, V.M. Muller, and Y.P. Toporov. Effect of contact deformations on the adhesion of particles. *Journal of Colloid and Interface Science*, 53(2):314–326, 1975.
 - [35] D. Tranchida and S. Piccarolo. On the use of the nanoindentation unloading curve to measure the Young’s modulus of polymers on a nanometer scale. *Macromolecular Rapid Communications*, 26(22):1800–1804, 2005.

- [36] I.N. Sneddon. The relation between load and penetration in the axisymmetric boussinesq problem for a punch of arbitrary profile. *International Journal of Engineering Science*, 3(1):47–57, 1965.
- [37] G. Haugstad. *Distance-Dependent Interactions*, pages 33–90. John Wiley & Sons, Inc., 2012.
- [38] F. Rico, P. Roca-Cusachs, N. Gavara, R. Farré, M. Rotger, and D. Navajas. Probing mechanical properties of living cells by atomic force microscopy with blunted pyramidal cantilever tips. *Physical Review E*, 72(2):021914, 2005.
- [39] P. Schön, S. Dutta, M. Shirazi, J. Noordermeer, and J.G. Vancso. Quantitative mapping of surface elastic moduli in silica-reinforced rubbers and rubber blends across the length scales by AFM. *Journal of Materials Science*, 46(10):3507–3516, 2011.
- [40] F. Deng and K.J. van Vliet. Prediction of elastic properties for polymer-particle nanocomposites exhibiting an interphase. *Nanotechnology*, 22(16):165703, 2011.
- [41] M. Qu, F. Deng, S.M. Kalkhoran, A. Gouldstone, A. Robisson, and K.J. van Vliet. Nanoscale visualization and multiscale mechanical implications of bound rubber interphases in rubber-carbon black nanocomposites. *Soft Matter*, 7(3):1066–1077, 2011.
- [42] A. Mostafa, A. Abouel-Kasem, M.R. Bayoumi, and M.G. El-Sebaie. The influence of CB loading on thermal aging resistance of SBR and NBR rubber compounds under different aging temperature. *Materials and Design*, 30(3):791–795, 2009.
- [43] L. Guo, G. Huang, J. Zheng, and G. Li. Effect of nanosilica on thermal oxidative degradation of SBR. *Journal of Thermal Analysis and Calorimetry*, 116(q):359–366, 2013.

Paper D

Formation of a tribo-modified surface layer on elastomers

M. Mokhtari, M.B. de Rooij, D.J. Schipper and R. Bosman

Submitted to the Journal of Tribology Letters

Formation of a tribo-modified surface layer on elastomers

M. Mokhtari, M.B. de Rooij, D.J. Schipper and R. Bosman

Surface Technology and Tribology, Faculty of Engineering Technology, University of Twente,
P.O. Box 217, 7500 AE Enschede, The Netherlands

Abstract

Many aspects of rubber friction are still far from being understood. Several studies have been devoted to comprehending the contribution of hysteresis to friction. However, the contribution from the real area of contact is not yet fully understood. One of the complexities arises from the modification of the top layer in contact with the counter surface. Shearing of a tribologically modified surface layer via a rigid rough counter surface plays an important role in the overall friction. In earlier studies, the importance of both the wear and the formation rates on the existence of such a layer was emphasized. However, so far no predictive model has been presented that can relate the tribological conditions together with the mechanical properties of the rubber to the formation of the tribofilm. In this study, the formation rate and consequently the thickness of the modified layer are connected to the tribological conditions (such as contact pressure, sliding velocity and roughness) and the mechanical properties of the rubber. The mechanism of the mechanical degradation of the rubber is explained. Some of the changes detected in the modified surface layer of a tire tread in comparison with the bulk of the rubber, using AFM in the peak-force tapping mode are reported. Next to the detected changes in the morphology, the possibility of the chain reorientation in the rubber network due to the applied mechanical loading is investigated. A multi-scale contact model is used to describe the pressure distribution at the rubber interface as a function of the tribological conditions. The subsurface energy field is then attained using the obtained pressure distribution. The subsurface energy field, together with the wear rate, will be used to estimate the modified layer formation rate and thickness. The proposed model is applied to a friction test. The model results are in good agreement with experiments.

1 Introduction

The friction between rubber and rigid counter surfaces has interested many researchers because of its great practical importance. The smart design of tires,

rubber seals, wiper blades, conveyor belts and syringes, requires detailed knowledge about rubber friction [1–6]. Several parameters should be considered in modeling rubber friction. Contact pressure, (sliding) velocity, temperature

and surface roughness, as well as morphology of the rubber compounds, are some of the main factors that all play a role in the friction of polymers in contact with solid surfaces. Although great interest has been shown over the last 50 years in studies focusing on the tribological behavior of rubber sliding contacts, the friction problem is not yet fully understood.

Rubber friction can be decomposed to two main contributors (see Eq. 1), categorized in particular by contributions from the area of contact and hysteresis [7]. The oscillating forces exerted from the surface asperities onto the rubber surface, induce the hysteresis component of the friction through internal damping in the bulk of the rubber.

$$F_f = F_{hys} + \tau_f A_{real} \quad (1)$$

In the formulation above F_f and F_{hys} are the overall and hysteresis component of friction forces. The friction force dealing with contribution from the real area of contact is shown by $\tau_f A_{real}$ where A_{real} is the real area of contact and τ_f is the shearing stress acting at the interface.

The hysteresis component of friction is modeled on the basis of different contact models. Among the present contact models, the contact model of Persson has the advantage that it does not exclude a priori any roughness wavelength from the analysis. In the contact model of Persson, the exact solution for the case of full contact is obtained and subsequently through application of boundary conditions, the solution for the partial contact problem is developed [2]. In contrast, multi-

asperity contact models are based on partial contacts where it is assumed that contact occurs on isolated asperities far from each other [8, 9]. However, the interaction between neighboring asperities is neglected, which is the main disadvantage of multi-asperity models, especially at high contact pressures or when applied to soft materials. On the other hand, in the contact model of Persson, the ill-posed boundary conditions [10] bring an overestimation in the asperity elastic energy and consequently, an underestimation in the calculated real area of contact [11]. A correction is applied to overcome this deficiency [12].

The contribution from the real area of contact is not as clear as hysteresis. This arises partially from accurately determining the real area of contact A_{real} through various contact models explained above. Both asperity contact models and the models based on Persson's methodology have been investigated and the results have been compared [13–15]. Another origin in the contribution from the real area of contact arises from the definition of the shear stress acting at the interface of the elastomer-rigid surface contacts. The shear stress is modeled using different methods, but under a common title of adhesion. Adhesion is generally related to the intermolecular attractive forces between the contacting bodies [16]. Adhesion of elastomers is modeled using both phenomenological and physical models. A comprehensive review on the adhesion theories of elastomers can be found in [17]. The mechanism of adhesive friction in elastomers is explained by two approaches, i.e. the process of attachment and deformation of molecular

chains addressed by Schallamach [18] and the crack propagation concept initiated by Savkoor [19]. The former concept was further developed in references [20–24] and the latter is established in references [25–28]. Both approaches are combined in a phenomenological physical model and formula [29, 30].

Modifications that occur at the top layer of elastomers are another complication in specifying the contribution of the real area of contact. These modifications make the mechanical properties of the rubber layer in contact different from the bulk and, therefore, the shearing of the top rubber layer alters as a function of the tribological conditions [31]. The importance of these modifications in determining the tribological behavior of the elastomers in contact with rough surfaces has been emphasized [32, 33].

Figure 1: A rough rigid ball (granite) in sliding contact with a rubber disk. Friction is decomposed to two main contributors, namely hysteresis and the contribution from real area of contact where shearing a thin modified surface layer plays an important role in the latter. A modified surface layer exists only when the balance condition between formation Q_f and wear Q_w rates is met [31].

1.1 Existence and Importance of the Tribologically Modified Surface Layers

Many researchers have shown that the composition and the tribological properties of the surfaces in contact change when compared with the original interface [34]. Elastomers are not an exception in this context [35–38]. These modified surface layers play an important role in determining the tribological behavior of the elastomers in contact as a result of alteration in τ_f (see Eq. 1). The existence of a tribologically modified surface layer on rubber samples was shown by Scanning Electron Microscopic (SEM) imaging [39]. Furthermore, a degradation in mechanical properties of such layer was proven using Atomic Force Microscopy (AFM) nanoindentations [33]. In addition, the mechanical properties of the modified layer depend on the frictional energy exerted on the rubber. It was shown that increasing the frictional energy results in an extra degradation. Moreover, part of the frictional energy is absorbed by heat generation and wear. The generated heat shifts the mechanical properties of the rubber [40] through increasing the temperature. Wear might completely remove the modified surface layer. Therefore, the balance between formation and wear of the modified layer controls the existence of the modified surface layer [31]. The asymmetric pressure distribution in the bulk of the material under a rough rigid semi-sphere in contact with a rubber half-space that generates the hysteresis component of friction is illustrated in Fig. 1. Moreover, the formation and wear rates of the

modified surface layer and the balance between them, which determines whether the tribologically modified surface layer exists, are schematically depicted. In addition, shearing of a modified layer by the rough counter surface as the second component of friction is shown.

The formation of a modified surface layer is rationalized by thermal and stress-induced degradation of the top rubber layer [40]. The standard expression describing activated processes has been used to model the formation process. In this study, the mechanism of modifications in elastomers due to frictional energy input is studied and a model which predicts both the modification rate and thickness of the modified layer as a function of tribological conditions and mechanical properties of the elastomer is proposed.

The outline of this paper is as follows: In Sect. 2, firstly the mechanical degradation of elastomers is explained. In this section, the morphology of the modified surface layer is studied via AFM using the peak-force tapping mode. The detected changes in the morphology are reported. In addition, the possibility of rubber network reorientation in the direction of sliding due to frictional loading is discussed. Subsequently, the model that consists of three parts is presented; in the first part, the pressure distribution at the interface, between the rubber and a counter surface, is governed. Then the subsurface energy distribution in the bulk of a rubber component as a function of the tribological loading is calculated from the normal pressure and frictional shear distributions. In the last part of the model, the obtained energy field together with the wear rate

are related to the formation rate and thickness of the modified surface layer. The presented model is applied to a pin-on-disk test to estimate the formation rate in Sect. 3. The model results are discussed in Sect. 4. Finally, the main conclusions of this study are summarized in Sect. 5.

2 Formation of a Tribologically Modified Surface Layer

The modification of the rubber surface in sliding contacts has been attributed to several different phenomena. However, no agreement between different studies was found on the determination of the driving phenomena as the source of the properties modification. Rubber degradation is categorized into mechanical, thermal and chemical degradation. In [36], tribochemical reactions and thermo-oxidative degradation of the rubber samples were assigned as the origin of the modifications of carbon black filled elastomers. However, similar experiments have been performed in [35] and it was shown that no thermo-oxidation processes occur because of friction tests. Next to oxidation, thermal and chemical degradation, subsurface layer formation due to mechanical degradation in the course of sliding friction has been reported and modeled for several other materials [41–43]. In polymers, mechanical degradation is recognized as severely changing the tribological behavior. Orientation softening is a well-known phenomenon in high molecular weight polyethylene that changes the wear rate by modifying the chain size and orientation of the polyethylene in

the wear track [44]. In elastomers, the molecular chain network also evolves as a function of the loading conditions. The evolution of the elastomer network is the source of the mechanical degradation. The authors believe that gaining a quantitative insight into the changes of the modified surface layer is only possible by a detailed study of several tribo systems. More studies are required to investigate and model plausible oxidation, chemical and thermal degradation of rubbers as a function of the frictional energy exerted on the surface layer during sliding contacts. In the literature, the significance of oxidation, thermal and chemical degradation of the rubbers is limited to a few experimental studies. For that reason, this study considers mechanical degradation of rubbers and other degradation mechanisms are neglected. Mechanical degradation of viscoelastic materials corresponding to rupture has been researched [45], however, the current study focuses on the mechanical degradation of the tribo-modified surface layers in the nondestructive regime.

The filler-polymer interaction is a determining factor in mechanical degradation of elastomers [45, 46]. Therefore, to model the changes occurring in the elastomer network, at first the rubber network should be considered. To design rubber components with desired properties, several reinforcement fillers are added to the rubber matrix. Carbon black and silica are the ones most frequently used in the tire industry. Filler particles induce notable inelastic effects, including the Mullins and the Payne effect, besides enhancing the overall properties of the system.

As shown in Fig. 2, the rubber chains are bonded together via chemical cross-linking. Cross-linked chains cannot move independently. In some micromechanical models [49], a fraction of chains is considered to be breakable and the rest to be elastic. The fraction of breakable chains is responsible for the network alteration. On the other hand, in alternative models [50], the material is assumed to be composed of different networks (namely the pure rubber network, the polymer-filler network and the filler-cross-link network), each with its own reference configuration. Each network is assumed to act parallel to the other networks with no interaction between them. The pure rubber network is assumed to be perfectly elastic. Two extra networks are made between filler particles and the rubber chains; fillers can bond to the cross-links or directly to a rubber chain.

Around the filler particles, a glassy bridge is formed which has a lower glass transition temperature than the polymer matrix. The bound rubber interphase is elastically harder than the rubber matrix [48] and plays an important role in reinforcement of the elastomers. At low strain values, because of the rupture of the glassy bridges around fillers (that consequently results in an increased distance between filler particles [51, 52]), the shear modulus degrades as a function of strain. These modifications are at least partially recoverable due to the progressive rebirth of the bonds, if the system is put at rest for a relatively long time. In a generalized network decomposition model [47], it is assumed that the breakage and the recreation of aggregates occur in the filler-cross-link network (see Fig. 2).

Figure 2: A filler reinforced rubber matrix is decomposed to different networks; purely elastic deformation occurs in the pure rubber network. Breakage of the aggregates, which is mainly recoverable, happens in the filler-cross-link network and degradation of the rubber develops in the filler-polymer network [47]. Around the filler particles, a glassy bridge is formed which has a lower glass transition temperature than the polymer matrix. The bound rubber interphase is elastically harder than the rubber matrix [48].

The (partial) recoverable strain softening property in elastomers is called the Payne effect [53]. It has been explained [31] that if the applied frictional energy is lower than a threshold, no modification occurs. This is due to the fact that at lower frictional energies, the strain is only sufficient to degrade the filler-cross-link network, which is mainly recoverable.

Once the applied macro strain is higher than a threshold (which differs for each elastomer composite and depends on several parameters such as filler type, filler size, rubber matrix component, filler content, cross-linking density, rubber-filler interaction, filler treatment, aggregation process, temperature and loading history) an evolution in the filler-polymer network occurs. The threshold for activating the degradation process is discussed in [54, 55]. The modifications in the filler-polymer network result in degradation of the material. Considering the fact that

such softenings do not happen in unfilled rubbers, it is inferred that the polymer-filler network and not the rubber network is modified. Several possible sources have been proposed for the degradation in the filler-polymer network. Bond rupture [56, 57], chain sliding [58], link breakage and matrix alteration [59], removal of entanglements [60], debonding and recreation of cross-links, chains residual stretch, chain breakage [61] breakage of filler cluster structure [62] and interface model concept [63] have been used to describe the softening phenomenon in the filler reinforced elastomers. Despite many proposed explanations, the degradation mechanism is not fully understood, which demonstrates the complexity of the problem.

The stress softening in filler-rubber network of elastomers is considered as a reversible phenomenon. The recovery of the stress softening is named healing.

Healing is a thermally activated process whereby the original stiffness is recovered over time after removal of the applied stress. It has been shown that healing is temperature dependent and at room temperature only a small recovery is observed [64]. Furthermore, in another study [65], a carbon black filled rubber showed only partial recovery after a long stress release time of 4 weeks. In a silica filled composite, the stress softening could not be recovered after 6 months [60]. Finally, it has been concluded that the stress softening is reversible when exposed to high temperature in vacuo or to solvent swelling [66]. In this study healing is neglected and only degradation of the filler-polymer network is considered.

The degradation in the filler-polymer network occurs only if the force magnitude, applied to a single chain, exceeds the effective interaction strength of polymer-filler bonds [67]. When the applied load is lower than this threshold, the filler-cross-link network is damaged which is recoverable. Several approaches have been suggested to model the distribution of forces of the molecular chains as a function of the applied strains. Consider two filler particles with distance r in between. Suppose that several chains with length L_i are connected at each end to one of the fillers. Each chain consists of n_i smaller segments of length l_i . In other words $L_i = n_i l_i$. Assume that a macro-stretch χ is applied to the rubber matrix. Due to strain amplification, a micro-stretch $\lambda = (\chi - C^x)/(1 - C^x)$ will be exerted on the polymer chains between aggregates [67], where C is the volume fraction of the filler and the exponent x is a function of the filler network. It is assumed

that the chain lengths follow a distribution function as schematically illustrated in Fig. 3. In practice, the number of segments of a chain n_i are limited between n_{min} and n_{max} where n_{min} is determined by the maximum strain previously applied. For a detailed discussion on the chain length distribution functions and limits of n_i see [67].

It has been shown [68] that the value of the critical force, F_c (the effective interaction strength of polymer-filler bonds) does not depend on the length of the chain, however, it differs for different aggregates (which depends on aggregate surface geometry, chain geometrical position with respect to the aggregate surface, etc.). Therefore, a distribution for the critical force F_c should be considered. This approach is similar to the approach presented in [45], however, a distribution of bond strengths $q(h)$ was considered and averaged. The chain force due to strain can be calculated by [67]:

$$F_i = \frac{kT}{l_i} \mathcal{L}^{-1}\left(\frac{r}{L_i}\right) \quad (2)$$

where $\mathcal{L}^{-1}$ is the inverse Langevin function. Having the chain length distribution and using Eq. 2, the elastic energy of each chain can be governed as depicted in Fig. 3. If the stored elastic energy in a chain is higher than an averaged bond strength value h , the chain debonds and does not contribute to the rubber elasticity. Filler-polymer degradation is assumed to be the result of chain debonding from and chain sliding on the fillers.

The degradation mechanism is explained in tensile loading above.

Figure 3: The distribution function of chains versus length of the chains between two filler particles inside the rubber matrix is shown schematically. The modification does not immediately occur by applying strain. Before a threshold that is related to the shortest available length of the polymer chain, no modification occurs (figure reproduced from [67]).

However, degradations do not only occur in tensile loadings but also under compression and shear [69, 70]. The rate of the chain debonding from and chain sliding on the filler particles at temperature T is assumed to be given by the standard expression of activated processes [40, 45]:

$$\Omega = \frac{akT}{\hbar} e^{-\frac{h-E}{kT}} \quad (3)$$

In the equation above, a is proportionality constant, k is the Boltzmann's constant, $\hbar$ is the reduced

Planck's constant and h , E are the required energy to break a single bond and the stored elastic energy in each bond due to the applied strain respectively. The debonded chains induce modification. Once the stored elastic energy distribution is defined, the rate of the modification is achieved by:

$$\Omega_{avg} = \frac{\int_{n_{min}}^{n_{max}} E(n)\Omega(n)dn}{\int_{n_{min}}^{n_{max}} E(n)dn} \quad (4)$$

In this study, for simplicity, only average values for h , E are considered and

Figure 4: Height map of a tire tread compound in the (a) wear track and (b) bulk of the material measured via peak force tapping mode AFM.

Eq. 3 is used to estimate the degradation rate.

Modifications of the mechanical properties of carbon black and silica reinforced rubber compounds inside the wear track due to the applied frictional energy have been studied by Atomic Force Microscopy (AFM) nano-indentations [33]. In this study, the effect of the rubber modification on the morphology of the degraded sections is studied. Peak-Force Tapping mode allows studying both the topography and some mechanical properties of the surface simultaneously. A silica reinforced rubber tread compound after controlled wet grip tests is studied by a Multi-Mode 8 AFM from Bruker with Nanoscope V controller and J vertical engage scanner. The measurements are performed with a probe which has a nominal spring constant of 0.35 N/m and a nominal tip radius of 20 nm . The spring constant of the probe's cantilever is estimated by thermal sweep method [71]. The AFM topography measurements both inside and outside the wear track are

presented in Fig. 4. A clear modification in the wear track of the tire tread in comparison with the bulk is noticeable. Several circular particles with relatively higher modulus of elasticity and lower adhesion (adhesion map is not shown) are randomly distributed along the surface of the wear track. The harder particles in the bulk are not clearly distinct from the soft phase. This result is in agreement with [38] where it was concluded that bare silica particles are present at the wear track of silica filled rubbers.

In polymers, molecular reorientation due to cumulative stresses brings about orientation softening [44]. Besides rubber network damage which is detectable via morphology changes, as shown above, the possibility of deformation induced anisotropy due to chain reorientation is investigated.

At locations closer to the center of the tire/road contact patch, the worn tread shows a nodular morphology as presented in Fig. 5. It is known that the contact pressure at the center of the

tire is higher than at the sides. The nodular morphology might be interpreted as the reorientation of the rubber chains; although some part of the modifications might be healed (as explained in [60, 64–66]) by the healing phenomenon, due to the irreversible part of the damage, an induced change in the material symmetry has been reported [72, 73]. Similar morphologies are seen in the tribologically modified surfaces of some alloys [74]. The nodular morphologies have been detected in thermosetting epoxies [75] too. However, the nodular morphology was attributed to an AFM artifact named dilation [76] which is caused by relatively large AFM tip or by relatively rough surface. The authors explain their reasoning by noticing that both the modulus and the adhesion were highest in topographic valleys [75]. However, this is not the case in our study, as illustrated in Fig. 5. It is not clear if the observed morphology is real and caused by the induced anisotropy in the material or is an artifact because of the rough surface of the worn tread.

2.1 Subsurface Mechanical Energy Distribution in the Contact Between a Rough Counter Surface and a Viscoelastic Half-Space

Consider a rigid rough surface in sliding contact with a rubber half-space. The rate of the mechanical energy (mechanical power) distributed at any point in the bulk of the rubber is related to the stress and strain rate distributions:

$$\begin{aligned} W(x, y, z, t) &= \int_{V_{tot}} w(x, y, z, t) dV \\ &= \int_{V_{tot}} \sigma(x, y, z, t) \frac{d\varepsilon(x, y, z, t)}{dt} dV \end{aligned} \quad (5)$$

The strains are related to the stresses by the mechanical properties of the rubber. To govern the subsurface mechanical energy distribution, at first the subsurface stress distributions should be calculated. The subsurface stresses at each point inside the rubber body are related to the pressure distribution at the surface of the real contact area; the influence coefficients connect the subsurface stresses to the surface pressure and the shear traction [77]. Based on experimental measurements performed earlier, the shear traction is estimated by the adhesive component of friction arising in the sliding contact. To calculate the normal pressure distribution at the real area of contact, an appropriate contact model should be used. In the Introduction, the preferable aspects of the Persson’s approach to asperity contact models, when applied to soft materials or at relatively high contact pressures, are briefly reviewed. Despite the advantage that many wavelengths of roughness are considered in the approach of Persson, subsurface stresses are not obtained. On the other hand, although the interaction between the asperities can be added to the current asperity models [11, 78], the complication of the interaction between neighboring micro contacts is not accurately solved [14]. All in all, as Greenwood has mentioned in a self-critical article, entitled “*Surface Roughness and Contact: An Apology*” [79], the initial definition of a peak corresponding to

Figure 5: Nodular morphology (a) and DMT map (b) of the tire tread at locations closer to the center of the tire. Line profiles of the height, the modulus E_s and the adhesion F_{adh} from part of a line of the image is presented in (c). Unlike the study in [75], the valleys in height correspond to local minimum and maximum of modulus and adhesion maps respectively.

the asperities was wrong and, instead, a pioneering Archard's concept in which roughness consists of "protuberances on protuberances" [80] should be used. Therefore, a non-statistical multi-scale model for contact which considers the effect of having asperities located on top of relatively larger asperities in a recurrent convention [81] is applied. Unlike asperity models, the aforementioned approach does not suffer from ambiguity of scale (in the asperity models based on the approach of Greenwood and Williamson [8] the average radius of curvature is dependent on the scale of observation).

The main assumptions and formulas of the model of Jackson and Streater [81] are reviewed below; it is assumed that asperities with smaller cross-sectional surface areas are located on top of the larger asperities. The frequency, corresponding to the wavelength of each level of asperities, is directly governed by the FFT of the roughness. The areal asperity density η_i at each frequency is governed by $\eta_i = 2f_i^2$, where f_i is the reciprocal of the wavelength. The radius of curvature R_i for each frequency level is $R_i = 1/(4\pi^2\beta_i f_i^2)$, where β_i is the amplitude corresponding to the given frequency, directly obtained from FFT of the roughness. The total load carried by asperities at each frequency level is constant. Moreover, it is assumed that the load at each frequency level is equally distributed among all the asperities at that level. Furthermore, the real area of contact at each frequency level cannot be higher than the contact area at the previous level. Once the number of asperities at each level and, consequently,

the carrying load by each asperity is determined, the contact area of each single asperity is calculated using an asperity model. The influence of neighboring asperities should be included in modeling the contact of soft materials, therefore, the contact model of a two dimensional wavy surface in contact with a flat [82] is used to calculate the contact area and pressure distribution at each level. The nominal contact area A_0 is the macroscopic area of contact and f_0 is the reciprocal of the wavelength corresponding to the length of contact at the nominal contact area.

To illustrate in more detail how the model estimates the modified surface layer thickness and its formation rate, a flowchart of the method is depicted in Fig. 6. The first part of the model corresponds to determining the pressure distribution via solving the contact problem through the model of Jackson and Streater [81] in combination with the contact model for a two dimensional wavy surface [82]. The contact should be considered at the onset of saturation where the real area of contact does not change by an increase in the frequency level. Once the final frequency level f_{sat} is determined, the pressure distribution in the apparent area of contact A_0 is determined by:

$$P(x, y) = \frac{A_0 \sigma_0}{A_{sat}} + 2\pi E_r \beta_{sat} f_{sat} \cos(2\pi f_{sat} x) \cos(2\pi f_{sat} y) \quad (6)$$

where σ_0 is the nominal contact pressure, A_{sat} is the real area of contact at the final frequency level and E_r is the reduced elastic modulus. In the second part

Figure 6: Flow chart of the model predicting the rate and thickness of the modified surface layer. The model is divided to three parts. Part I deals with calculating the pressure distribution at the surface of the rubber as a function of the tribological conditions (reproduced from [81]). Part II corresponds to calculation of the subsurface energy field from the normal pressure and tangential shear distribution. In Part III, the available mechanical energy which is reduced by the wear of the material is used to estimate the rate and thickness of the modified surface layer.

Figure 7: Normalized shifted loss and storage shear modulus of elasticity as a function of frequency for a BR/SSBR elastomer reinforced with carbon black.

of the model, the pressure distribution together with the tangential shear stress distribution (which is governed by multiplication of the normal pressure and the coefficient of friction) are used to calculate the subsurface mechanical energy field by the method explained in reference [77] and in the Appendix.

In the last part of the model, the subsurface energy field is related to the formation rate by Eq. 3. The subsurface energy decreases drastically by an increase in the depth of the material. The thickness of the modified surface layer is estimated by the depth at which a severe decrease in the mechanical energy is calculated. One should subtract the thickness of the worn layer from the estimated thickness of the modified surface layer to evaluate the available thickness of the modified layer.

3 Application of the Formation Model to a Friction Test

The friction between a rubber disk and a rough granite sphere is measured by a pin-on-disk setup. The sliding velocity is 5 *mm/s* and the nominal contact pressure is 0.2 *MPa*. The rubber matrix includes 30 parts per hundred rubber (phr) butadiene rubber (BR) and 70 phr solution styrene-butadiene rubber (S-SBR). In addition the rubber sample is filled with 70 phr of carbon black particles. The mechanical properties of the rubber disk are measured using dynamical mechanical analysis (DMA). DMA in temperature sweep mode at a fixed frequency of 10 *Hz* under dynamic and static strains of 0.1 and 1 % respectively is used to determine the glass transition temperature of the rubber sample. The shear modulus $G(\omega)$

Figure 8: Frequency spectrum of the granite surface. The roughness is measured using confocal microscopy and AFM in contact mode.

is measured in oscillatory shear mode at a constant strain amplitude of 0.1 % where the sample is fixed at both interfaces and sheared at different frequencies between 1 and 200 Hz . The whole procedure is then repeated for different temperatures (the temperature is varied between -20 and $85\text{ }^{\circ}C$). The measured glass transition temperature and the selected reference temperature $T_{ref} = 27^{\circ}C$ are used to shift the measured shear modulus $G(\omega)$ against frequency ω both horizontally and vertically. The normalized shear modulus as a function of frequency is shown in Fig. 7.

Two different scanning techniques of confocal microscopy and atomic force microscopy (AFM) in the contact mode are used to measure the roughness of the granite sphere. The resulting frequency spectrum of the surface is shown in Fig. 8.

The transition of the measured friction coefficient in the running-in phase is shown in Fig. 9. The measured friction gets stable only after approximately 210 laps. The top rubber layer degrades gradually during these 210 contacts. In other words, during the running-in phase, the shear stress τ_f at the interface decreases gradually and finally gets stable. To estimate the required time for degradation of the top rubber layer during the friction test the following method is used; at each single contact event, the time required for the granite to travel through the contact length (at the nominal contact area A_0) is the ratio between the nominal contact length and the sliding velocity (this is illustrated in Fig. 10 where $dt = L/v$). The length of nominal contact is estimated by the Hertz contact theory using rubber mechanical properties corresponding to the roughness frequency

level f_0 . Therefore the whole required time for degrading the top layer of the rubber sample, under aforementioned tribological conditions, is 210 times the required time for a single contact event dt . The required time to form a tribologically modified surface layer locally is estimated to be ≈ 5 s.

Figure 9: Transient coefficient of friction.

The multi-scale contact model of Jackson and Streater [81] in combination with contact mechanics of a wavy surface [82] and the frequency spectrum are used to calculate the area of contact at each frequency level. The modulus of elasticity of viscoelastic materials is frequency dependent (as shown in Fig. 7), therefore the elasticity increases by each frequency level f_i . An increase in the elasticity decreases the contact area. In addition, the exciting frequency applied by the roughness asperities is dependent on the sliding velocity and the angle ϕ between the sliding velocity and the wave vector or, in other words, $\omega_i \approx v \cos \phi / f_i$. At each frequency level, asperities are assumed to be randomly distributed. Therefore

the average value of elasticity modulus $E(\omega_i) = \int_0^{2\pi} \pi E(2\pi v \cos \phi / f_i) d\phi / 2\pi$ at each frequency level is used (see Fig. 6). The ratio of the real area of contact to the nominal contact area for each frequency is plotted against the magnification factor $\zeta = f_i / f_0$ and is illustrated in Fig. 11.

Figure 10: The time dt required for the granite to travel through the nominal contact length L at each contact event is $dt = L/v$.

The real area of contact decreases gradually with an increase in frequency level and reaches a constant value. The contact is considered at the onset of saturation where the contact area does not change, even if smaller asperities are considered. In other words, asperities smaller than the asperity wavelength corresponding to the onset of saturation are in full contact with the elastomer. The nominal contact area is filled with asperities (with the wavelength correlating to the frequency level at the onset of saturation), each carrying equal force such that the summation of the forces is equal to the nominal force. The stress components at each point in the bulk of the material are related to the surface

Figure 11: The ratio between contact area at each frequency to the nominal contact area as a function of magnification factor.

pressure distribution using the method explained in [77] (see the Appendix).

Once the stress components, and consequently, strains (strains are governed via Lamé constants) at each point are known, the numerical derivative of the strain $d\varepsilon/dt$ should be calculated. If the sliding velocity v_s is assumed to be constant, the time derivative of the strain can be calculated by:

$$\dot{\varepsilon} = \frac{\varepsilon_{t+\Delta t} - \varepsilon_t}{\Delta t} = v_s \frac{\varepsilon_{x+\Delta x} - \varepsilon_x}{\Delta x} \quad (7)$$

Using Eq. 5 and Eq. 7, the exerted energy due to frictional sliding contact in the bulk of the rubber can be calculated as a function of the depth in the bulk. The degradation of the rubber occurs in the direction where the highest energy is applied to the molecular chains [55]. In the loading conditions considered in this problem (normal pressure in z direction

and friction applied in x direction), shear in x - z plane induces the highest energy in the bulk. The energy density field due to shear in x - z plane for the above-mentioned tribological loading, as a function of depth, is presented in Fig. 13 via curve E_1 for a single contact. In the same figure, the effect of an increase in the nominal contact pressure on the subsurface energy field is shown via curve E_2 which corresponds to the energy distribution for a nominal contact pressure of 1 MPa under the same other tribological conditions. For both conditions, a heat partition factor [83] of 0.4 is used. As expected, the distributed energy in the bulk for a higher contact pressure is higher.

To determine the rate of the modification and the thickness of the modified surface layer, the information on distributed energy in the bulk is insufficient. The modified layer is not

Figure 12: A rigid rough surface is shown schematically in sliding contact with a rubber half-space. The rough counter surface is assumed to be rough on several scales. Asperities at each level are considered to be a two dimensional wavy surface. Each asperity at a specific wavelength is assumed to be covered with smaller asperities on top. The sliding velocity is assumed to be constant, therefore the time derivative of strain is related to the spatial derivative of strain, which is calculated by the difference between the strains at each point and another point with distance $\Delta x = v_s \cdot \Delta t$. The normal stress in z direction inside the bulk of the viscoelastic material in x - z plane and at a fixed y value is shown schematically.

only subjected to modification, but also it simultaneously wears off [31]. Therefore, it is crucial to know the averaged thickness of the worn layer in each contact event (rate of the worn layer) to firstly certify if the modified surface layer exists. The rate of the worn layer thickness also regulates the rate of the modification, because the worn layer thickness (in each contact event) determines the maximum available energy applied to the top layer. The average thickness of the worn layer per contact event is determined experimentally. The averaged specific wear rate for contact pressure of 0.2 MPa during the whole

measurement is $9.47 \times 10^{-3} \text{ mm}^3/\text{Nm}$. The rubber disk is worn with a rate of $0.08 \text{ }\mu\text{m}$ in each contact event. This is shown by the red line W_1 in Fig. 13. In other words, at each contact event, a layer with thickness of $0.08 \text{ }\mu\text{m}$ of the rubber disk will not find the opportunity to be modified.

In order to estimate the rate of the degradation, the energy exerted on a single polymer chain should be calculated. The energy exerted on each polymer chain is dependent on the cross-link density. With a lower cross-link density, the applied mechanical energy is distributed

Figure 13: Distributed energy density due to shear in x - z plane as a function of the depth of the bulk in a single contact for two nominal contact pressures.

among a lesser number of chains and therefore the degradation rate increases. On the other hand, a higher cross-link density decreases the threshold at which irreversible degradation occurs. The cross-link density is assumed to be in the order of $\approx 10^{22}/\text{cm}^3$ which is a typical value for rubbers.

Considering the wear rate, the maximum available energy that can degrade rubber is used to estimate the modification rate (see Fig. 13). The distributed energy decreases drastically in the first $2.8 \mu\text{m}$ which is approximately in the order of the thickness of the modified surface layer previously reported [39]. Once the applied energy to a chain is calculated, using $h \approx 2.5 \times 10^{-19} \text{ J}$, the degradation rate is governed to be $\Omega \approx 1/4 \text{ s}^{-1}$. In other words, the rubber modifies after 4 s of contact under aforementioned

tribological conditions. The governed time is in agreement with the calculated formation rate for the friction test.

4 Discussion

The estimated formation rate from the model and from measurement agree. However, a slight difference between the two rates is seen.

- The difference between the formation rates is attributed to several other complex phenomena such as healing; the difference is not considered in this model for the sake of simplicity. As mentioned in Sect. 2, the stress softening is reversible when exposed to high temperature in vacuo or to solvent swelling.

- In the modification model presented, the effect of heat generation and flash temperature was neglected. The flash temperature can change the mechanical properties of the rubber compound and, therefore, the contact and the subsurface energy distribution would differ. In addition, a higher temperature can enhance both the healing and the degradation rates.

The effect of an increase in the normal pressure which increases the subsurface energy field was shown in Fig. 13. With an increase in the normal pressure, the depth at which the mechanical energy decreases drastically (this depth is related to the thickness of the modified surface layer) is increased too. In other words, an increase in the normal pressure can potentially modify a thicker layer of the rubber with a higher modification rate. However, with an increase in the pressure, wear rate might also increase. This reduces the available modification energy. As discussed in [31], the necessary condition for the existence of the modified layer is the balance between the formation and wear rates.

In this study, in addition to rubber degradation due to chain debonding from and chain sliding on the filler, chain reorientation along the direction of sliding was investigated. Reorientation of the chains results in an anisotropic modified layer [54, 73]. Therefore, the problem of contact between a rough rigid counter surface and an isotropic viscoelastic half-space modifies to the contact between a layered material (where the first layer is transversely isotropic and the second layer

is isotropic) and a rigid rough surface. However, considering the thickness of the modified layer and typical indentations of the roughness asperities, it seems that the asperities of the rigid surface indent through the modified layer into the bulk. Therefore, the contact area and hysteresis formulations for the isotropic material are still valid.

5 Conclusions

The rubber friction is decomposed to two main contributors; namely, hysteresis and contribution from real area of contact. Although the hysteresis component is well elaborated, the contribution of contact area has received less attention. The composition and tribological properties of a rubber in contact with a rigid surface are subject to change during frictional sliding contact. The shearing of a thin modified layer to the rough counter surface plays an important role in the total friction. In this study, a physical model is presented to model the degradation of the top rubber layer as a function of the tribological conditions and mechanical properties of the rubber. The degradation is assumed to occur in the filler-polymer network and the healing is neglected. The model consists of three parts; the pressure distribution at the rubber interface is calculated using a multi-scale contact model. The subsurface stresses and consequently energy fields due to the normal pressure and tangential shear applied at the surface are governed. Finally, the modification rate and the thickness of the degraded layer are calculated using both the subsurface energy rate field and the wear rate. The

presented model is applied to a pin-on-disk test. The calculated formation rate is in agreement with the experiment and the model estimates a thickness in the order of typical measured values.

Acknowledgements

The authors would like to gratefully acknowledge Dr. Sissi de Beer for AFM measurements, many useful discussions and suggestions. This project is carried out in the framework of the innovation program “GO Gebundelde Innovatiekracht” and funded by the “European Regional Development Fund”, “Regio Twente” and “Provincie Overijssel”. The project partners Apollo Tyres Global R&D B.V., University of Twente (Tire-Road Consortium), Reef Infra, Stemmer Imaging B.V. and the Provincie Gelderland are gratefully acknowledged.

Appendix: Subsurface Stress Calculation in a Half-Space Loaded on Surface

Consider a half-space loaded by a normal pressure distribution $P(x, y)$ in the z direction and a shear stress $t_x = \mu_x P(x, y)$ along the x direction. The pressure distribution is firstly discretized by rectangular cells with size $2a \times 2b$. If the surface of a half-space is loaded both in the normal direction z and in the tangential direction along x axis, as shown in the figure below, the subsurface stresses can be calculated by superposition of stresses due to normal and tangential loading.

Figure A. 1: The two-dimensional normal stress and tangential shear stress applied on the surface of a half-space is discretized by rectangular cells with size $2a \times 2b$. The pressure at each rectangular cell is uniformly distributed.

The subsurface stress field due to a uniform pressure P in the normal direction over a rectangle area with sides $2a \times 2b$, centred at the origin, is governed by:

$$\sigma_{ij} = \frac{P}{2\pi} [F_{ij}(x+a, y+b, z) - F_{ij}(x+a, y-b, z) + F_{ij}(x-a, y-b, z) - F_{ij}(x-a, y+b, z)] \quad (\text{A.1})$$

with the following functions:

$$F_{xx}(x, y, z) = 2\nu [\tan^{-1} \frac{xz}{Ry} - \tan^{-1} \frac{x}{y} - \tan^{-1} \frac{y}{x} + \tan^{-1} \frac{yz}{Rx} + \frac{xyz}{R(x^2 + z^2)}] \quad (\text{A.2})$$

$$F_{yy}(x, y, z) = F_{xx}(y, x, z) \quad (\text{A.3})$$

$$F_{zz}(x, y, z) = -\tan^{-1} \frac{y}{x} - \tan^{-1} \frac{x}{y} + \tan^{-1} \frac{yz}{Rx} + \tan^{-1} \frac{xz}{Ry} - \frac{xyz}{R(x^2 + z^2)} - \frac{xyz}{R(y^2 + z^2)} \quad (\text{A.4})$$

$$F_{xy}(x, y, z) = -(1 - 2\nu) \log(R + z) - \frac{z}{R} \quad (\text{A.5})$$

$$F_{xz}(x, y, z) = \frac{z^2 y}{R(x^2 + z^2)} \quad (\text{A.6})$$

$$F_{yz}(x, y, z) = \frac{z^2 x}{R(y^2 + z^2)} \quad (\text{A.7})$$

The subsurface stress field due to a uniform shear stress $t_x = \mu_x P(x, y)$ over a rectangle area with sides $2a \times 2b$, centered at the origin, is governed by:

$$\begin{aligned} \sigma_{ij} = \frac{t_x}{2\pi} [& G_{ij}(x + a, y + b, z) \\ & - G_{ij}(x + a, y - b, z) + G_{ij}(x - a, y - b, z) \\ & - G_{ij}(x - a, y + b, z)] \end{aligned} \quad (\text{A.8})$$

with the following functions:

$$\begin{aligned} G_{xx}(x, y, z) = 2 \log(R + y) + \frac{x^2 y}{R(x^2 + z^2)} \\ - (1 - 2\nu) \frac{y}{R + z} \end{aligned} \quad (\text{A.9})$$

$$\begin{aligned} G_{yy}(x, y, z) = 2\nu \log(R + y) + \frac{y}{R} \\ + (1 - 2\nu) \frac{y}{R + z} \end{aligned} \quad (\text{A.10})$$

$$G_{zz}(x, y, z) = \frac{z^2 y}{R(x^2 + z^2)} \quad (\text{A.11})$$

$$G_{xz}(x, y, z) = -\tan^{-1} \frac{yx}{Rz} + \frac{xyz}{R(x^2 + z^2)} \quad (\text{A.12})$$

$$\begin{aligned} G_{xy}(x, y, z) = \log(R + x) - \frac{x}{R} \\ + (1 - 2\nu) \frac{x}{R + z} \end{aligned} \quad (\text{A.13})$$

$$G_{yz}(x, y, z) = -\frac{z}{R} \quad (\text{A.14})$$

6 References

- [1] K.A. Grosch. *The relation between the friction and visco-elastic properties of rubber*, volume 274. 1963.
- [2] B.N.J. Persson. Theory of rubber friction and contact mechanics. *The Journal of Chemical Physics*, 115(8):3840–3861, 2001.
- [3] G. Heinrich, M. Klüppel, and T.A. Vilgis. Evaluation of self-affine surfaces and their implication for frictional dynamics as illustrated with a Rouse material. *Computational and Theoretical Polymer Science*, 10(1-2):53–61, 2000.
- [4] B. Lorenz and B.N.J. Persson. Leak rate of seals: Comparison of theory with experiment. *EPL (Europhysics Letters)*, 86(4):44006, 2009.
- [5] B.N.J. Persson and M. Scaraggi. On the transition from boundary lubrication to hydrodynamic lubrication in Åsoft contacts. *Journal of Physics: Condensed Matter*, 21(18):185002, 2009.
- [6] G. Bóдай and T.J. Goda. Friction force measurement at windscreen wiper/glass contact. *Tribology Letters*, 45(3):515–523, 2012.
- [7] D.F. Moore. *The friction and lubrication of elastomers*, volume 9 of *International series of monographs on materials science and technology*. Pergamon Press, 1972.
- [8] J.A. Greenwood and J.B.P. Williamson. *Contact of Nominally Flat Surfaces*, volume 295. 1966.

- [9] A.W. Bush, R.D. Gibson, and T.R. Thomas. The elastic contact of a rough surface. *Wear*, 35(1):87–111, 1975.
- [10] W. Manners and J.A. Greenwood. Some observations on Persson’s diffusion theory of elastic contact. *Wear*, 261(5-6):600–610, 2006.
- [11] L. Afferrante, G. Carbone, and G. Demelio. Interacting and coalescing Hertzian asperities: A new multiasperity contact model. *Wear*, 278-279:28–33, 2012.
- [12] B.N.J. Persson. On the elastic energy and stress correlation in the contact between elastic solids with randomly rough surfaces. *Journal of Physics: Condensed Matter*, 20(31):312001, 2008.
- [13] G. Carbone and F. Bottiglione. Contact mechanics of rough surfaces: a comparison between theories. *Meccanica*, 46(3):557–565, 2011.
- [14] V.A. Yastrebov, G. Anciaux, and J.F. Molinari. From infinitesimal to full contact between rough surfaces: Evolution of the contact area. *International Journal of Solids and Structures*, 52:83–102, 2015.
- [15] W.B. Dapp, N. Prodanov, and M. H. Müser. Systematic analysis of Persson’s contact mechanics theory of randomly rough elastic surfaces. *Journal of Physics Condensed Matter*, 26(35):355002, 2014.
- [16] P. Wriggers and J. Reinelt. Multi-scale approach for frictional contact of elastomers on rough rigid surfaces. *Computer Methods in Applied Mechanics and Engineering*, 198(21-26):1996–2008, 2009.
- [17] D.F. Moore and W. Geyer. A review of adhesion theories for elastomers. *Wear*, 22(2):113–141, 1972.
- [18] A. Schallamach. A theory of dynamic rubber friction. *Wear*, 6(5):375–382, 1963.
- [19] A.R. Savkoor. *Dry adhesive contact of elastomers*. PhD thesis, University of Delft, The Netherlands, 1987.
- [20] Y.B. Chernyak and A.I. Leonov. On the theory of the adhesive friction of elastomers. *Wear*, 108(2):105–138, 1986.
- [21] M.K. Chaudhury. Rate-dependent fracture at adhesive interface. *The Journal of Physical Chemistry B*, 103(31):6562–6566, 1999.
- [22] C. Drummond, J. Israelachvili, and P. Richetti. Friction between two weakly adhering boundary lubricated surfaces in water. *Physical Review E*, 67(6):066110, 2003.
- [23] T. Baumberger and C. Caroli. Solid friction from stick-slip down to pinning and aging. *Advances in Physics*, 55(3-4):279–348, 2006.
- [24] B.N.J. Persson and A.I. Volokitin. Rubber friction on smooth surfaces. *The European Physical Journal E*, 21(1):69–80, 2006.
- [25] P.G. de Gennes. Soft adhesives. *Langmuir*, 12(19):4497–4500, 1996.
- [26] A. Le Gal, X. Yang, and M. Klüppel. Evaluation of sliding friction and contact mechanics of elastomers based on dynamic-mechanical analysis. *The Journal of Chemical Physics*, 123(1):014704, 2005.
- [27] B.N.J. Persson, O. Albohr, G. Heinrich, and H. Ueba. Crack propagation in rubber-like materials. *Journal of Physics: Condensed Matter*, 17(44):R1071, 2005.
- [28] B.N.J. Persson, I.M. Sivebaek, V.N. Samoilov, Z. Ke, A.I. Volokitin, and Z. Zhenyu. On the origin of amonton’s friction law. *Journal of Physics: Condensed Matter*, 20(39):395006, 2008.
- [29] S. Momozono, K. Nakamura, and K. Kyogoku. Theoretical model for adhesive friction between elastomers and rough solid surfaces. *The Journal of Chemical Physics*, 132(11):114105, 2010.
- [30] S. Momozono, H. Takeuchi, Y. Iguchi, K. Nakamura, and K. Kyogoku. Dissipation characteristics of adhesive kinetic friction on amorphous polymer surfaces. *Tribology International*, 48:122–127, 2012.

- [31] M. Mokhtari, D.J. Schipper, N. Vleugels, and J.W. M. Noordermeer. Existence of a tribo-modified surface layer on sbr elastomers: Balance between formation and wear of the modified layer. *Tribology Letters*, 58(2):1–13, 2015.
- [32] M. Mokhtari, D.J. Schipper, and T.V. Tolpekina. On the friction of carbon black-and silica-reinforced br and s-sbr elastomers. *Tribology Letters*, 54(3):297–308, 2014.
- [33] M. Mokhtari and D.J. Schipper. Existence of a tribo-modified surface layer of BR/S-SBR elastomers reinforced with silica or carbon black. *Tribology International*, Article in press, 2014.
- [34] S. Jacobson and S. Hogmark. Surface modifications in tribological contacts. *Wear*, 266(3-4):370–378, 2009.
- [35] L. Martínez, R. Nevshupa, D. Felhös, J.L. de Segovia, and E. Romin. Influence of EPDM elastomers with different carbon black contents. *Tribology International*, 44(9):996–1003, 2011.
- [36] J. Karger-Kocsis, A. Mousa, Z. Major, and N. Békési. Dry friction and sliding wear of EPDM rubbers against steel as a function of carbon black content. *Wear*, 264(3-4):359–367, 2008.
- [37] J.M. Degrange, M. Thomine, P. Kapsa, J.M. Pelletier, L. Chazeau, G. Vigier, G. Dudragne, and L. Guerbé. Influence of viscoelasticity on the tribological behaviour of carbon black filled nitrile rubber (nbr) for lip seal application. *Wear*, 259(1-6):684–692, 2005.
- [38] M.-J. Wang and Y. Kutsovsky. Effect of fillers on wet skid resistance of tires. Part II: Experimental observations on effect of filler-elastomer interactions on water lubrication. *Rubber Chemistry and Technology*, 81(4): 576–599, 2008.
- [39] N.V. Rodriguez, M.A. Masen, and D.J. Schipper. Tribologically modified surfaces on elastomeric materials. *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology*, 227(5): 398–405, 2013.
- [40] B.N.J. Persson. Rubber friction: role of the flash temperature. *Journal of Physics: Condensed Matter*, 18(32):7789, 2006.
- [41] V. Panin, A. Kolubaev, S. Tarasov, and V. Popov. Subsurface layer formation during sliding friction. *Wear*, 249(10-11):860–867, 2001.
- [42] S. Tarasov, V. Rubtsov, and A. Kolubaev. Subsurface shear instability and nanostructuring of metals in sliding. *Wear*, 268(1-2):59–66, 2010.
- [43] J. Shang, W. Ma, and J. Lu. Formation of laminar structure under unlubricated friction of Cu-SiO₂ composite. *Tribology Letters*, 48(2):249–254, 2012.
- [44] R.K. Lee, L.A. Korduba, and A. Wang. An improved theoretical model of orientation softening and cross-shear wear of ultra high molecular weight polyethylene. *Wear*, 271(9-10):2230–2233, 2011.
- [45] W.G. Knauss. *Rupture phenomena in viscoelastic materials*. PhD thesis, California Institute of Technology, 1963.
- [46] T. Nakazono and A. Matsumoto. Mechanical aging behavior of styrene-butadiene rubbers evaluated by abrasion test. *Journal of Applied Polymer Science*, 120(1):379–389, 2011.
- [47] R. Dargazany, V.N. Khiêm, and M. Itskov. A generalized network decomposition model for the quasi-static inelastic behavior of filled elastomers. *International Journal of Plasticity*, 63:94–109, 2014.
- [48] M. Qu, F. Deng, S.M. Kalkhoran, A. Gouldstone, A. Robisson, and K.J. van Vliet. Nanoscale visualization and multiscale mechanical implications of bound rubber interphases in rubber-carbon black nanocomposites. *Soft Matter*, 7(3): 1066–1077, 2011.

- [49] D. De Tommasi, G. Puglisi, and G. Saccomandi. A micromechanics-based model for the mullins effect. *Journal of Rheology*, 50(4):495–512, 2006.
- [50] S. Govindjee and J. Simo. A micro-mechanically based continuum damage model for carbon black-filled rubbers incorporating Mullins effect. *Journal of the Mechanics and Physics of Solids*, 39(1): 87–112, 1991.
- [51] L. Staniewicz, T. Vaudey, C. Degrandcourt, M. Couty, F. Gaboriaud, and P. Midgley. Electron tomography provides a direct link between the payne effect and the inter-particle spacing of rubber composites. *Scientific Reports*, 4:7389, 2014.
- [52] S. Merabia, P. Sotta, and D.R. Long. A microscopic model for the reinforcement and the nonlinear behavior of filled elastomers and thermoplastic elastomers (Payne and Mullins effects). *Macromolecules*, 41(21): 8252–8266, 2008.
- [53] A.R. Payne. Dynamic properties of heat-treated butyl vulcanizates. *Journal of Applied Polymer Science*, 7(3):873–885, 1963.
- [54] M. Itskov, A. Ehret, R. Kazakevičiūtė-Makovska, and G. Weinhold. A thermodynamically consistent phenomenological model of the anisotropic Mullins effect. *ZAMM - Journal of Applied Mathematics and Mechanics*, 90(5):370–386, 2010.
- [55] Y. Merckel, M. Brieu, J. Diani, and J. Caillard. A Mullins softening criterion for general loading conditions. *Journal of the Mechanics and Physics of Solids*, 60(7):1257–1264, 2012.
- [56] A.F. Blanchard and D. Parkinson. Breakage of carbon-rubber networks by applied stress. *Industrial & Engineering Chemistry*, 44(4): 799–812, 1952.
- [57] F. Bueche. Molecular basis for the Mullins effect. *Journal of Applied Polymer Science*, 4(10):107–114, 1960.
- [58] R. Houwink. Slipping of molecules during the deformation of reinforced rubber. *Rubber Chemistry and Technology*, 29(3):888–893, 1956.
- [59] G. Marckmann, E. Verron, L. Gornet, G. Chagnon, P. Charrier, and P. Fort. A theory of network alteration for the Mullins effect. *Journal of the Mechanics and Physics of Solids*, 50(9):2011–2028, 2002.
- [60] D.E. Hanson, M. Hawley, R. Houlton, K. Chitanvis, P. Rae, E.B. Orler, and D.A. Wroblewski. Stress softening experiments in silica-filled polydimethylsiloxane provide insight into a mechanism for the Mullins effect. *Polymer*, 46(24):10989–10995, 2005.
- [61] J.A.C. Harwood, L. Mullins, and A.R. Payne. Stress softening in natural rubber vulcanizates. Part II. stress softening effects in pure gum and filler loaded rubbers. *Journal of Applied Polymer Science*, 9(9): 3011–3021, 1965.
- [62] G. Kraus, C.W. Childers, and K.W. Rollmann. Stress softening in carbon black-reinforced vulcanizates. Strain rate and temperature effects. *Journal of Applied Polymer Science*, 10(2):229–244, 1966.
- [63] Y. Fukahori. New progress in the theory and model of carbon black reinforcement of elastomers. *Journal of Applied Polymer Science*, 95(1):60–67, 2005.
- [64] L. Mullins. Effect of stretching on the properties of rubber. *Rubber Chemistry and Technology*, 21(2):281–300, 1948.
- [65] Z. Rigbi. *Reinforcement of rubber by carbon black*, volume 36 of *Advances in Polymer Science*, chapter 2, pages 21–68. Springer Berlin Heidelberg, 1980.
- [66] J. Diani, B. Fayolle, and P. Gilormini. A review on the mullins effect. *European Polymer Journal*, 45(3):601–612, 2009.
- [67] R. Dargazany and M. Itskov. A network evolution model for the anisotropic mullins effect in carbon black filled rubbers. *International Journal of Solids and Structures*, 46(16):2967–2977, 2009.

- [68] G. Huber and T.A. Vilgis. Polymer adsorption on heterogeneous surfaces. *The European Physical Journal B - Condensed Matter and Complex Systems*, 3(2):217–223, 1998.
- [69] S.R. Rickaby and N.H. Scott. Cyclic stress-softening model for the mullins effect in compression. *International Journal of Non-Linear Mechanics*, 49:152–158, 2013.
- [70] S.R. Rickaby and N.H. Scott. Orthotropic cyclic stress-softening model for pure shear during repeated loading and unloading. *IMA Journal of Applied Mathematics*, 79(5):869–888, 2014.
- [71] J.L. Hutter and J. Bechhoefer. Calibration of Atomic Force Microscope tips. *Review of Scientific Instruments*, 64(7):1868–1873, 1993.
- [72] J. Diani, M. Brieu, and P. Gilormini. Observation and modeling of the anisotropic visco-hyperelastic behavior of a rubberlike material. *International Journal of Solids and Structures*, 43(10):3044–3056, 2006.
- [73] S.R. Rickaby and N.H. Scott. Transversely isotropic cyclic stress-softening model for the mullins effect. *Proc. R. Soc. A*, 468:4041–4057, 2012.
- [74] C.G. Figueroa, I. Ortega, V.H. Jacobo, A. Ortiz, A.E. Bravo, and R. Schouwenaars. Microstructures of tribologically modified surface layers in two-phase alloys. *IOP Conf. Series: Materials Science and Engineering*, 63(012018), 2014. 6th International Conference on Nanomaterials by Severe Plastic Deformation.
- [75] D. Haba, J. Kaufmann, A.J. Brunner, K. Resch, and C. Teichert. Observation of elastic modulus inhomogeneities in thermosetting epoxies using afm – discerning facts and artifacts. *Polymer*, 55(16):4032–4040, 2014.
- [76] J.S. Villarrubia. Morphological estimation of tip geometry for scanned probe microscopy. *Surface Science*, 321(3):287–300, 1994.
- [77] S. Liu and Q. Wang. Studying contact stress fields caused by surface tractions with a discrete convolution and fast fourier transform algorithm. *Journal of Tribology*, 124(1):36–45, 2002.
- [78] M. Paggi and M. Ciavarella. The coefficient of proportionality κ between real contact area and load with new asperity models. *Wear*, 268(7-8):1020–1029, 2010.
- [79] J.A. Greenwood and J.J. Wu. Surface roughness and contact: An apology. *Meccanica*, 36(6):617–630, 2001.
- [80] J.F. Archard. Elastic deformation and the laws of friction. *Proc. R. Soc. A*, 243(1233):190–205, 1957.
- [81] R.L. Jackson and J.L. Streater. A multi-scale model for contact between rough surfaces. *Wear*, 261(11-12):1337–1347, 2006.
- [82] K.L. Johnson, J.A. Greenwood, and J.G. Higginson. The contact of elastic regular wavy surfaces. *International Journal of Mechanical Sciences*, 27(6):383–396, 1985.
- [83] J. Bos. *Friction heating of tribological contacts*. PhD thesis, University of Twente, The Netherlands, 1995.

Existence of a tribo-modified surface layer on SBR elastomers: balance between formation and wear of the modified layer

M. Mokhtari, D.J. Schipper, N. Vleugels, J.W.M. Noordermeer
Tribology Letters (2015) 58:22

Tribol Lett (2015) 58:22
DOI 10.1007/s11249-015-0496-3

ORIGINAL PAPER

Existence of a Tribo-Modified Surface Layer on SBR Elastomers: Balance Between Formation and Wear of the Modified Layer

Milad Mokhtari · Dirk J. Schipper · Nadia Vleugels ·
Jacques W. M. Noordermeer

Received: 20 December 2014 / Accepted: 15 February 2015 / Published online: 22 March 2015
© The Author(s) 2015. This article is published with open access at Springerlink.com

Abstract In most of the tribological contacts, the composition and tribological properties of the original interface will change during use. The tribo-film, with modified properties compared to the bulk, are dynamic structures that play a significant role in friction. The existence of a tribo-modified surface layer and its importance on the overall friction of elastomers has been shown both theoretically and experimentally before. The characteristics of the modified surface layers deserve specific attention since the tribological properties of elastomers in contact with a rough counter-surface are determined by these modified surfaces together with the properties of bulk of the material. Both the formation of the modified layer and the break down (wear) of it are of importance in determining the existence and thickness of the tribo-modified layer. In this study, the importance of the wear is emphasized by comparing two styrene butadiene rubber-based elastomers in contact with a granite sphere. A current status of perception of the removal and the stability of the modified surface layers on rubbers is introduced as well as experimental work related to this matter and discussion within literature. Pin-on-disk friction tests are performed on two SBR-based samples in contact with a granite sphere under controlled environmental conditions to form the modified surface layer. Although the hysteresis part of the

friction force which has a minor contribution in the overall friction is not markedly different, the total measured friction coefficient differs significantly. Mechanical changes both inside and outside the wear track are determined by atomic force microscope nano-indentations at different timescales to examine the modified surface layer on the test samples. The specific wear rates of the two tribo-systems are compared, and the existence of the modified surface layer, the different measured friction coefficient and the running-in distances toward steady-state friction are explained considering different wear rates. A conceptual model is presented, correlating the energy input into the tribo-system and the existence of a modified surface layer.

Keywords Friction · Modified surface layer · Balance between formation and wear · SBR · AFM nano-indentation · Rubber friction

List of symbols

F_f	Total friction force (N)
F_{vis}	Hysteresis contribution of friction force induced by viscoelastic losses (N)
τ_s	Frictional shear stress (Pa)
A_{real}	Real area of contact (m^2)
μ	Total coefficient of friction
F_N	Nominal normal load (N)
p_0	Nominal contact pressure (Pa)
A_0	Nominal area of contact (m^2)
μ_{vis}	Viscoelastic or hysteresis coefficient of friction
$P(q)$	Real to nominal area of contact ratio as a function of wave vector
ω	Frequency of the applied load to the rubber (rad/s)
λ	Length scale of the roughness under study (m)
q	Amplitude of the roughness wave vector ($1/m$)

M. Mokhtari (✉) · D. J. Schipper
Surface Technology and Tribology, Faculty of Engineering
Technology, University of Twente, P.O. Box 217,
7500 AE Enschede, The Netherlands
e-mail: m.mokhtari@utwente.nl; m.mokhtari@gmail.com

N. Vleugels · J. W. M. Noordermeer
Electromechanical Technology and Engineering, Faculty of Engineering
Technology, University of Twente, P.O. Box 217,
7500 AE Enschede, The Netherlands

Notation

F_f	Total friction force	(N)
F_{vis}	Hysteresis contribution of friction force	(N)
F_N	Nominal normal load	(N)
A_{real}	Real area of contact	(m ²)
A_0	Nominal area of contact	(m ²)
$A(q)$	Apparent contact area when the surface is smooth on wave vectors $> q$	(m ²)
$P(q)$	Real to the nominal area of contact ratio	(-)
$C(q)$	Power spectral density of the roughness	(m ⁴)
q	Amplitude of the roughness wave vector	(1/m)
q_0	Lower wave vector cutoff related to the longest wave length	(1/m)
q_1	Higher wave vector cutoff related to the shortest wave length	(1/m)
E	Modulus of elasticity	(Pa)
E_{in}	Tribological energy input	(J)
s	Sliding distance	(m)
Q_f	Formation rate of the modified surface layer	(m/s)
Q_w	Wear rate	(m/s)
k	Specific wear rate	(mm ³ /Nm)
a_T	Temperature-frequency viscoelastic horizontal shift factor	(-)

ω	Frequency of the applied load to the rubber	(rad/s)
λ	Length scale of the roughness under study	(m)
ϕ	Angle between the velocity vector and the wave vector $\vec{q}$	(rad)
σ_0	Nominal contact pressure	(Pa)
μ_f	Total coefficient of friction	$(-)$
μ_{hys}	Viscoelastic or hysteresis coefficient of friction	$(-)$
τ_f	Frictional shear stress	(Pa)
δ_{total}	Thickness of the modified surface layer at balance	(m)
δ_f	Modified surface layer thickness, neglecting wear	(m)
δ_w	Thickness of the worn layer	(m)
ζ	Magnification factor	$(-)$
ν	Poisson's ratio	$(-)$

Existence of a tribo-modified surface layer on SBR elastomers: balance between formation and wear of the modified layer

M. Mokhtari, D.J. Schipper, N. Vleugels*, J.W.M. Noordermeer*

Surface Technology and Tribology, Faculty of Engineering Technology, University of Twente,
P.O. Box 217, 7500 AE Enschede, The Netherlands

*Elastomer Technology and Engineering, Faculty of Engineering Technology, University of
Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

Abstract

In most of the tribological contacts, the composition and tribological properties of the original interface will change during use. The tribo-films, with modified properties compared to the bulk, are dynamic structures that play a significant role in friction. The existence of a tribo-modified surface layer and its importance on the overall friction of elastomers has been shown both theoretically and experimentally before. The characteristics of the modified surface layer deserve specific attention since the tribological properties of elastomers in contact with a rough counter-surface are determined by these modified surfaces together with the properties of bulk of the material. Both the formation of the modified layer and the break down (wear) of it are of importance in determining the existence and thickness of the tribo-modified layer. In this study, the importance of the wear is emphasized by comparing two styrene butadiene rubber-based elastomers in contact with a granite sphere. A current status of perception of the removal and the stability of the modified surface layers on rubbers is introduced as well as experimental work related to this matter and discussion within literature. Pin-on-disk friction tests are performed on two SBR-based samples in contact with a granite sphere under controlled environmental conditions to form the modified surface layer. Although the hysteresis part of the friction force which has a minor contribution in the overall friction is not markedly different, the total measured friction coefficient differs significantly. Mechanical changes both inside and outside the wear track are determined by atomic force microscope nano-indentations at different time scales to examine the modified surface layer on the test samples. The specific wear rates of the two tribo-systems are compared, and the existence of the modified surface layer, the different measured friction coefficient and the running-in distances toward steady-state friction are explained considering different wear rates. A conceptual model is presented, correlating the energy input into the tribo-system and the existence of a modified surface layer.

1 Introduction

Friction needs to be accurately accounted for in a smart design of various rubber engineering components including but not limited to tires, rubber seals, wiper blades, conveyor belts and syringes [1–4]. Even today, there remains an incomplete understanding of the rubber friction problem, in spite of the fact that great interest has been dedicated by studying the tribological behavior of rubber sliding contacts over the last 50 years, which marks the difficulty of the problem.

Classifying the friction force between rubber and a rough surface, two main contributors are commonly described, i.e., the adhesion component and the hysteresis component [5]. Adhesion is related to the attractive forces between the contacting bodies [6]. Cyclic deformation of the rubber dissipates energy via the internal damping in the bulk of the material and generates the hysteresis component of friction [2]. Other contributors to rubber friction are energy dissipation due to crack opening [7] and energy dissipation in shearing of a thin viscous film [8]. The significant role of interfacial interactions in determining the wet sliding friction of elastomer compounds has been noted by Pan [9]. The friction force contributions mentioned before are summarized in terms of two main forces: (1) the contributions related to the viscoelastic deformation of the rubber, and (2) the contributions related to the real area of contact as defined in Eq. 1. One cannot indicate one contributor as the main contributor to the friction as a generalized rule, but depending on the tribological conditions,

hysteresis or contribution from the real area of contact can play a dominant role in determining the overall friction.

$$F_f = F_{vis} + \tau_f A_{real} \quad (1)$$

where F_f , F_{vis} are the forces concerning the total friction and the contribution from the hysteresis losses respectively and the product $\tau_f A_{real}$ represents the force in the real area of contact where τ_f , A_{real} are the frictional shear stress and real area of contact.

1.1 Contact and Friction of Rubbers

Several contact models have been proposed and examined for various materials [2, 10–12]. Among them, the asperity contact theory, first addressed by Greenwood and Williamson [10], has attracted attention of several researchers for a long time and has been used to describe rough surfaces in contact. Neglecting the interaction between neighboring asperities is the main disadvantage of such models. Rubbers are considered as elastically soft materials that are flexible and, therefore, can deform much easier than most of the engineering materials such as metals. Thus, the effect of the asperities on each other cannot be neglected. The interaction between the asperities can be added to the current asperity models [13, 14]; however, these approaches remain quite approximate [15]. On the other hand, Persson’s contact theory does not pre-exclude any scale of roughness (unlike asperity contact models) from the contact analysis [2], it considers the contact in the limit of full contact and

further extends the analysis to the partial contact by imposing a boundary condition. Although Manners and Greenwood [16] raise some concerns about the boundary conditions applied in Persson's theory, the rubber behavior (a hyperelastic material with the ability to bend and fill out the roughness on at least small wave lengths) is more analogous to Persson's analysis, than the asperity contact models (where it is assumed that contact occurs on segregated islands, far from each other, which are named asperities and do not have any influence on each other because of the far distances in between).

However, Persson's contact theory as like as other models is an approximation (because of the assumptions which are made to simplify the complex problem of the contact between rubber-like materials and rigid rough surfaces) to the physical reality that occurs. It has been subject to comparison with other contact models and has been analyzed [17] extensively. The results of comparisons can lead to guidelines for enhancing the theory.

The basic equations of the hysteresis coefficient of friction as well as the real area of contact, based on Persson's contact and friction theory, are summarized below [7]:

$$\mu_{hys} \approx \frac{1}{2} \int_{q_0}^{q_1} dq q^3 C(q) P(q) \times \int_0^{2\pi} d\phi \cos \phi \operatorname{Im} \left[\frac{E(qv \cos \phi)}{(1 - \nu^2) \sigma_0} \right] \quad (2)$$

where the function $P(q) = A(q)/A_0$ is given by

$$P(q) = \frac{2}{\pi} \int_0^\infty dx \frac{\sin x}{x} \exp \left[-x^2 G(q) \right] \quad (3)$$

where

$$G(q) = \frac{1}{8} \int_{q_0}^q dq q^3 C(q) \int_0^{2\pi} d\phi \left| \frac{E(qv \cos \phi)}{(1 - \nu^2) \sigma_0} \right|^2 \quad (4)$$

The contribution to the overall friction due to the force of shearing a thin fluid-like film formed by segments of rubber molecules [8] has been suggested to be modeled as:

$$F_{shear} = \tau_f A \quad \text{with} \quad \tau_f = \tau_0 (a_T v)^\alpha \quad (5)$$

where a_T is the temperature-frequency viscoelastic shift factor and τ_0 is basically a fitting parameter. One can find more about the origin of the formulas in [7].

The present study investigates the importance of shearing the modified surface layer and its contribution to the overall friction, and highlights the nature of a dynamic process which involves formation and removal of the modified surface layer.

1.2 Thin Modified Surface Layer

The composition and tribological properties of the original interface changes during use in most tribological contacts. This has been shown for various materials under various tribological conditions [18]. However, there are not many studies on the existence and the properties of the modified surface layer in contact with elastomers with a rigid rough counter-surface. It is worth emphasizing that these

modified surfaces play an important role in determining the tribological behavior. The important role of shearing the top rubber layer in the overall friction is demonstrated in some tribological systems [19]. It has been shown that τ_f may change due to degradation of the top rubber layer in contact with the counter-surface, and therefore, the overall friction changes [20].

The rubber surface that is in contact with the counter-surface undergoes changes in mechanical properties (and chemical compositions) in comparison with the bulk or with the non-contact parts of the rubber surface [21–27]. Therefore, the mechanical properties of the modified surface layer should be used in modeling the friction and not the properties of the bulk of the material (see Fig. 1). This is especially important in tribo-systems where the contribution from shearing the top rubber layer is controlling the friction [20]. Moreover, not much research has been performed on understanding the physical properties of the tribo-modified surface layers on elastomers. In addition, the dynamics of the formation, removal and the stability of the tribo-modified surface layers on rubbers (which is the result of a balance between formation and wear of the modified surface layer) are still not well understood. The formation process (and rate) of the modified layer is not discussed in the present study. However, the modified layer is also subject to wear. The generated modified surface layer might be completely gone due to wear if the wear rate is equal to or higher than the modification rate. The generated modified surface layer, i.e., the mechanical properties, is studied experimentally. The

mechanical properties of the modified surface layers are dependent on the tribological conditions; it has been shown that a more severe tribological condition might lead to more loss of elastic modulus [20]. Moreover, wear is also dependent on the tribological conditions, and it can change dramatically depending on the tribological conditions. Therefore, the friction behavior, wear and tribo-film formation are interrelated for the studied tribo-systems. Gaining a quantitative insight into the interfacial layer existence and the change in properties demands a detailed study of several tribo-systems. The present study focuses on the important role of wear on the existence of such a layer.

Figure 1: Rough granite ball is shown in contact with a rubber disk. The contact is considered on different scales. Viscoelastic losses together with shearing of the granite to the rubber determine the friction. Shear occurs between a modified surface layer and rough granite.

2 Materials and Experimental Methods

2.1 Materials

The rubber formulations employed in this study are based on a solution-polymerized styrene butadiene rubber (SSBR Buna VSL VP PBR 4045 from Lanxess, Leverkusen, Germany), type of elastomer with a styrene content of 25 %, a vinyl content of 25 % and a butadiene content of 50 %. Two samples are prepared. Sample (1) is unreinforced vulcanized SBR rubber, and sample (2) is reinforced with 3 parts per hundred rubber (phr) aramid fibers. The fibers which were supplied by Teijin Aramid BV, the Netherlands, have an initial length of 3 *mm* and a fiber diameter of 10–12 microns. Moreover, 3-octanoylthio-1-propyltriethoxysilane (NXT) from Evonik GmbH is used as coupling agent for sample (2) to provide sufficient chemical bonding between the rubber matrix and the fibers. The ethoxy part of the used coupling agent molecule reacts with the fibers, while the thiol part goes through a reaction with the rubber. In order to enhance the fiber/rubber adhesion, the fibers were coated with an epoxy-amine coating. No coupling agent was used in preparation of the first sample. The fibers were randomly oriented, so the mechanical properties do not differ along different axes. Moreover, the fibers were selected to be sufficiently thin and closely spaced, so that the materials appear homogeneous on the length scales which matter for friction.

Table 1: Rubber formulation of prepared samples with the amounts of components indicated in weight parts of component per hundred weight parts of the rubber (phr).

Compound	Sample 1	Sample 2
Description	phr	phr
S-SBR	100	100
Aramid fiber	0	3
NXT	0	1
Sulfur	1.4	1.4
ZnO	2.5	2.5
Stearic acid	2.5	2.5
TBBS ^a	1.7	1.7

^aN-tert-butylbenzothiazole-2-sulphenamide is used as accelerator.

An overview of the rubber compounds prepared with the corresponding amounts (phr) of the components is given in Table 1.

The compounds were prepared on a 350-mL Brabender 350S internal mixer using a two-stage mixing procedure (50 °C, 1:1.13 rotor speed ratio); the fibers and the zinc oxide are added to the loaded rubber after 1 and 2.5 *min*, respectively. Then, after 3 *min*, the residue is swept back in the hopper. The fibers are dispersed on a Polymix 80T mill for 30 *min* at 130 °C. After the dispersion of the fibers on the mill, the first-stage master batch is returned to the mixing chamber for a second stage and mixed with the curatives up to a temperature of 100 °C at 75 *rpm* for 3 *min*.

The compounds are then vulcanized in a Wickert press WLP 1600 under a pressure of 100 *bar* and at 160 °C, according to their $t_{90} + 2$ *min* optimum vulcanization time, as determined in a Rubber Process Analyzer RPA 2000

of Alpha Technologies, following the procedure described in ISO 3417.

2.2 Viscoelasticity of Compounds

The dynamic properties of the rubber samples were measured by Dynamical Mechanical Analysis in a Metravib DMA 2000 dynamic spectrometer in temperature sweep mode, under dynamic and static strains of 0.1 and 1 %, respectively, at a fixed frequency of 10 *Hz*, over a wide temperature range (-90 to +120 °C) with strip specimens of 2 *mm* thickness and 35 *mm* length to determine the glass transition temperatures of the samples. The measured loss tangent, which is the ratio between the loss and storage moduli, is shown as a function of temperature for the two samples in Fig. 2.

Figure 2: Measured loss tangent as a function of temperature for both samples.

In order to create dynamic mechanical master curves, frequency-dependent elasticity modulus measurements in tension mode were taken at different temperatures between -30 and 50 °C, each varying the frequency between 1

and 200 *Hz*. The glass transition temperature and the selected reference temperature $T_{ref} = 27$ °C are used to shift the measured elastic modulus $E(\omega)$ versus frequency ω both horizontally and vertically. The calculated master curves for the moduli of elasticity as a function of frequency are shown in Fig. 3 for both samples. The reinforced sample (2) has a higher elasticity modulus than sample (1) but the mechanical characteristics of the two samples are not grossly different, especially at higher frequencies. The loss tangent which has been used traditionally as a measure for the hysteresis in the rubber samples is approximately similar for lower temperatures; however, sample (1) shows higher values for higher temperatures, see Fig. 2.

2.3 Friction Tests

The friction between the prepared rubber disks and a granite ball with a diameter of 30 *mm* and a root-mean-square roughness of 2.1 μm was measured by a ball-on-disk setup under controlled environmental conditions: The temperature is kept constant at 27 °C and the relative humidity at 50 %. The sliding velocity is 5 *mm/s*, and the nominal contact pressure between the granite and the rubbers is 0.175 *MPa*. The roughness of the granite sphere was measured using two different scanning techniques, confocal microscopy and atomic force microscopy (AFM) in the contact mode. The measurements obtained by both techniques as well as the calculated power spectral density of the roughness of the granite ball governed by each method are shown in Fig. 4. The surface of the granite ball is prepared by

Figure 3: Shifted storage (a) and loss (b) moduli of elasticity as a function of frequency.

sand blasting. As shown, the granite surface is self-fractal. It is noteworthy that confocal microscopy and atomic force microscopy measurements provide consistent measures.

The slope of the power spectrum in the self-affine fractal region corresponds to the Hurst exponent $H = 0.87$ or fractal dimension $D_f = 3 - H = 2.13$ that is very typical for most surfaces [28]. The measured steady-state coefficient of friction under dry conditions is shown in Fig. 5 (blue bars). In addition, the contribution from the hysteresis component of friction is decoupled from the total friction and measured by a simple experiment; the rubber surface was wetted by a very thin layer of oil (Ondina 927 with a dynamic viscosity of 78 *mPas* at 20 °C) such that the lubricated tribo-system remains in the boundary lubrication regime. The measured hysteresis contribution to the

total friction is also shown in Fig. 5 (red bars). Although the dynamic properties of the samples are not very different, the measured coefficients of friction differ drastically. However, the hysteresis part of the friction is approximately similar for all the samples. This is because hysteresis is dependent on the dynamical properties of the rubber samples (and roughness which is similar in all tribo-systems), but the total friction is also dependent on the real area of contact (that is also dependent on viscoelasticity and the roughness of the sample) and the frictional shear stress τ_f , as given in Eq. 1. Therefore, the frictional shear stress should be the source of the difference in the measured total friction for samples (1) and (2).

Another major difference between the two studied tribological systems is the running-in phase: The measured friction coefficient between sample (1) in contact with the rough granite ball becomes

Figure 4: Rough contact surface obtained by use of a confocal microscope in the wave-vector range $1.58 \times 10^4 \text{ m}^{-1} \leq q \leq 9.77 \times 10^5 \text{ m}^{-1}$ (a), by use of an atomic force microscope in the range $9.77 \times 10^5 \text{ m}^{-1} \leq q \leq 7.07 \times 10^8 \text{ m}^{-1}$ (b) and the calculated power spectral density of the roughness (c).

constant (steady state) after a short run-in distance and hardly changes anymore; however, the measured friction coefficient decreases gradually and becomes stable only after a long run-in distance for sample (2) as shown in Fig. 6.

Figure 5: Total and hysteresis component of friction (measured by pin-on-disk test rig) and the run-in distance for samples (1) and (2) before the measured friction is stabilized.

Figure 6: Measured coefficient of friction and its transient shown versus sliding distance.

3 Numerical Results

The hysteresis coefficient of friction, based on Eq. 2 and using the measured roughness and mechanical properties of the samples, is calculated for both samples and shown as a function of velocity in Fig. 7. The calculated coefficient of friction matches with the measured hysteresis component of friction shown with red bars in Fig. 5. As mentioned before, the hysteresis part of the friction is not very different simply because of their nearly similar mechanical properties.

Figure 7: Hysteresis coefficient of friction as a function of sliding velocity, calculated for both samples.

Moreover, the ratio between the real area of contact and the apparent contact area, for a sliding velocity of $v = 5 \text{ mm/s}$, as a function of the magnification factor $\zeta = q/q_0$, is calculated using Eq. 3. The numerical results are presented in Fig. 8.

Considering the fact that sample (1) is elastically softer, it deforms more, and therefore, the calculated real area of contact for sample (1) is higher than for sample (2). However, this difference in the

calculated contact area cannot explain the differences shown in the measured friction coefficients. Based on Eq. 5, the shear strength should be taken into account to explain the difference in friction.

Figure 8: Variation of real area of contact over nominal contact area as a function of magnification for sliding velocity of $v = 5$ mm/s for both samples.

4 AFM Nano-indentations

As discussed earlier, the contribution to friction from the real area of contact plays an important role in determining the overall friction in the studied tribo-system. Hence, the properties of the top rubber layer in contact with the granite sphere should be studied. There are not many studies where existence of a modified surface layer on top of the rubber has been explored. In [25], scanning electron microscopy (SEM) imaging was used to visualize such a layer. No quantitative data, except about the thickness of the layer, could be derived from SEM imaging; therefore, atomic force microscope (AFM) nano-indentations were used to investigate

the mechanical properties of the modified surface layer [20]. The mechanical properties of the wear track of both samples were studied using AFM nano-indentations and compared with the bulk or non-contact sections of the rubber disk. In order to apply low loads and consequently bring about low penetration depths, a cantilever with a low spring constant (a nominal spring constant of 0.10 N/m) was used.

To avoid surface roughness effects in determining the elastic modulus from nano-indentation results, a featureless, smooth region of the rubber was selected. The absolute roughness of the regions selected for nano-indentation was in the order of a few nm on a $1\text{ }\mu\text{m} \times 1\text{ }\mu\text{m}$ scale. Further, no evident residual imprint was detected after penetration which suggests no occurrence of plastic deformation due to indentation. Thus, only phenomena with viscoelastic nature are active during indentation. The deflection sensitivity was measured by indenting an elastically hard material, i.e., silicon at various indenter rates. The procedure proposed by Green [29] was used to measure the spring constant of the cantilever. Nano-indentations were performed with loads ranging from about 0.04 – 187 nN and indentation rates in the range 21 – 3.6×10^8 nm/s.

The contact model of a blunted pyramidal tip indenting an elastic half-space [30] was used to analyze the force-indentation depth diagrams. Considering the fact that the unloading part of the force-indentation depth diagrams is not advantageous for quantitatively characterizing the studied surfaces [31], the elasticity modulus of the samples

was obtained by the loading part of the indentation tests.

The calculated moduli of elasticity for both samples are shown as a function of indenter rate in Fig. 9. The nano-indentation results do not reveal any changes in the mechanical properties of sample (1), though the wear track of sample (2) has different mechanical properties in terms of elastic modulus. This change is more noticeable when indenting the rubber with a higher velocity.

5 Discussion

The AFM nano-indentation results presented in Sect. 4 demonstrate the absence of the modified surface layer on sample (1); the elastic moduli inside and outside the wear track are approximately similar. It was shown that formation of such a layer and its properties are dependent on the tribological conditions and consequently the mechanical energy that has been applied to the rubber surface [20]. Considering the fact that the coefficient of friction of sample (1) is higher than for sample (2), it may be concluded that the frictional work generated in contact with sample (1) with the granite is higher in comparison with the sample (2) granite tribo-system. Nonetheless, the frictional work is not only dissipated in tribo-material evolution but also in wear particle generation.

The wear debris of both samples in contact with the granite is powdery and “dusty-like” as shown in Fig. 10. The specific wear rates are $k_1 = 1.83 \times 10^{-1} \text{ mm}^3/\text{Nm}$ and $k_2 = 3.87 \times 10^{-3} \text{ mm}^3/\text{Nm}$

for samples (1) and (2), respectively. Sample (1) has a much worse resistance to wear in comparison with sample (2). This is evident, when comparing the specific wear rates which differ by even two decades of magnitude. This can be explained by the concept of the crack mean-free path, using theory of powdery rubber wear [32]; it has been suggested that reducing the crack mean-free path results in reduction of the wear rate. Unreinforced rubber compound, because of lack of (strong) inhomogeneities which can scatter the crack tip and reduce the crack mean-free path, has a very bad wear resistance. On the other hand, in a reinforced rubber when the crack tip reaches a filler particle cluster, it may bend by $\sim 90^\circ$ rather than penetrate through the filler particle. More particularly, the smaller wear rate for sample (2) is due to much larger energy (per unit area) required to propagate a crack in the reinforced rubber, as discussed in [33].

The frictional energy can be dissipated by different mechanisms such as frictional heating, elastic (and or plastic) deformations or fracture of one or both bodies in contact, the formation of modified surface layers and tribo-materials, making or breaking adhesive bonds and wear. In the contact between an elastomer and a rigid surface, wear, formation of tribo-modified surface layers and heat generation are the main modes of energy dissipation. In the current study, the sliding velocity is kept low such that heat generation is negligible. Therefore, the main forms of energy dissipation are formation of the modified surface layer and wear. The tribological energy input exerted into the tribo-system is defined as

Figure 9: Time dependence of elastic modulus for: (a) sample (1), (b) sample (2), both inside and outside the wear track, measured by AFM nano-indentations.

Figure 10: Scanning electron microscope images of rubber wear particles: (a) sample (1), (b) sample (2).

the product of the friction force F_f and worked length s

$$E_{in} = \sum F_f s = F_N \int \mu s ds \quad (6)$$

The concept of formation and removal of a thin layer with different properties than the bulk of the material, the competition between these two phenomena and the balance between them has been studied for other materials such as ceramics [34] or steel components in the boundary lubrication regime and at presence of lubricant additives [35]. The sliding resistance of an elastomer in contact with a rigid rough surface is dependent on the nature of the interface which is prone to changing because of the frictional energy dissipation during use. Subsequently, wear should be considered in the context of friction of elastomers. The necessity of embedding wear models into friction models has been shown for other materials [36]. The balance of the modified surface layer writes:

$$\frac{d\delta_{total}}{dt} = Q_f - Q_w \quad (7)$$

where δ_{total} is the thickness of the modified surface layer, Q_f is the formation rate of the modified surface layer and the Q_w is the wear rate. Under steady-state conditions, $d\delta_{total}/dt = 0$, and therefore, $Q_f = Q_w$. More experimental studies are required to model the formation of the modified surface layer theoretically, and therefore, the formation rate is not studied in the present study. However, it is known that the formation rate is a function of the tribological conditions [20] (normal pressure, sliding velocity, roughness and

temperature). Wear can be addressed by Archard's formulation [37]:

$$Q_w = k\sigma_0 v \quad (8)$$

where the wear rate is directly proportional to the applied pressure σ_0 multiplied by the sliding speed v . The proportionality constant k is dependent on the normal pressure σ_0 . The balance presented in Eq. 7 can also be written as a balance in thickness: $\delta_{total} = \delta_f - \delta_w$, $\delta_w = k(\sigma_0)\sigma_0 s$, $\delta_f = f(T, \sigma_0, R, v)$, where R is a measure for roughness. Two different conditions are conceivable: (1) $\delta_f > \delta_w$ and (2) $\delta_f \leq \delta_w$. Existence of a tribo-modified surface layer and the frictional energy of the tribo-system can be correlated as illustrated in Fig. 11. δ_f and δ_w are shown schematically in Fig. 11-a, and δ_{total} which is the difference between the thicknesses of the formed modified surface layer and the worn layer is shown in Fig. 11-b. Three different conditions are explained using Fig. 11-b; the rubber is exposed to wear as soon as it becomes in contact with a counter-surface. However, in order to generate a thin modified surface layer, sufficient amount of energy should be exerted to the rubber surface. This is shown schematically in Fig. 11 where the thickness of the formed modified surface layer is nonzero only when the energy input rate is higher than a minimum value required to modify the surface. This energy level differs for different compounds. The thickness of the formed modified surface layer and the layer thickness worn away both increase by an increase in the energy input. Yet, the existence of the modified surface layer depends on the ratio between δ_f and

δ_w . If the wear rate is higher than the formation rate (condition (2)), the whole modified layer is worn, and therefore, no modified surface layer is present (this condition is demonstrated using green line in Fig. 11-b). However, if $\delta_f > \delta_w$, the modified surface layer exists. Under this condition, an increase in energy input rate (which increases both δ_f and δ_w) can bring about two conditions; as shown in Fig. 11-b, the first situation is that with an increase in energy input, the thickness of the layer worn away increases more than the thickness of the formed modified surface layer, and therefore, the total modified surface layer thickness will decrease and will be completely removed (blue line). The second situation is when both thicknesses increase proportionally such that the modified surface layer exists for higher energy input rates (black line).

Considering the size of typical stones used in asphalt roads in comparison with the typical thickness of the modified surface layers on rubbers [25], the modified surface layer does not change the hysteresis part of the friction remarkably. This can be shown theoretically [38] and has also been proven experimentally (compare Sects. 2.3 and 3). Nonetheless, the modified surface layer can notably change the contribution from real area of contact by alteration of the shear stress and consequently, the overall friction. Accordingly, the existence and the mechanical properties of the modified surface layer are crucial for correctly modeling friction.

The difference in wear rates can explain the differences seen in the measured friction coefficients. Consider Fig. 6, where the measured friction for

sample (1) is stabilized and does not change anymore just after a short sliding distance. Conversely, the measured friction signal stabilizes after a much longer distance for the reinforced sample (2). Because of the high wear rate of sample (1) in contact with the granite counter-surface, the tribo-system does not find the opportunity to form a modified surface layer. Therefore, no significant difference is seen in mechanical properties of the wear track and outside the wear track for sample (1). However, a competition occurs between generation and wear of the modified layer in the contact between sample (2) and the rigid rough counter-surface, in the run-in phase, till the formation and wear rate of such a layer are in balance. As a result of such a balance, the measured friction stabilizes (note the difference in run-in distance, presented by green bars in Fig. 5). Hence, the main condition for the existence of a modified surface layer is the balance between the formation and wear rate of it.

6 Summary and Conclusions

The composition and tribological properties of a rubber-rigid surface interface are subject to change during use, especially under dry and boundary lubrication conditions. Although the changes of the interfaces and formation of the tribo-films have been studied for different materials, research on modified rubber surfaces due to interaction between the rubber surface and counter-surface did not receive much attention. The existence of a modified surface layer on rubbers in

Figure 11: Schematic division of the exerted energy to the rubber surface (in the form of frictional energy) into different situations regarding existence of a modified surface layer.

contact with a rigid rough surface has been shown [20, 25]; however, the dynamics of the modified surface layer formation, surface layer removal and the stability of the modified surface layer is still not satisfactorily studied.

A current perception of the removal and the stability of the modified surface layers on rubbers are introduced alongside experimental work and discussion of the literature. Two rubber samples were prepared, and their dynamic mechanical properties were measured using DMA. The mechanical properties of the samples and thereupon the hysteresis contribution to the friction do not differ much; however, their measured friction in contact with a granite rough surface showed a clear difference. Both theory and experiments validated that the hysteresis part of the friction is not the source of such difference. AFM nano-indentations

showed that a modified surface layer with different mechanical properties from the bulk of the material does exist on the wear track of sample (2). However, no such layer could be identified on sample (1). Moreover, the specific wear rate of sample (1) is two decades of magnitude higher than for sample (2). It has been concluded that the existence of a modified surface layer and its definitive role on friction is not only determined by the tribological conditions [20], but that wear also plays a crucial role in this argument. A conceptual model is presented, dividing the energy input to the rubber surface to different zones concerning the existence of a tribo-film. The model suggests that the modified surface layer is formed if only the energy input is sufficient to make such a surface modification. An increase in the input energy results in a more degradation of the rubber; however, more increase in

energy input might result in excessive wear of the modified layer so that no modified layer remains. In such a way, the decisive importance of wear on the existence of a modified surface layer is demonstrated.

7 References

- [1] K.A. Grosch. The relation between the friction and visco-elastic properties of rubber. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, 274(1356):21–39, 1963.
- [2] B.N.J. Persson. Theory of rubber friction and contact mechanics. *Journal of Chemical Physics*, 115(8):3840–3861, 2001.
- [3] G. Bóдай and T.J. Goda. Friction force measurement at windscreen wiper/glass contact. *Tribology Letters*, 45(3):515–523, 2012.
- [4] M. Mofidi, B. Prakash, B.N.J. Persson, and O. Albohr. Rubber friction on (apparently) smooth lubricated surfaces. *Journal of Physics Condensed Matter*, 20(8):085223, 2008.
- [5] D.F. Moore. *The friction and lubrication of elastomers*. Pergamon Press, Oxford, New York, 1972.
- [6] P. Wriggers and J. Reinelt. Multi-scale approach for frictional contact of elastomers on rough rigid surfaces. *Computer Methods in Applied Mechanics and Engineering*, 198(21-26):1996–2008, 2009.
- [7] B. Lorenz, B.N.J. Persson, S. Dieluweit, and T. Tada. Rubber friction: Comparison of theory with experiment. *European Physical Journal E*, 34(129):11129, 2011.
- [8] B. Lorenz, B.N.J. Persson, G. Fortunato, M. Giustiniano, and F. Baldoni. Rubber friction for tire tread compound on road surfaces. *Journal of Physics: Condensed Matter*, 25(9):095007, 2013.
- [9] X-D. Pan. Wet sliding friction of elastomer compounds on a rough surface under varied lubrication conditions. *Wear*, 262(5-6):707–717, 2007.
- [10] J.A. Greenwood and J.B.P. Williamson. Contact of nominally flat surfaces. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, 295(1442):300–319, 1966.
- [11] C. Putignano, L. Afferrante, G. Carbone, and G. Demelio. A new efficient numerical method for contact mechanics of rough surfaces. *International Journal of Solids and Structures*, 49(2):338–343, 2012.
- [12] D.J. Haines and E. Ollerton. Contact stress distributions on elliptical contact surfaces subjected to radial and tangential forces. *Proceedings of the Institution of Mechanical Engineers*, 177(1):95–114, 1963.
- [13] M. Paggi and M. Ciavarella. The coefficient of proportionality κ between real contact area and load, with new asperity models. *Wear*, 268(7-8):1020–1029, 2010.
- [14] L. Afferrante, G. Carbone, and G. Demelio. Interacting and coalescing hertzian asperities: A new multiasperity contact model. *Wear*, 278-279(0):28–33, 2012.
- [15] V.A. Yastrebov, G. Anciaux, and J-F. Molinari. From infinitesimal to full contact between rough surfaces: Evolution of the contact area. *International Journal of Solids and Structures*, 52:83–102, 2015.
- [16] W. Manners and J.A. Greenwood. Some observations on persson's diffusion theory of elastic contact. *Wear*, 261(5-6):600–610, 2006.
- [17] W.B. Dapp, N. Prodanov, and M.H. Müser. Systematic analysis of persson's contact mechanics theory of randomly rough elastic surfaces. *Journal of Physics Condensed Matter*, 26(35):355002, 2014.
- [18] S. Jacobson and S. Hogmark. Surface modifications in tribological contacts. *Wear*, 266(3-4):370–378, 2009.

- [19] M. Mokhtari, D.J. Schipper, and T.V. Tolpekina. On the friction of carbon black- and silica-reinforced BR and S-SBR elastomers. *Tribology Letters*, 54(3):297–308, 2014.
- [20] M. Mokhtari and D.J. Schipper. Existence of a tribo-modified surface layer of BR/S-SBR elastomers reinforced with silica or carbon black. *Tribology International*, Article in press(2014).
- [21] L. Martínez, R. Nevshupa, D. Felhös, J.L. de Segovia, and E. Román. Influence of friction on the surface characteristics of EPDM elastomers with different carbon black contents. *Tribology International*, 44(9):996–1003, 2011.
- [22] J.M. Degrange, M. Thomine, P. Kapsa, J.M. Pelletier, L. Chazeau, G. Vigier, G. Dudragne, and L. Guerbé. Influence of viscoelasticity on the tribological behaviour of carbon black filled nitrile rubber (NBR) for lip seal application. *Wear*, 259(1-6):684–692, 2005.
- [23] J. Karger-Kocsis, A. Mousa, Z. Major, and N. Békési. Dry friction and sliding wear of EPDM rubbers against steel as a function of carbon black content. *Wear*, 264(3-4):359–367, 2008.
- [24] T. Nakazono and A. Matsumoto. Mechanical aging behavior of styrene-butadiene rubbers evaluated by abrasion test. *Journal of Applied Polymer Science*, 120(1):379–389, 2011.
- [25] N.V. Rodriguez, M.A. Masen, and D. J. Schipper. Tribologically modified surfaces on elastomeric materials. *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology*, 227(5): 398–405, 2013.
- [26] M.-J. Wang and Y. Kutsovsky. Effect of fillers on wet skid resistance of tires. Part I: Water lubrication vs. filler-elastomer interactions. *Rubber Chemistry and Technology*, 81(4): 552–575, 2008.
- [27] M.-J. Wang and Y. Kutsovsky. Effect of fillers on wet skid resistance of tires. Part II: experimental observations on effect of filler-elastomer interactions on water lubrication. *Rubber Chemistry and Technology*, 81(4): 576–599, 2008.
- [28] B.N.J. Persson. On the fractal dimension of rough surfaces. *Tribology Letters*, 54(1):99–106, 2014.
- [29] C.P. Green, H. Lioe, J.P. Cleveland, R. Proksch, P. Mulvaney, and J.E. Sader. Normal and torsional spring constants of atomic force microscope cantilevers. *Review of Scientific Instruments*, 75(6):1988–1996, 2004.
- [30] F. Rico, P. Roca-Cusachs, N. Gavara, R. Farré, M. Rotger, and D. Navajas. Probing mechanical properties of living cells by atomic force microscopy with blunted pyramidal cantilever tips. *Physical Review E*, 72(2):021914, 2005.
- [31] D. Tranchida and S. Piccarolo. On the use of the nanoindentation unloading curve to measure the Young's modulus of polymers on a nanometer scale. *Macromolecular Rapid Communications*, 26(22):1800–1804, 2005.
- [32] B.N.J. Persson. Theory of powdery rubber wear. *Journal of Physics Condensed Matter*, 21(48):485001, 2009.
- [33] B.N.J. Persson. Model study of brittle fracture of polymers. *Physical Review Letters*, 81(16):3439–3442, 1998. PRL.
- [34] M. Valefi, M. de Rooij, M. Mokhtari, and D.J. Schipper. Modelling of a thin soft layer on a self-lubricating ceramic composite. *Wear*, 303(1-2):178–184, 2013.
- [35] A. Morina and A. Neville. Understanding the composition and low friction tribofilm formation/removal in boundary lubrication. *Tribology International*, 40(10-12):1696–1704, 2007.
- [36] P.J. Blau. Embedding wear models into friction models. *Tribology Letters*, 34(1):75–79, 2009.

- [37] J.F. Archard. Contact and rubbing of flat surfaces. *Journal of Applied Physics*, 24(8):981–988, 1953.
- [38] B.N.J. Persson. Contact mechanics for layered materials with randomly rough surfaces. *Journal of Physics: Condensed Matter*, 24(9):095008, 2012.

List of Publications

Journal papers

- M. Valefi, M.B. de Rooij, M. Mokhtari, D.J. Schipper. Modelling of a thin soft layer on a self-lubricating ceramic composite. *Wear* (2013) 303:178-184.
- M. Mokhtari, D.J. Schipper and T.V. Tolpekina. On the Friction of Carbon Black- and Silica-Reinforced BR and S-SBR Elastomers. *Tribology Letters* (2014) 54:297-308.
- M. Mokhtari, D.J. Schipper. Existence of a tribo-modified surface layer of BR/S-SBR elastomers reinforced with silica or carbon black. *Tribology International* (2014), Article in press.
- M. Mokhtari, D.J. Schipper, N. Vleugels, J.W.M. Noordermeer. Existence of a tribo-modified surface layer on SBR elastomers: balance between formation and wear of the modified layer. *Tribology Letters* (2015) 58:22.
- M. Mokhtari, D.J. Schipper, N. Vleugels, J.W.M. Noordermeer. Transversely isotropic viscoelastic materials: Contact mechanics and friction. *Submitted to Tribology International* (8-2015).
- M. Mokhtari, M.B. de Rooij, D.J. Schipper and R. Bosman. Formation of a tribo-modified surface layer on elastomers. *Submitted to Tribology Letters* (8-2015).

Conference proceedings

- M. Mokhtari, D.J. Schipper and T.V. Tolpekina. Friction of Carbon Black and Silica Reinforced Elastomers. *Proceedings of 5th World Tribology Conference. September 2013, Turino, Italy, ISBN:978-88-90818-50-9.*
- M. Mokhtari, D.J. Schipper. On the existence of a friction-modified surface layer of BR/SSBR elastomers reinforced with different silica or carbon black contents. *Proceedings of Nordtrib, 2014, Aarhus, Denmark, ISBN:978-87-92765-26-0.*
- M. Mokhtari, D.J. Schipper. Existence of a Friction-modified Surface Layer on SBR Elastomers: Competition Between Formation and Wear of the Surface Layer. *Presented at 1st STLE Tribology Frontiers Conference, 26-28 October, 2014, Chicago.*
- M. Mokhtari, D.J. Schipper, N. Vleugels, J.W.M. Noordermeer. Contact mechanics and friction of transversely isotropic viscoelastic materials. *Proceedings of International Tribology Conference. September 2015, Tokyo, Japan.*
- M. Mokhtari, D.J. Schipper. Importance of texture and tread rubber properties in determining tire/road wet friction. *Proceedings of International Tribology Conference. September 2015, Tokyo, Japan.*