TAILORING RUBBER COMPOUND AND PROCESSING FOR BALANCING THE PROPERTIES OF AIRCRAFT TIRE RETREADS

Indriasari

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AIRCRAFT TIRE RETREADS**

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DISSERTATION

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INTRODUCTION

1.1 INTRODUCTION

The demand for aircraft (AC) tires, including retreaded ones, increases following the constantly growing air passenger traffic [1, 2]. India and China are projected to emerge as the leaders in the market of AC tires in the near future, surpassing the US aviation industry by 2022. Based on the aircraft type, the market of AC tires/retreaded tires is separated into commercial and military applications. The commercial segment had a share of 54.34% in 2018 due to the increasing number of air passenger traffic and the growing number of aircrafts manufactured worldwide [3]. The global AC tire market was valued at US\$ 1,260 million in 2017 [1], while the global retreaded tire market was valued at US\$ 692 million in 2018 [2].

The global market of AC tires/retreaded tires can be divided into bias ply and radial tires. Bias ply tires dominated the market with a share of 61% in 2018. However, based on the forecast from 2019 till 2025, the share of radial tires is expected to grow. These tires offer low weight, but tend to be less retreadable than bias ply tires. The radial tires help to reduce operating cost, generate less heat, and last longer than bias ply tires [3].

The tires are one of the most complex engineered components of an aircraft. They need to withstand heavy loads at high velocities and extreme temperatures during service. Due to the severe operating conditions of AC tires, thus short service life, it is common that AC tires are retreaded. Tire retreading, also known as remolding or recapping, is the process to replace the worn tread with a new one. Retreading AC tires is a very economical and ecological solution.

Based on the process, the retreading market is segmented into pre-cure and mold-cure technology. Pre-cure is a tire retreading process in which the tread of the worn-out tire is removed before a new already vulcanized tread with a new tread pattern is wrapped and spliced around the carcass by making use of a bonding agent known as a cushion gum. Thus, the process enables tire manufacturers to produce different sizes and treads at the same time. In the mold-cure tire process, the original tread is removed, and unvulcanized rubber is wrapped around the carcass and vulcanized. Due to the low investment costs, pre-cure dominated the global market in 2017 [2].

An AC tire life is measured by the number of flight cycles. For example, the average number of flight cycles of a set of tires on a Boeing 737 (B737) airplane is around 250 to 300 under ideal conditions. In reality, it is difficult to reach those numbers. Factors such as temperature, runway types, and operational conditions (speed, load, pressure) have a great

influence on the durability of a tire. Table 1.1 depicts the AC tire consumption per type of aircraft by the Garuda Indonesia Airline (GIA) company in 2015 [4]. The B737 aircraft is the most frequently used type at GIA with a total number of 280 aircrafts. The B737 Next Generation (NG) main tires are to be changed when they reach 194 flight cycles or approximately every one month and six days. GIA consumed 25,450 tires with a value of US\$ 13.4 million in 2015. This demonstrates the benefit for the airline, if the service life of AC tires can be increased.

Table 1.1 Garuda Indonesia AC tire consumption in 2015 [4].

Aircraft type & position	Tires/ aircraft	Number of aircrafts	Aircraft utilization (flight cycles/yr.)	Rate removal of tires/yr.	Tire service life (flight cycles/tire)	Cost/tire (US\$)	Total tires/ yr.	Total cost/yr. (US\$)
A330 Nose	2	26	927	4	232	713	208	148,335
A330 Main	8			3	309	1,115	624	695,885
A320 Nose	2	100	2084	8	261	436	1600	697,680
A320 Main	4			8	261	812	3200	2,597,600
B747-400 Nose	2	3	704	6	117	699.5	36	25,184
B747-400 Main	16			6	117	699.5	288	201,470
B737 classic Nose	2	65	1142	6	190	167	780	129,948
B737 classic Main	4			6	190	385	1560	600,678
B737 NG Nose	2	215	1935	11	176	167	4730	788,018
B737 NG Main	4			10	194	478.5	8600	4,115,530
ATR-72 Nose	2	70	1635	6	273	281	840	236,334
ATR-72 Main	4			5	327	953	1400	1,334,700
CRJ-1000 Nose	2	18	1818	12	152	810	432	349,942
CRJ-1000 Main	4			9	202	1,336	648	865,858
B777 Nose	2	9	799	4	200	810	72	58,324
B777 Main	12			4	200	1,336	432	577,238
Total							25,450	13,432,723

In 2000, the Federal Aviation Administration (FAA) signed an executive order that required federal agencies to replace Original Equipment Manufacturer (OEM) tires with retreaded tires rather than new tires whenever possible. In the United States, almost all major airlines use retreaded tires and nearly 80% of all AC tires in use nowadays are retreads. The FAA released strict and clear guidelines to support the use of retreaded AC tires in 2006. Most retreading plants throughout the world are franchised, licensed, or affiliated with the major suppliers. With the same standard procedure of testing, FAA's Technical Standard Order (TSO) TSO-C62, retreaded tires have demonstrated to provide the same reliability and performance as original equipment tires [5].

1.2 BACKGROUND OF THE THESIS

The development of AC tire retreads aims at extending the service life. The tire can be retreaded up to 7 times with an average number of flight cycles of up to 200/retread. In terms of material improvement, compound formulation development provides a means to improve existing products and also to develop new products: Designing rubber formulations for cool running and higher heat resistance, thus decreased tread wear, for higher ultraviolet-protection to improve the tire's ability to resist weather, for increased tire resistance to contaminated runways (oil, grease, ice, snow), and for lowered tire damage from cuts or tear; just a few examples of increasing the performance and service life of AC tire retreads. The properties of the tread rubbers are determined not only by the right composition of the formulation, but also by correct processing in terms of mixing conditions and addition sequence during mixing. Hence, proper selection of rubber ingredients and processing parameters are essential to balance the properties, i.e., low hysteresis, decreased treadwear, high stress-strain properties, and ease in processability.

1.3 AIM OF THE THESIS

The research covered in this thesis aimed at providing a comprehensive study related to the development of rubber processing and formulations for AC tire retreads. The objectives of the research are listed below:

1. To use a reliable method to optimize rubber mixing for different types of filler systems: Carbon Black (CB), Silica (SI) and a hybrid of Carbon Black/Silica (CB/SI) by identifying and optimizing the most significant factors to produce a rubber material with the desired properties and consistent quality for AC tire retreads.
2. To investigate the effect of different addition sequences of specific materials, in this case Zinc Oxide (ZnO) and DiPhenyl Guanidine (DPG), on the properties of a NR/BR blend reinforced by a hybrid CB/SI filler system for AC tire retreads.
3. To select a suitable type of Butadiene Rubber (BR) to be blended with Natural Rubber (NR) to be used in AC tire retread formulations. It is essential to investigate the macro- and micro-structure of the polymers and how these properties influence the final properties.
4. To select a suitable type of oligomeric resin to be used as an additive to improve processing, tackiness of the compounds as well as the final properties crucial for AC tire retreads.
5. To characterize the aging properties of AC tire retreads to give valuable information on how these selected materials perform at high service temperatures.

1.4 STRUCTURE OF THE THESIS

Chapter 1: **Introduction**

This chapter describes the demand of AC tires including retreaded ones, followed by the background of this project and the aim of the thesis.

Chapter 2: **Literature review**

Chapter 2 reviews the developments of AC tires/retreaded tires, the structure of these tires, the operation conditions and problems related to AC tire treads/retreads, the retreading process and the procedure for testing and certification. The types of rubbers and fillers, vulcanization systems and resins used in the formulations, as well as several examples of compounding of AC tire treads are reviewed based on patents.

Chapter 3: **Defining key factors for improving properties of aircraft tire retreads produced from carbon black-filled NR/BR blends**

CB is the most common reinforcing filler used in AC tire tread formulations. For CB-reinforced NR/BR compounds, the processing parameters such as mixing temperature, time, rotor speed, addition sequence, and ram pressure are important factors that need to be controlled as they can influence both, processing as well as vulcanizate properties. In the present study, the type of BR, mixer set temperature, rotor speed, and filler mixing time were selected as the key factors, and investigated for CB-filled NR/BR blends. Properties such as Mooney Viscosity (MV), Payne Effect (PE), $\tan \delta$ at 100°C as an indication of hysteresis/heat build-up, and stress-strain properties were chosen as the responses. A complete Design of Experiment (DOE) procedure comprising a two-level full factorial setup for screening followed by an optimization process and confirmation runs are performed.

Chapter 4: **Optimization of the mixing parameters for NR/BR blends with a hybrid carbon black/silica and a silica filler system**

The following factors are investigated:

- Two types of BR: High-Cis BR (HC BR) and High-Cis Long-Chain Branched BR (HC LCB BR)
- Two types of fillers: a hybrid CB/SI and SI
- Silanization temperature
- Silanization time

in order to optimize the properties of AC tire retreads.

Chapter 5: The effect of zinc oxide and diphenyl guanidine addition sequence on processing, mechanical and dynamic properties

Partial substitution of CB by SI needs to be accompanied by adjustment of the manufacturing process, as the rubber performance is not only determined by the right choice of the formulation ingredients, but also by correct processing such as optimum parameter settings and addition sequence. This study investigates the influence of the addition sequence of ZnO and DPG to CB/SI-filled NR/BR blends on the compound as well as mechanical and dynamic properties of the vulcanizates.

Chapter 6: The influence of different types of butadiene rubber on processing, mechanical and dynamic properties of aircraft tire retreads

The properties of compounds and vulcanizates are strongly affected by the polymer choice. The polymer architecture determines the performance of the final properties as well as the processability. Therefore, proper selection of the polymers to be blended with NR determines the best compromise in compound and vulcanizates properties. Four types of BR, namely High-Cis BR (HC BR), High-Cis Long-Chain Branched BR (HC LCB BR), Low-Cis star-branched BR (LC BR) and High-Vinyl (HV BR), are investigated to study their effect on processing, mechanical and dynamic properties in a hybrid CB/SI filler system.

Chapter 7: Incorporation of resins for improving the properties of aircraft tire retreads

This chapter focuses on the evaluation of the effect of oligomeric resins on processing, mechanical and dynamic properties of a NR/HC LCB BR blend with different filler systems, and their potential to improve the properties of AC tire retreads. Two types of resin, namely a modified Terpene Phenol (TP) and an aromatic hydrocarbon C9 resin (C9), are investigated concerning their effect on $\tan \delta$ at different temperatures, stress-strain properties and processability depending on the filler systems: CB, CB/SI and SI.

Chapter 8: Aging properties of aircraft tire retreads

This chapter investigates the aging properties of AC tire retread vulcanizates. A higher service temperature causes accelerated aging for most rubbers. This means that the generated heat in aviation tires accelerates the degradation of the mechanical and dynamic properties of the rubber. The amount of degradation by aging is dependent on a set of variables, e.g., exposure to oxygen/ozone, elevated temperatures, and time. Two series of rubber formulations are investigated to study the effect of aging on ultimate and dynamic properties:

Series 1: vulcanizates of NR blended with different types of BR reinforced by a CB/SI filler system, and

Series 2: vulcanizates of NR blended with HC LCB BR and reinforced by different filler systems: CB, CB/SI and SI.

Chapter 9: **Summary**

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LITERATURE REVIEW

2.1 RECENT DEVELOPMENTS IN AIRCRAFT TECHNOLOGY

The aircraft industry is looking for technologies to continuously innovate its products, businesses and services. This industry aims to design more efficient and advanced aircrafts. Using new composite materials to make the aircraft lighter and more fuel-efficient, or re-designing aircrafts by imitating nature's best examples such as birds and sharks to design winglets/sharklets to improve aerodynamics are some examples of innovation in the development of the new generation of aircrafts [1]. The aviation industry contributes about 2% to the global CO₂ emissions. The aircraft manufacturers are committed to improve fleet efficiency with at least 1.5% annually in order to achieve a carbon neutral growth from 2020 on and reducing net CO₂ emissions by 50% till 2050 relative to 2005 [2]. Driven by fuel costs and environmental pressure, the trend towards electrical power systems for propulsion is also progressing in the aircraft industry [3]. Airbus initiated a zero-emissions project to bring the electric aircraft into reality under the 'E-Fan X project' to explore the possibilities to develop hybrid-electric propulsion.

A direct consequence of the rise of aircraft production is the demand for more robust and safe aircraft components [4]. One of these components is the main landing gear system. Aircraft landing gear systems are designed to support the entire weight of an aircraft on the ground and enables the aircraft for taxiing, landing, and takeoff [2]. These systems account for over 7% of the total weight of the aircraft and represent nearly 20% of the overall maintenance costs, which makes them a significant component of an efficient aircraft [4]. Designing aircraft tires is an immense effort. The tire manufacturer designs a tire according to the requirements of the customers and other regulations [5]. After the tires passed all mandatory tests and met the requirements of the aircraft manufacturer, the tires are brought into production.

2.2 CONSTRUCTION OF AIRCRAFT TIRES

Based on the construction, there are two types of aircraft (AC) tires: radial and bias, the same as for passenger and truck tires. Figures 2.1 and 2.2 show the structures of bias ply and radial AC tires.

Figure 2.1 Structure of bias ply AC tire [6].

Figure 2.2 Structure of radial AC tire [6].

The difference lies in the direction of the cord plies. In bias tires, the carcass plies are arranged in the range of 30 to 60 degrees, while in radial tires, the cord plies are 90 degrees to the centerline or direction of rotation of the tire. The advantages of radial over bias tires are a lower heat build-up because no sidewall flex is transmitted to the tread, and greater comfort to users due to the flexibility and strength of the tire so that the tire absorbs considerable shock and impact. This type of tires helps in reducing operating cost, generates less heat, and lasts longer than bias tires.

2.3 OPERATING CONDITIONS OF AC TIRES INCLUDING RETREADED TIRES

Dissimilar to tires used for cars, trucks or busses, AC tires experience their main impact during relatively short time intervals such as takeoff, landing and taxiing, and undergo comparatively severe conditions. AC tires are designed to support a substantially high load; however, the size of AC tires should be as small as possible as they should be light. Figure 2.3 shows the operating range of AC tires and other tire applications in terms of speed versus load. Most tires are designed to work at high speed with a relatively low load or vice versa. For example, racing cars can reach 400 km/h, but the load per tire is relatively small, and Off-The-Road (OTR) trucks operate at a low speed, but the load can reach up to 100 tons/tire. Meanwhile, AC tires used for narrow- or wide-body aircrafts are designed for a combination of large loads (20 to 30 tons/tire) and high speeds as fast as tires of racing cars: the speed can reach 380 km/h [7].

Figure 2.3 Tire operating range (load versus speed) of various vehicle applications [7].

AC tires operate at a relatively high speed coupled with a substantial load. Table 2.1 depicts the difference between AC tires and Passenger Car Tires (PCT) with the same size. From this table, it can be seen that the load on an AC tire can reach six times the load on PCT, with the velocity of the AC tire over two times faster than the velocity of the PCT. It is also clear that the operating pressure of AC tires is almost six times higher compared to the one of PCT, and the deflection is 32%, which is almost three times higher than the deflection of a PCT.

Table 2.1 Similar size tire comparison of aircraft versus passenger [6].

Parameter	AC tire	PCT
Size	27 x 7.75 – 15	P205/75R15
Diameter (in/cm)	27.0/68.6	27.1/68.8
Section width (in/cm)	7.75/19.7	7.99/20.3
Ply rating	12	–
Load rating (lb./kg)	9650/4377	1598/724.8
Pressure (Psi/MPa)	200/1.38	35/0.24
Deflection (%)	32	11
Max speed (mph/km/h)	225/362	112/180
Load/tire weight	244	78

During takeoff, the tire should be able to endure not only the load but also the forces produced by a high angular speed while resisting heat generation and wear. During landing, the AC tire has to sustain heavy loads and impact forces as well as deceleration from a relatively high speed to stop the airplane during braking at a very short period of time. It undergoes sudden temperature rising. Heat generation in an AC tire is much higher than in any other tire. Figure 2.4 shows the effect of different wheel rotation conditions on the temperature distribution on the surface of an AC tire simulated by ANalysis SYStem (ANSYS) [1]. The initially static wheel, in Figure 2.4(a), recorded the highest temperature in its contact area at 307°C. The small area surrounding the contact patch had a temperature of 260°C, and the majority of the tread temperature was less than 165°C. The static wheel had the highest temperatures, because the affected area was fully sliding with a speed equal to the aircraft's forward speed until the longitudinal friction force increased to spin the wheel and change its position. The hottest spot represents the most affected area, it became sticky and heavy wear occurred.

Figure 2.4 AC tire tread temperature profiles of a Boeing 747-400 at 0 rad/sec (a); 60.5 rad/sec (b); 121 rad/sec (c) [8].

Figure 2.5 shows a comparison of tire wear for a typical landing (0 rad/sec), for 50% (60.5 rad/sec) and 100% rolling (121 rad/sec). The highest wear of a typical landing occurs when the wheel touches the ground with zero rotational speed. When the wheel is initially rotated at 50% and 100% of its free-rolling speed, the total tire rubber wear is reduced by 37% and 51% respectively, which increases the tire's service life [9].

The AC tire's service life is measured by the number of flight cycles. For example, the ideal number of flight cycles of a Boeing 737 with one set of tires is around 250 to 300. In reality, it is difficult for AC tires to reach those ideal numbers. Factors such as temperature, runway types, operational conditions (speed, load, pressure) have a large influence on the durability of the tire. Due to the necessity of frequent replacement, it is very common for AC tires to be retreaded.

Figure 2.5 Total wear of a tire under initially static conditions, 50% and 100% pre-rotated wheel vs. time simulated by ANSYS for a Boeing 737-400 at a landing speed of 75.6 m/s [9].

2.4 RETREADING AC TIRES

The term retreading refers to the method of restoring a worn tire for operation by renewing the tread rubber, or by renewing the tread rubber plus the reinforcing plies (bias) or protector ply (radial) [10]. During the retreading process, the remaining tread part is removed and replaced by a new one. Tire retreading is an effort to extend the service life of AC tires. Cross retreading is the practice of one manufacturer retreading tire casings of other tire manufactures, in addition to its own casings [10]. This practice is based upon customer agreements and manufacturer restrictions. The current practice of cross retreading applies only to bias casings, not to radial AC tires. The Federal Aviation Administration (FAA), European Aviation Safety Agency (EASA), Directorate General of Civil Aviation (DGCA) and regulatory organizations in other countries require retreading and/or repair of AC tires to be performed only by a certified facility [11-13]. The certification is determined by the governing authority under which the operator is authorized.

Figure 2.6 depicts the steps of the mold-cure aircraft tire retreading process. In this process, the original tread is removed, and raw rubber is wrapped around the tire. First of all, a worn tire is inspected visually as well as by the Non-Destructive Inspection (NDI) Shearography. These inspections ensure that the tire meets the retreading specifications. The accepted tire is then placed in the buffing machine, in which the remaining old tread is removed from the tire casing. The new fabric reinforcement/protector ply (if required) and the new tread are adhered to the casing to cover it perfectly. The tire is then loaded into the curing mold. Lastly, the cured tire undergoes balancing and final inspection using the NDI Shearography.

Figure 2.6 Tire retreading process [14].

The following list outlines some of the conditions which can disqualify a tire from being retreaded [15]:

1. Any injuries to the beads or in the bead area.
2. Weather or ozone cracking of tread or sidewall that results in exposed body cords.
3. Protruding bead wire or kinked bead.
4. Ply separation.
5. Internal damage or broken cords.
6. Flat spots and skid burn that have penetrated to the top carcass ply. Wearing the tire beyond the protector ply or reinforcing plies can leave insufficient interface rubber to allow retreading.
7. Punctures that penetrate the inner liner.
8. Excessive brake heat damage, such as experienced in a rejected takeoff.
9. Tires that are heavily oil contaminated.
10. Tires that have experienced a major pressure loss.

The retreading qualification process refers to the Technical Standard Order TSO-C62e. Retreaded tires selected for use on a specific aircraft must demonstrate suitability through appropriate laboratory tests. The tire must withstand the dynamometer cycles as shown in Table 2.2 [16]: all AC tires including retreaded tires must withstand 58 dynamometer cycles as a demonstration of overall performance, plus 3 overload dynamometer cycles as a demonstration of the casing's capability under overload. The 58 dynamometer cycles consist of 50 takeoff and landing cycles and 8 taxi cycles. The overload cycles consist of 2 taxi cycles at 1.2 times rated load and 1 overload takeoff cycle starting at 1.5 times rated load. The dynamometer cycles can be done in any order. However, if the overload takeoff cycle is not run as the last one, the tire must not show detectable signs of deterioration after the cycle completion other than the normally expected tread surface abrasion as depicted in Figure 2.7.

Table 2.2 Dynamometer test cycles for AC tires [16].

Test conditions	Number of Cycles (Rated load)	Number of Cycles (overload)	Rated load	Overload
Taxi during takeoff/landing	8	2	100%	120%
Takeoff & landing	50	-	100%	-
Takeoff	-	1	-	150%
Total cycles	61		-	-

Figure 2.7 Normal wear on an AC tire tread [6].

2.5 PROCEDURES AND REGULATIONS FOR RETREADING AC TIRES

Retreading of AC tires can only be done in a certified facility. A certified facility can apply one of certification processes below:

1. Type Certificate (TC) or Supplement Type Certificate (STC) is a type of certificate which is issued by a regulatory authority such as the Federal Aviation Association (FAA, USA), European Aviation Safety Agency (EASA, Europe), Civil Aviation Safety Authority (CASA, Australia), Directorate General Civil Aviation (DGCA, Indonesia) or similar regulatory organizations in other countries. The TC is issued to signify the airworthiness of the approved design or "type" of an aircraft part to be manufactured [17, 18]. The STC defines a product design change, and states how the modification affects the existing type design.
2. Technical Standard Order (TSO) is a minimum performance standard for specified materials, parts, and appliances used on civil aircrafts. Applicant for this type of certificate can be a manufacturer or any person. Receiving a TSO authorization means that the applicant is authorized to manufacture the article based on the TSO standard, but it does not include the approval to install and use the article in the aircraft [17].
3. Part Manufacture Approval (PMA) is an approval granted by a regulatory authority to a manufacturer of aircraft parts [17].
4. Maintenance organizations approval is an approval for organizations to carry out maintenance under both, the Civil Aviation Safety Regulations (CASR) 1998 and Civil Aviation Regulations (CAR) 1988 (CAR 30 maintenance) [19]. Applicants for this type of certificate are for example the Garuda Maintenance Facility (GMF) AeroAsia in Indonesia, SAMCO Aircraft Maintenance in The Netherlands, Heston Maintenance Repair and Overhaul in Australia (Heston MRO).

2.6 PROBLEMS RELATED TO AC TIRE TREADS/RETREADS

The tread is the outer part of the tire and in direct contact with the ground. Due to the extreme conditions AC tires experience during operation, their treads must be designed to resist high abrasion, excessive heat build-up and to provide excellent traction while braking. Figure 2.8 depicts the physical properties of AC tire treads, for which improvements are desirable. The properties in focus for improvements are hysteresis (rebound or $\tan \delta$ at 100°C), tread wear (abrasion resistance), stiffness (tensile and dynamic shear modulus), tear resistance, and processability (e.g. smooth rubber extrudates) [20].

Figure 2.8 Crucial properties of AC tire treads [20].

During operation, AC tire treads are subjected to continuous deformations under substantial load and high frequencies. This combination of severe operation conditions leads to a high generation of heat. Heat generation is a dynamic property, in which the mechanical energy, which is applied to a material, is converted into heat.

Heat generation leads to a higher temperature of AC tires: heat build-up. It is one of the critical parameters in AC tire treads that need to be taken into account in their development. Depending on the mode of deformation, the modulus can be represented by G' , G'' , and G^* , when the deformation is in shear. G' is the "storage shear modulus"; G'' the "loss or viscous shear modulus"; and G^* the "complex modulus in shear". The symbol E is used when the mode of deformation is compression or elongation. The viscous part is the component responsible for mechanical energy loss. The correlations are given in Equations 2.1 – 2.3 [21, 22]:

$$|G^*| = \sqrt{G'^2 + G''^2} \quad \text{Equation 2.1}$$

$$\tan \delta = G''/G' \quad \text{Equation 2.2}$$

$$E^* = 2(1 + \nu)G^* \sim 3G^* \quad \text{Equation 2.3}$$

δ is called the phase angle and ν is the Poisson ratio accounting for volume change on deformation. As the latter is commonly practically absent for rubbery materials, is $\nu \sim 0.5$ [22]. The tangent of the phase angle: $\tan \delta$, as a function of temperature can be used as an indicator of tire performance [21, 23-25], as shown in Figure 2.9. At sufficiently low temperature (or high frequency), the natural movements of polymer segments are so slow or frozen, that they cannot follow the mechanically imposed motions anymore. The polymer behaves as a glass. At the transition from glassy to rubbery state, either by raising the

temperature or decreasing the frequency, excessive friction happens inside the polymer so that $\tan \delta$ reaches a maximum. Consequently, the $\tan \delta$ peak can be used as an indication of the glass transition temperature (T_g) and abrasion resistance, the latter related to the ability of the polymer to absorb deformation and consequent energy absorption without damage. At temperatures above T_g or lower frequencies, $\tan \delta$ decreases again. $\tan \delta$ in the transition region from glassy to rubbery can be used as an indication of low temperature properties such as ice traction. In this zone, several relaxation processes occur, including long polymer chain relaxations, rearrangement of short segments including branching, and reorientation of pendant side groups [21]. Elastomers are generally used in the rubbery state at a temperature above the transition zone, in the plateau region. In the rubbery region, the chains and chain segments slip past each other. In the terminal region at even higher temperature or lower frequencies, the polymers behave as (highly viscous) liquids, and movement of polymer chains past each other occurs. The deformation in the terminal region is irrecoverable [26].

Figure 2.9 $\tan \delta$ as a function of temperature as tire performance indicator [24].

A high temperature increase has directly physical consequences, i.e. a decrease of tensile strength: see Figure 2.10, accelerated treadwear, decreased static and elastic moduli in filled vulcanizates. A more severe consequence of high peak temperatures is a thermo-chemical effect: Depending on the type of polymers, the presence of oxygen in combination with a high temperature leads to oxidation, which may cause chain scission and softening of Natural Rubber (NR). Alternatively, these may also lead to hardening due to the formation of additional crosslinks as in Butadiene Rubber (BR) or Styrene-Butadiene Rubber (SBR) [21, 27, 28]. In severe cases, thermal degradation of rubber can lead to explosive rupture (blow-out).

Figure 2.10 The effect of temperature on the reduction of tensile strength [29].

At a very high localized temperature, smearing of rubber might occur. The smearing increases as the load and the sliding velocity increase. Even though rubbers do not have an apparent melting point, smearing can occur under tire sliding conditions, as proven by black deposits left on the road/runway. Figure 2.11 shows the effect of surface temperature of an abrasive plate on the loss of rubber after 100 revolutions for NR and Emulsion Styrene Butadiene Rubber (ESBR) tread compounds [30]. It can be seen from the graph that the loss of NR begins to rise rapidly at 300°F (150°C), while ESBR shows a gradual loss even up to 400°F (204°C). The abrasive plate was heavily smeared by NR at 320°F (160°C).

Figure 2.11 Weight loss of rubber as a function of surface temperature [30].

2.7 TYPES OF RUBBER

2.7.1 NATURAL RUBBER

Eng et al. reported that Natural Rubber (NR) molecules consist of an ω -terminal group, two or three trans-1,4 isoprene units, 10000 – 30000 cis-1,4 isoprene units, and an α -terminal moiety as shown in Figure 2.12 [31]. The α -terminal moiety is arranged from mono- or di-phosphate groups linked with phospholipids [32, 33]. The ω -terminal moiety was postulated to be a modified dimethylallyl unit linked with a functional group to create crosslinks through intermolecular hydrogen bonding [34].

Figure 2.12 Structure of NR [31].

NR from *Hevea brasiliensis* latex consists for 30 – 45 wt% of cis-1,4 polyisoprene, 3 – 5 wt% of non-rubber constituents, with the remaining part being water. The non-rubber constituents comprise proteins, amino acids, carbohydrates, phospholipids, amines, nucleic acids, as well as inorganic or mineral components [35]. Amnuaypornsrri et al. [36] proposed that the non-rubber constituents composed of proteins and phospholipids are presumed to be major constituents to form temporary network nodes by interaction with rubber chains at both chain ends as shown in Figure 2.13.

Figure 2.13 Proposed structure of the temporary network in NR [36].

The non-rubber constituents, particularly proteins and phospholipids, are natural accelerators and cause shorter cure times and higher crosslink densities compared to deproteinized NR [37]. Proteins and phospholipids are presumed to form a naturally occurring network, and the network plays a significant role in strain-induced crystallization [35]. This phenomenon results in high reinforcement appearing as a strong increase of the modulus on stretching, as well as a high tensile strength [38]. Figure 2.14 shows the stress strain curves

of NR and SBR. Stretching a piece of NR at room temperature turns the amorphous rubber into a semi crystalline material. The strain-induced crystallization in NR leads to an upturn at high strains and enhances the ultimate properties, while SBR does not show this phenomenon [39].

Figure 2.14 Stress-strain curves of NR and SBR [39].

NR also exhibits high tear strength and tack for tire building, and low hysteresis under dynamically loaded conditions [40]. The high strength of NR has a beneficial effect on supporting the substantial load when used as aircraft tires. An excellent tear strength provides aircraft tires more resistance to cutting, chipping or chunking (pieces of the tread rubber are torn from the tire). Lower hysteresis reduces the heat build-up and results in a lower service temperature, in this way enhancing durability [20]. The problems of NR are its tendency to thermal degradation and the limited flexibility at very low temperatures, as it has a higher glass transition temperature (T_g) compared to high-cis BR. Hence, blending of NR with a polymer with a lower T_g is usually done to prevent a rapid change of properties with temperature during operation.

The concentration of NR in an elastomer blend for treads depends on the specific application of the tires. According to the usage, there are two main types of tires: those for commercial vehicles and those for consumer applications. Figure 2.15 depicts the range of NR contents for each class of tires. It can be seen that for consumer tires such as for Radial Light Truck (RLT) and passenger cars, a lower concentration of NR is used than for tires used for commercial vehicles: Radial Medium Trucks (RMT), Off-The-Road (OTR), and aircrafts.

Figure 2.15 NR content as percentage of total tire weight and relationship to the tire performance triangle [41].

Table 2.3 describes the level of NR in several components of a tire, which is reported by The Malaysian Natural Rubber Producers Association and Smithers Scientific Services [41].

Table 2.3 NR content (phr) in selected types of tires and tire components [41].

Component	Automobile Tires	Radial Medium Truck Tires	Bias Truck Tires
Non-silica tread	45	90	50
Base	70	100	-
Sidewall	45	55	40
Wire Coat	100	100	70

The range of NR contents in tire treads can vary from 10 to 100 parts per hundred rubber (phr) depending on the desired final properties. For example, up to 100 phr of NR can be used for making commercial truck tire treads when hysteresis and tear strength are the most important features. Other tires need blending of NR with BR for resistance to abrasion and fatigue or blending with SBR for traction and stiffness [41].

Tables 2.4 and 2.5 show the classification of the NR grades Ribbed Smoked Sheet (RSS) and Technical Specified Rubber (TSR). There is a correlation between types of NR and their properties: RSS is superior to TSR regarding physical properties such as tensile strength. The treatments of latex to produce dry rubber causes differences in the final characteristics. For example, TSR from latex (TSR L) or the first grade of RSS (RSS 1X) are commonly used in the production of transparent rubber articles. If the mixing capacity is limited and batch to batch uniformity is desired, a Constant Viscosity (CV) rubber is the best choice. If a high flex resistance is wanted, a TSR 5 would be the most convenient one [41].

Table 2.4 Classification of RSS rubber [41].

RSS	Rubber mildew	Wrapping mildew	Opaque spots	Over-smoked spots	Oxidized spots	Burned sheets	Comments
1X	No	No	No	No	No	No	Dry, clean, no blemish
1	Very slightly	Very slightly	No	No	No	No	Dry, clean, no blemish
2	Slight	Slight	No	No	No	No	No sand or foreign matter
3	Slight	Slight	Slight	No	No	No	No sand or foreign matter
4	Slight	Slight	Slight	Slight	No	No	No sand or foreign matter
5	Slight	Slight	Slight	Slight	N/A	No	N/A

Table 2.5 Specifications for TSR defined in ISO [41].

Property	Grade					
	TSR CV	TSR L	TSR 5	TSR 10	TSR 20	TSR 50
Dirt content, max, wt%	0.05	0.05	0.05	0.1	0.2	0.5
Ash content, max, wt%	0.6	0.6	0.5	0.75	1	1.5
Nitrogen content, max, wt%	0.6	0.6	0.5	0.6	0.6	0.6
Volatile matter, max, wt%	0.8	0.8	0.8	0.8	0.8	0.8
Initial Wallace plasticity, Po	30	30	30	30	30	
Plasticity retention index (min)	60	60	60	50	40	30
Color, max Lovibon units		6				
Mooney viscosity	60 + 5					

2.7.2 BUTADIENE RUBBER

Butadiene Rubber (BR) is a polymer which consists of only one type of monomer: 1,3 butadiene. The latter can form three different types of linkages, namely cis-1,4 (m), trans 1,4 (n) and 1,2-vinyl (o) as seen in Figure 2.16.

Figure 2.16 Chemical structure of BR [38].

Nowadays, most BRs are made by a solution process, using either a transition metal complex from Titanium (Ti), Nickel (Ni), or Cobalt (Co), or an alkyl metal like butyl-lithium, as a catalyst. The usage of Ziegler-Natta transition metals and alkyl-lithium can produce very distinct products. Transition metal catalysts produce a high-cis configuration BR, while BR made by using butyl-lithium generates a polymer with a medium to high-vinyl content. A high-cis BR typically has a cis content higher than 95%. Table 2.6 shows typical compositions of different types of BR.

Table 2.6 Typical compositions of various BR types [38].

Catalyst used	Cis (%)	Trans (%)	Vinyl (%)
Nickel (Ni)	98	1	1
Neodymium (Nd)	97	2	1
Cobalt (Co)	97	2	1
Titanium (Ti)	92	4	4
Butyl-lithium (Li)	36	54	10

It is imperative to select a proper type of BR for a particular application since the type of BR will determine the properties of a final product. High-cis BR imparts excellent abrasion resistance, low rolling resistance but poor wet skid resistance. It also features better “green strength” which is important in the tire building process, and it increases cut growth resistance which is one of the important aspects of tire performance [42]. High-vinyl BR provides good wet skid resistance and low rolling resistance, but abrasion resistance is poor. The balance of wet skid, rolling and abrasion resistance can be achieved by using a medium-vinyl BR [43].

The problem related to compounding with a major portion of high-cis Nd-BR is poor processability, and the incorporation of the filler into a compound containing a highly linear Nd-BR is also difficult.

2.8 FILLERS

Rubbers in general cannot be used alone to produce end-products, because they do not have sufficient strength. Hence, fillers are added to rubber compounds to improve properties such as tensile and tear strength as well as abrasion resistance of the vulcanizates. Fillers are divided into three categories according to their reinforcing effect: non-reinforcing, semi-reinforcing and reinforcing. The key parameters influencing the reinforcement efficiency of fillers are:

1. Primary particle size

Figure 2.17 depicts the classification of fillers based on their primary particle size. Precipitated silica has a very small particle size below 0.05 micron, while Carbon Black (CB) has particles sizes in the range of 0.01 to 0.5 micron. Precipitated silica and CB with a particle size below 0.1 micron are classified as reinforcing fillers and can significantly improve rubber properties. Semi- and non-reinforcing fillers have particle sizes in the range of 0.1 to 5 micron and 5 to 100 microns, respectively. Fillers with a particle size larger than 10 micron are generally avoided, because they cause a localized stress concentration leading to elastomer rupture on flexing or stretching [44].

Figure 2.17 Filler classification based on particle size [44].

2. Specific surface area

The specific surface area of fillers can be measured by different adsorption methods. For silica, it can be determined by using three different methods: Nitrogen Surface Area (NSA), Statistical Thickness Surface Area (STSA) and Cetyl-Trimethyl-Ammonium Bromide (CTAB) adsorption. The first two measurements are based on the theory of Brunauer-Emmet-Teller (BET). Compared to CTAB and STSA, which measure the external surface of filler particles, the NSA method measures the outer and inner surface of a filler, thus provides the overall surface area. Currently, the CTAB method is most relevant for silica; this method was withdrawn for the measurement of CB surface area according to ASTM D3765 because of poor testing precision and labor-intensity [45]. Specific surface area increases with decrease of particle size.

3. Filler structure

Fillers seldomly appear as individual primary particles; they form in general clusters in the form of aggregates or agglomerates. CB can cluster through Van der Waals forces, while silica forms larger units through hydrogen bonding. The "structure" of fillers is used to describe the aggregate shape, size and density. DiButylPhthalate (DPB) adsorption according to ASTM D6845 was used in the past to measure the structure. This method is replaced by the oil-adsorption method using paraffinic oil according to ASTM D2414 due to toxicity of DBP. The higher the structure, the higher the reinforcement.

2.8.1 CARBON BLACK

Carbon Black (CB) is the most widely used filler in the rubber field because of its capability to reinforce elastomers. It is composed of carbon atoms, of which a small portion carries functional groups as shown in Figure 2.18.

Figure 2.18 Surface structure of CB [46].

Figure 2.19 shows the morphology of CB. The primary carbon particles tend to form aggregates or agglomerates. Aggregates are the smallest stable structural units of CB. CB is supplied in the form of compacted agglomerates. During mixing, the CB agglomerates are broken up to the dimension of aggregates.

Figure 2.19 Morphology of CB [47].

2.8.2 SILICA

Silica (SI) is composed of siloxane and silanol groups. Silanol groups are very polar and chemically active. The degree of chemical interaction between SI and the rubber matrix relies on the type of functionality on the filler surface. Silanol groups are present on the surface of SI primary particles in three different forms as shown in Figure 2.20. Isolated and geminal silanols are the most reactive ones [48].

Figure 2.20 Three different forms of silanol groups on the SI surface [48].

The difference in polarity between the surface of SI and the rubber matrix creates a major problem in rubber compounding. With the development of coupling agents such as bifunctional organosilanes, which act as a bridge between the SI surface and the rubber matrix, filler-rubber interaction can be improved. Generally, there are three types of sulfur-functionalized silanes which are most commonly used in sulfur-cured rubber compounds: see Figure 2.21. The coupling agents have double functionalities: The organo-functional groups can react with the rubber matrix, and the ethoxy groups split off and create a reactive site on the silicon atom able to couple with silanol groups of the SI to form a chemical bond.

Where R = -CH₃, -C₂H₅, alkylpolyether; x = 2 – 8; PG = CN, octanoyl

Figure 2.21 Representative sulfur-functional silanes [48].

2.9 VULCANIZATION AGENTS

Sulfur is the most widely used vulcanization chemical for unsaturated rubbers such as NR, BR, and SBR. During the vulcanization process, the individual rubber molecules are crosslinked to form a three-dimensional network of interconnected chains through sulfur crosslinks as described in Figure 2.22. However, vulcanization of rubber using sulfur alone is very slow. Therefore, accelerators are added to boost the vulcanization.

Figure 2.22 Model of an NR-sulfur network [49].

Sulfur vulcanization systems typically consist of 3 to 10 phr Zinc Oxide (ZnO), 1 to 4 phr stearic acid, 0.5 to 4 phr accelerators and 0.5 to 3 phr sulfur. Proper selection of accelerators for a particular rubber compound is an essential task, since the type as well as the amount of accelerator significantly influence the processing and vulcanizate properties of the rubber compound. The changes in vulcanizate properties as a function of crosslink density are depicted in Figure 2.23. As the crosslink density of the vulcanizate increases, properties such as static modulus, dynamic modulus at high velocities and hardness increase. Hysteresis,

permanent set and friction coefficient decrease as the crosslink density increases. Other properties such as tear strength and tensile strength show a maximum value and then decrease [50].

Figure 2.23 Vulcanizate properties as a function of the degree of crosslinking [50].

Vulcanization systems with a high sulfur dosage and low accelerator dosage are denoted as Conventional Vulcanization (CV) systems, and the counterpart as Efficient Vulcanization (EV) systems. Semi EV is a system, in which sulfur and accelerator concentrations are in-between those of a CV and an EV system: see Table 2.7.

Table 2.7 Classification of sulfur vulcanization systems [49].

Vulcanization system	Conventional (CV)	Semi-Efficient (Semi EV)	Efficient (EV)
Sulfur dosage, phr	2 – 3.5	1 – 1.7	0.4 – 0.8
Accelerator dosage, phr	0.4 – 1.2	1.2 – 2.4	2 – 5
Accelerator/Sulfur ratio	0.1 – 0.6	0.7 – 2.5	2.5 – 12

Typical CV systems form polysulfidic crosslinks which exhibit higher tensile, tear and flex-fatigue resistances. EV systems feature a high number of monosulfidic crosslinks, and such vulcanizates are characterized by better heat stability and lower compression set than polysulfidic systems. Table 2.8 summarizes the influence of the selected cure system on the properties of the vulcanizates.

Table 2.8 Effect of cure systems on crosslink types and vulcanizate properties [49].

Cure System	Conventional (CV)	Semi-Efficient (Semi EV)	Efficient (EV)
Poly + disulfidic crosslinks, %	95	50	20
Monosulfidic crosslinks, %	5	50	80
Cyclic sulfidic concentration	High	Medium	Low
Reversion resistance	Low	Medium	High
Heat aging resistance	Low	Medium	High
Flex-Fatigue resistance	High	Medium	Low
Heat build-up	High	Medium	Low
Tear resistance	High	Medium	Low
Compression set	High	Medium	Low

2.10 THE USE OF NR/BR BLENDS FOR AC TIRE TREADS/RETREADS

Stephens [51] developed two compounds, a top cap and a sub-tread as depicted in Figure 2.24, to provide an AC tire which resists casing-damage and chunking out as well as providing improved wear resistance, as seen in Table 2.9. A blend of NR and BR is used to improve wear resistance. The sub-tread is composed of NR, which provides low heat and thus less temperature generation during tire operation.

Figure 2.24 Cross sectional view of an AC tire [51].

Table 2.9 Top cap and sub-tread formulation [51].

Component	Top cap	Sub-tread
	Parts per hundred rubber (phr)	
NR	60	100
BR	40	-
ZnO	5	4
Stearic acid	2	2
CB N375	52	-
CB N110	-	30
CB N326	-	25
Process oil	8	-
Tackifier resin	4	-
Antidegradants	2.5	3.5
Sulfur	2.2	1
2-(4-Morpholiniothio)- Benzothiazole (MBS)	1	1.5
Properties:		
Hardness (IRHD)	63	65
Resilience @50°C (%)	69	65
Abrasion resistance index (ARI)	140	90
Tear strength (MPa)	23	38

Another development in AC tire tread formulations is shown in Table 2.10, based on a patent of Sandstrom et al. [20]. The development focuses on enhancing the abrasion resistance and hysteresis, and it provides a smooth rubber extrudate and minimum defects during tire assembly.

Table 2.10 AC tire tread rubber compositions [20].

Material	Sample 1	Sample 2	Sample 3
1 st non-productive mixing step			
Cis 1,4 BR (Budene®1280)	80	75	70
RSS#2	20	25	30
CB N347	40		
Paraffinic wax	2	1.5	
Rubber process oil and fatty acid	10		7
ZnO	3		
2 nd non-productive mixing step			
Tackifying resin	3		
Antidegradant	2.5		
Silica coupling agent	3.5	4	
Silica	17.5	20	
Productive mixing step			
Sulfur	1.2	1.4	1.2
Accelerators (sulfenamide, guanidine type)	2.4	2.7	2.7
Properties			
G' at 100°C, 10% strain, 1 Hz (MPa)	1.392	1.773	1.541
Tan δ 100°C, 10% strain, 1 Hz	0.127	0.130	0.136
Tensile strength (MPa)	16.27	16.17	17.57
Elongation at break (%)	521	501	537
Hardness shore A			
23°C	67	73	70
100°C	60	55	62
Rebound (%)			
23°C	47	45	44
100°C	58	55	55
Tear strength (MPa)	29.5	43.5	31.5
Abrasion resistance, relative volume loss	49	58	76

Based on the patent, an AC tire tread should have a relative abrasion resistance (volume loss relative to the reference rubber) of less than about 80%, and a hot rebound value at 100°C in the range of 45 – 70%. In addition, the AC tire tread rubber should have a tan δ value (100°C, 10% strain, 1 Hz) in the range of 0.07 to 0.17. Preferably, the AC tire tread has a storage modulus (100°C, 10% strain, 1Hz) in the range of 0.750 to 2 MPa and an Instron Tear (100°C) value from 13.5 to 54.5 MPa.

2.11 RESINS

Resins are oligomers which have a weight-average molecular weight (M_w) in the range of 800 to 4000. They can function as processing aids, plasticizers, extenders, reinforcing agents, and tackifiers [52], of which the latter one is the most important one. Tack is the ability of two materials to withstand separation after bringing their surfaces into contact for a short time under light pressure [53]. Figure 2.25 shows the process that happens when two surfaces are brought into contact under light pressure. The surfaces have a rough topography on a microscale level with entrapped gases between them, which will diffuse to the top compound (blue) or with adsorbed gas inside the compound (yellow). The actual contact occurs in the area where asperities of one surface meet those of the other. The molecular contact of polymeric chains between two surfaces will be prevented until the gases diffuse into the bulk of the material. The material must undergo viscous flow and displace the entrapped gases to increase the contact area. After achieving molecular contact, the interdiffusion of polymeric chains from each surface may take place [54]. The bond that is formed between polymeric chains of the two surfaces is capable of resisting stress before rupture.

Figure 2.25 The process of two surfaces brought into contact for a short time under a light pressure [54].

Two types of resins are available: naturally derived resins and hydrocarbon resins originating from coal distillation or steam cracking of heavy petroleum feedstock. Terpenes and rosins are examples of natural resins produced from the distillation of pine gum and the side stream of the Kraft pulping process. Another source of terpene such as D-limonene is orange juice or peel extract. Coumarone-indene resins are the most popular hydrocarbon resins obtained from the coal tar fractionation process. C5 aliphatic and C9 aromatic are examples of petroleum-based resins. The classification of resins is depicted in Figure 2.26.

Figure 2.26 Classification of resins [55].

2.11.1 RESIN STRUCTURES

Rosins

Rosins consist of turpentine oil and colophony. They have a chemical composition of $C_{19}H_{29}COOH$. Figure 2.27 shows the structure of rosins including abietic and pimaric types. Abietic acid is primarily present in rosins. The melting point of the monomers varies from 150 to 175°C, while the glass transition temperature (T_g) is in the range of 65 to 80°C [56]. Rosin esters are very effective tackifiers and compatible with many polymers. Because of their superior stickiness, rosin esters are used in a wide variety of products including sealants, hot melts, pressure sensitive adhesives, printing inks, varnishes and lacquers.

Abietic-type

Pimaric-type **Figure 2.27** Rosin types [57].**Terpenes**

Terpene resins are derived from natural terpene monomers, a byproduct from paper and pulp production and citrus juice production. Figure 2.28 shows the chemical structure of monoterpenes. Of the 14 most commonly occurring monoterpenes (α -pinene, β -pinene, Δ^3 -carene, d-limonene, camphene, myrcene, α -terpinene, β -phellandrene, sabinene, p-cymene, ocimene, α -thujene, terpinolene, and γ -terpinene), the first six are usually found to be the most abundant ones.

Figure 2.28 Chemical structures of monoterpenes [58].**Terpene phenol**

Terpene phenol resins are copolymers of a terpene and phenol. The reaction proceeds via a Friedel-Craft mechanism, which results in the linkage of two or three terpene molecules in the para- and ortho-position of the phenol molecule. A typical structure of terpene-phenol resin is shown in Figure 2.29. Terpene-phenol resins are often categorized according to their melting point, molecular weight and hydroxyl value. The softening points of terpene phenol resins are in the range of 75 – 150°C [56].

Figure 2.29 Structure of terpene-phenol resin [59].

C5 aliphatic resins

C5 aliphatic resins are derived from hydrocarbons consisting of a five-carbon chain with two double bonds known as piperylene. It is obtained as by-product of naphtha cracking. Figure 2.30 shows the various monomers of C5 aliphatic resins.

Figure 2.30 Chemical structures of monomers in C5 aliphatic resin [60].

Aromatic resins: C9 aromatic and Coumarone Indene

Figure 2.31 shows the chemical structures of monomers in an aromatic hydrocarbon resin. The main monomers are of styrene and indene types. Aromatic C9 resins are derived from a fraction of naphtha cracking, while coumarone indene is derived from coal-tar. They differ only in the proportion of indene-type structures, which are present at higher concentrations in coumarone indene, typically around 48% of indene. C9 resin in general has the following composition: 2 wt% of styrene, 4 wt% of α -methylstyrene, 20 wt% of vinyltoluene, 6 wt% of dicyclopentadiene, 20 wt% of indene, 5 wt% of methylindenes, 5 wt% of naphthalene, 38 wt% of other nonreactive aromatics [56].

Figure 2.31 Chemical structures of monomers in aromatic hydrocarbon resin [56].

2.11.2 PROPERTIES OF RESINS

Several properties of resins provide valuable information about their suitability for specific applications:

Softening point

The softening point is defined as the temperature at which the resin flows under a given load on heating. The resins are non-crystalline, thus amorphous materials which soften gradually over a range of temperatures. The softening point is controlled by the average molecular weight of the resin. The softening point is also related to the intrinsic viscosity, hardness and brittleness of resins [56, 61].

Glass transition temperature

Resins are amorphous polymers exhibiting a glass transition (T_g) due to the reduction of molecular mobility by the collapse of free volume with decreasing temperature [56]. T_g values of resins are around 30 to 90°C. In contrast, NR and high-cis BR for example have a T_g around -60 and -100°C, respectively. The addition of a resin to a rubber compound affects the T_g . In immiscible systems, two separate T_g peaks will appear; one related to the rubber and the other related to the resin. In a homogeneous system, the T_g will shift according to the Fox Equation 2.4 [62].

$$\frac{1}{T_g} = \frac{w_A}{T_{gA}} + \frac{w_B}{T_{gB}} \quad \text{Equation 2.4}$$

Where w_A, w_B are weight fractions of the resin and the rubber, respectively. T_{gA}, T_{gB}, T_g are the glass transition temperatures of the resin, the rubber and the resin-rubber blend, respectively.

Thermal stability

The thermal stability of resins is an important property, especially when they are used in applications where heat is applied, for example in hot melts (mixing), hot-applied road marking plastics, jointing, sealants, bituminous roofing compounds, and similar applications [61]. The degradation of resin may result in property changes such as deterioration of tack and peel strength as well as flexibility, and in oxidation, while depolymerization may also occur.

Viscosity

Dilute Solution viscosity

Dilute solution viscosity is the viscosity of a dilute solution of polymers. The solution viscosity of resins is influenced by many factors such as: concentration, softening point, average molecular weight, molecular weight distribution, the chemical composition of the resin, and the type of solvent. Resins with similar softening points may have different molecular weight distributions, thus may be different in viscosity of the solution. The molecular weight distribution has a tremendous influence on the resin solution viscosity. The narrower the molecular weight distribution, the higher the viscosity of the resin solution [56].

Melt viscosity

Melt viscosity measures the viscosity of a solid resin when it is in the molten state. Melt viscosity is important in rubber compounding, where modifying resins are used as tackifiers. They are used as viscosity regulators to facilitate mixing (processing aid). Melt viscosity is influenced by the softening point, average molecular weight and its distribution, and resin type [61].

Solubility

Solubility parameters are often used to predict the compatibility of polymers, chemical resistance, swelling of cured elastomers by solvents, permeation rates of solvents, and even to characterize the surfaces of pigments, fibers, and fillers [63]. The solubility of a polymer in various solvents is particularly determined by its chemical structure. Polymers will dissolve in solvents whose solubility parameters are close to their own. Hildebrand defined the solubility parameter δ as the square root of the cohesive energy density, Equation 2.5 [64]. The Cohesive Energy Density (CED), Equation 2.6, is the vapor energy U divided by a unit volume of the material V . ΔH_{vap} is the enthalpy of vaporization, R is the ideal gas constant, and T is the temperature. Table 2.11 shows the molar vaporization energy U and molar volume for group contributions V .

$$\delta = (\text{CED})^{1/2} \quad \text{Equation 2.5}$$

$$CED = \frac{U}{V} = \frac{(\Delta H_{vap} - RT)}{V} \quad \text{Equation 2.6}$$

Table 2.11 Group contributions to the molar vaporization energy and molar volume at 25°C [65].

Group	ΔU (KJ/mol)	V (cm ³ /mol)
-CH ₃	4.71	33.5
-CH ₂ -	4.94	16.1
>CH-	3.43	-1.0*
>C<	1.47	-19.2*
H ₂ C-	4.31	28.5
-CH=	4.31	13.5
>C=	4.31	-5.5*
HC≡	3.85	27.4
-C≡	7.07	6.5
Phenyl	31.9	71.4
Phenylene (ortho, meta, para)	31.9	52.4
Ring closure, 5 or more atoms	1.05	16
Ring closure, 3 or 4 atoms	3.14	18
Conjugated in ring, for each double bond	1.67	-2.2*

*Negative molar volume: contribution of the group is less when mixed than in a pure state

Hansen proposed the solubility parameter by counting several individual contributions such as atomic dispersion force E_D , polar cohesive energy E_P , and hydrogen bonding E_H . The total cohesion energy E , is shown in Equation 2.7.

$$E = E_D + E_P + E_H \quad \text{Equation 2.7}$$

The total Hansen solubility parameter δ as shown in Equation 2.8 is obtained from the sum of the square roots of each contribution divided by the molar volume V , Equation 2.9.

$$\delta = \delta_D + \delta_P + \delta_H \quad \text{Equation 2.8}$$

$$\delta = \left(\frac{E}{V}\right)^{1/2} = \left(\frac{E_D}{V}\right)^{1/2} + \left(\frac{E_P}{V}\right)^{1/2} + \left(\frac{E_H}{V}\right)^{1/2} \quad \text{Equation 2.9}$$

The difference in solubility parameters ($\delta_1 - \delta_2$) must be small for miscibility or dissolution over the entire volume fraction range. Polymer miscibility is possible only when the difference in solubility parameters $< 1.8 \text{ J}^{1/2}/\text{cm}^{3/2}$ [66].

Small [67] developed a group contribution method for calculating solubility parameters based on molar attraction F as shown in Equations 2.10 – 2.11.

$$E_{coh} = \frac{(\Sigma F)^2}{V} \quad \text{Equation 2.10}$$

$$\delta_{small} = \left(\frac{E_{coh}}{V} \right)^{1/2} = \sum \frac{F}{V} \quad \text{Equation 2.11}$$

Flory-Huggins parameter (χ)

The Flory-Huggins parameter χ_{12} has been used for many years to describe the polymer-solvent interaction. The χ_{12} can be derived from the Hildebrand solubility parameters for a nonpolar solvent and a nonpolar polymer [63]:

$$\chi_{12} = \frac{[V(\delta_1 - \delta_2)^2]}{RT} + \beta \quad \text{Equation 2.12}$$

where V is the molar volume of the solvent, δ is the Hildebrand solubility parameter for the solvent (1) and polymer (2), R is the gas constant, T is the absolute temperature, and β is an empirical constant. β has a generally accepted average value near 0.34. The χ_{12} can be calculated using Hansen solubility parameters which include dispersive, polar and hydrogen bonding [63] effects as depicted in Equation 2.13.

$$\chi_{12} = \frac{V [(\delta_{D2} - \delta_{D1})^2 + 0.25(\delta_{P2} - \delta_{P1})^2 + 0.25(\delta_{H2} - \delta_{H1})^2]}{RT} \quad \text{Equation 2.13}$$

According to the value of χ_{12} , there are three different kind of behaviors:

- $\chi_{12} < 0.5$: the polymer chain is expanded: polymer in a good solvent;
- $\chi_{12} = 0.5$: the repulsive effect is cancelled by the attractive effect of polymer/solvent interactions, known as theta condition;
- $\chi_{12} > 0.5$: there is separation into two coexisting phases, one richer in polymer but poorer in solvent than the other [68].

2.11.3 RESINS IN TIRE FORMULATIONS

Hilner [69] reported the improvement of dynamic mechanical properties of cured SBR compounds with the addition 10 phr of various hydrocarbon resins to replace 10 phr of separately added aromatic process oil. The SBR used in this study contains 37.5 phr of aromatic oil. Table 2.12 shows the formulation used in this study. The use of C9 and aliphatic-modified C9 resin improve wet grip and high-speed performance, while maintaining rolling resistance at a comparable level for the compound with separately added aromatic oil as shown in Table 2.13.

Table 2.12 Composition of tread compound [69].

Ingredient	Base formulation (phr)	Resin Based (phr)
SBR (Buna EM1712)	137.5	137.5
CB N339	80	80
ZnO	3	3
Stearic acid	2.5	2.5
Sulfur	1.8	1.8
N-Isopropyl-N'-Phenyl-1,4-PhenylenDiamine (IPPD)	1.5	1.5
N-Cyclohexyl-2-Benzothiazole Sulfenamide (CBS)	1.2	1.2
DiPhenyl Guanidine (DPG)	0.4	0.4
Aromatic process oil	10	-
Resin	-	10

Table 2.13 Dynamic mechanical properties of vulcanizates containing hydrocarbon resins or aromatic oil [69].

	Rolling resistance	Wet grip	High-speed performance
Petroleum-based C9 resin	+++	+++	++
Aliphatic-modified C9 resin	++	++	++
Coumarone-indene resin	+	-	+
Aromatic process oil	+++	--	a

Note:

-- = worse than -

- = worse than a

a = average

+ = better than a

++ = better than +

+++ = better than ++

Resins can significantly improve the service life of AC tires. One of the types of AC tire damage is chevron cutting as shown in Figure 2.32, which is caused by cross-grooved runways. These grooves help drain water from runways and prevent hydroplaning, but they can severely damage the tire: the edges of the grooves can cut the AC tire when the tire touches the ground. During landing, as the tire is loaded and accelerated, large forces are exerted on the tire, which cause the chevron cutting. It was proven in a field test of AC tire treads manufactured with rubber compositions having both a polyterpene resin and a polythiosulfate anti-reversion agent, that these additives provide a tire tread that better withstands chevron cutting as well as wear [70].

Figure 2.32 Chevron cutting [10].

A comparison of test results between a compound without resin and anti-reversion agents R, and a rubber mixture consisting of a polyterpene and a poly-thiosulfate anti-reversion agent F1 is seen in Table 2.14. Both compounds were mixed in a factory scale mixer and then used to manufacture AC tires. These AC tires were then mounted on a nose and main landing gear and tested concerning their wear resistance in terms of Landing per Tread (LPT) and their resistance to chevron cutting. It seems that a compound having a polyterpene and a poly-thiosulfate anti-reversion agent withstood a higher number of landings and field chevron cutting index compared to a compound without those materials.

Table 2.14 Rubber formulations for AC tire treads and testing results [70].

Composition	R	F1
NR	70	70
BR	30	30
CB N234	54	55
Mild Extracted Solvate (MES) oil	6	0
Polylimonene resin L120	0	8
Additives: Wax, N-Phenyl-Para-Phenylenediamine (6PPD), 2,2,4-TriMethyl-1,2-dihydroQuinoline (TMQ)	3	3
Stearic acid and ZnO	8	8
N-Tert-Butyl-2-Benzothiazole Sulfenamide (TBBS)	0.81	0.81
Sulfur	1.35	1.35
Poly-thiosulfate anti reversion agent	0	1.5
Physical properties:		
LPT Index for Nose Tires	100	112
LPT Index for Main Tires	100	108
Field Chevron Cutting Index*	100	145

* higher=better

2.12 MOTIVATION OF THE THESIS

Tires are one of the main components of aircrafts that undergo frequent replacement due to the severe conditions during utilization. Retreading AC tires is by far the most environmentally friendly and efficient way of extending the service life of AC tires. It is also economical since it saves more than 50% of the costs compared to a new tire. Almost all airline companies in the world use retreaded tires to reduce their operating costs.

The ultimate goal of improvements of retreading technologies and systems is to provide a high and consistent quality of retreaded tires. The development of innovative tread materials aims at cooler running and higher heat-resistance, while simultaneously improve tire service life. Heat generation, thus a high temperature increase within the tires, has direct consequences for other crucial properties such as tensile strength and tread wear. From a compounding point of view, it is imperative to provide rubber formulations with low hysteresis at the temperature and frequency ranges of service. The selection of ingredients determines the final properties of rubber products. Besides the ingredients, the correct processing in terms of mixing conditions and addition sequence during mixing also determines the properties. Therefore, proper selection of ingredients and optimized processing to balance the properties of AC tire retreads: low hysteresis while maintaining high stress-strain properties and ease of processing, are the goals of the study reported in this thesis.

Rubber processing

The first part of the study is dedicated to investigating the factors influencing the mixing behavior of:

- i) CB-filled NR/BR blends;
- ii) SI-filled and a hybrid CB/SI-filled NR/BR blends.

To enhance the properties of AC tire retreads, it is essential to investigate the parameters for rubber mixing influencing the material properties for those specific filler systems. The aim is to carefully optimize the parameter settings to successfully produce the desired or intended property profiles, with consistency in quality and minimum time expense (efficient). A Design of Experiments (DOE) approach is used because it covers many factors and a wide range of settings at the same time. The results are statistically accountable. Moreover, DOE is a widely used approach for optimizing quality and product performance. The outcome of this mixing optimization enables the rubber manufacturer to produce AC tire retreads in a similar high quality as the material produced in the research stage.

Addition sequence

Several researchers found that ZnO and DPG can interact with SI. The addition sequence of ZnO and DPG is investigated in compounds with a hybrid CB/SI filler system to study the effect on the rubber properties of AC tire retreads. It is essential to elucidate how different addition sequences affect the rubber properties. Finally, it will be possible to identify the best addition sequence of ZnO and DPG suitable for AC tire retreads.

Properties of polymers and resins

Related to the material selection, the investigations are divided into:

- i) A first investigation to study the effect of different types of BR in terms of macro- and micro-structure on the properties of AC tire retreads. It is also essential to have a better understanding of how the structure of polymers influence the properties in unfilled and filled systems.
- ii) The second focus of this part of the investigation is related to the use of resins in different filler systems. Two types of resins with different polarity, solubility, viscosity and softening point are used in order to study how the resins interact with polymers as well as with different filler systems, and how they influence the compound and the final properties of AC tire retreads.

Aging properties

Due to high service temperatures of AC tires, the tread/retread is prone to aging/oxidation. The knowledge about aging of these rubber vulcanizates will lead to better understanding of the influence on the material properties during service.

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DEFINING KEY FACTORS FOR IMPROVING PROPERTIES OF AIRCRAFT TIRE RETREADS PRODUCED FROM CARBON BLACK-FILLED NR/BR BLENDS*

ABSTRACT

Carbon Black (CB) is the most common reinforcing filler used in aircraft tire tread formulations. For CB-reinforced Natural Rubber/Butadiene Rubber (NR/BR) blends, material and processability parameters are important factors that need to be controlled as they can influence both, processing as well as vulcanizate properties. It is essential to investigate and optimize the key factors in order to achieve the target properties while maintaining an acceptable trade-off for other characteristics. In the present study, the type of BR, mixer set temperature, rotor speed, and filler mixing time were selected as input factors. A complete Design of Experiments (DOE) process is performed, comprising the following: a two-level full factorial setup for initial screening, Response Surface Method (RSM) for optimization, and validation runs for confirmation.

This evaluation procedure is used to study the impact of factors and their interactions on the properties of CB-filled NR/BR compounds and vulcanizates. From the DOE optimization and later confirmed by the DOE validation, rotor speed and filler mixing time are the most significant factors in improving Mooney Viscosity (MV), Modulus at 300% elongation (M300%), hysteresis ($\tan \delta$) as well as in reducing Payne Effect (PE). In the case of Tensile Strength (TS), high mixer set temperature has an adverse effect, thus deteriorating the properties. Therefore, it is recommended to mix at a temperature of 50°C and during a moderate filler mixing time of 7 mins combined with a rotor speed of 130 rpm. In terms of type of BR, a High-Cis and Long-Chain Branched grade (HC LCB BR) shows better processability, lower PE and $\tan \delta$ compared to a linear High-Cis grade (HC BR), while maintaining acceptable M300% and TS.

3.1 INTRODUCTION

Aircraft (AC) tire treads experience severe operating conditions in which they must be able to endure high forces upon landing of an aircraft: the tire touches the ground with zero rotational speed which creates high friction under substantial load, thus causing high temperatures within the AC tire tread. During takeoff, aircrafts also experience significant forces from rapid acceleration to relatively high speeds under load [1]. Because of these extreme working conditions, AC tire treads need to be resistant against heat generation and wear. Based on the simulation done by Alroqi et al. at zero rotational speed during landing, the temperature of a tire tread in the main area of contact is around 300°C, while the majority of the tread temperature is less than 165°C [2].

The selection of compound ingredients plays a crucial role in the performance of AC tire treads. The main requirements for AC tire treads are low hysteresis, superior tensile and tear strength, good retreadability, good adhesion to the underlayer, and high wear resistance [1]. Therefore, the treads of AC tires generally contain Natural Rubber (NR). This polymer is essential in AC tire tread compounds due to several advantages such as superior tensile and tear properties, low tire temperature (hysteresis) under dynamic load, as well as good component-to-component adhesion and green strength for tire retreadability [3]. Another essential requirement is high wear resistance; therefore, a blend of NR and Butadiene Rubber (BR) is typically used for AC tire treads. BR gives better low temperature flexibility, higher resilience, and superior abrasion resistance compared to most other tire rubbers. Reinforcing fillers such as high surface area Carbon Black (CB), in particular High Abrasion Furnace (HAF), Intermediate Super Abrasion Furnace (ISAF) and Super Abrasion Furnace (SAF) types, can be added to enhance abrasion resistance.

Besides ingredients, processing of rubber is also a crucial aspect in material preparation. Research has shown that variation of the controlled mixing parameters of the internal mixer such as mixing time [4-8], rotor speed [4], mixing set temperature [4, 8] and fill factor [7, 9] significantly influence the rubber properties. A proper selection of these mixing parameters will further optimize the properties of rubber materials.

It is therefore essential to investigate and optimize the compounding and processing key factors in order to achieve the target properties while maintaining an acceptable trade-off for other characteristics. Design of Experiments (DOE) is used for this purpose instead of a conventional experimental method, which is done by varying all relevant factors simultaneously. Moreover, an approach such as One Factor At a Time (OFAT) does not lead to a real optimum for the investigated system and fails for choosing the optimum setting conditions. Although OFAT can directly reveal how certain factors affect the product performance, it very poorly covers the whole factor space and does not disclose if there are interactions between specific factors [10]. In contrast, by a DOE approach, the entire factor space can be explored using as many factors as necessary at the same time. Thus, a more substantial space volume response is covered, and factor interactions will also be revealed

[11]. Some applications of DOE in rubber technology are described in literature, aiming at modelling and optimizing the properties of rubber materials [10, 12-17].

In the present study, four factors: the type of BR, mixer set temperature, rotor speed and filler mixing time are selected and investigated in CB-filled NR/BR blends. Aiming to identify the most significant factor for balancing the properties of AC tread compounds, a complete DOE process comprises a two-level full factorial setup for screening. The properties of AC tire treads such as Mooney Viscosity (MV), Payne Effect (PE), hysteresis ($\tan \delta$ 100°C, 10%, 1 Hz), and stress-strain properties are chosen as the responses. Finally, after the screening process, the two most notable factors were optimized and validation runs for confirmation performed.

3.2 EXPERIMENTAL

3.2.1 MATERIALS

The rubber types used are NR: Ribbed Smoked Sheet (RSS-1) obtained from Weber & Schaefer GmbH & Co. KG, Germany; BR: High-Cis BR (HC BR) CB 22, as well as High-Cis Long-Chain Branched BR (HC LCB BR) Nd 22 EZ from ARLANXEO, Germany. Other compounding ingredients are high structure CB N234 from CABOT, USA, and Treated Distillate Aromatic Extract (TDAE) oil from Hansen & Rosenthal, Germany. N-Cyclohexyl-2-Benzothiazole Sulfenamide (CBS), 2,2,4-TriMethyl-1,2-dihydroQuinoline (TMQ), N-Phenyl-para-Phenylenediamine (6PPD), Zinc Oxide (ZnO), stearic acid and sulfur are of technical quality.

For DOE screening purposes, it was decided to use two types of BR as given in Table 3.1 to study the effect of the type of BR on the properties. The compound formulation used for this study is depicted in Table 3.2, adopted from a patent for AC tire tread formulations [18].

Table 3.1 Properties of Butadiene Rubbers.

Properties	HC BR	HC LCB BR
Catalyst type	Neodymium	Neodymium
ML(1+4)100°C, MU	63	63
Cis content, %	min 96	min 96
Branching	highly linear	Long-chain branched
Weight average molecular weight (Mw), g/mol	6.0×10^5	5.3×10^5
Mw/Mn	2.0	2.2

Table 3.2 Rubber compound formulations.

Ingredients	Level -1 (phr)	Level +1 (phr)
NR	70	70
HC BR	30	-
HC LCB BR	-	30
CB N234	55	55
ZnO	5	5
Stearic acid	3	3
6PPD	2	2
TMQ	1	1
TDAE	7.5	7.5
Sulfur	1.5	1.5
CBS	1.5	1.5

3.2.2 COMPOUND PREPARATION

For the DOE screening, mixing was performed in an internal mixer (Brabender Plasticorder 350s, Brabender GmbH & Co KG, Germany) with mixer set temperature, rotor speed, and filler mixing time varied according to the defined experimental design (see Table 3.4, DOE screening method in section 3.2.4). The mixer was operated at a fill factor of 70%.

Two-stage mixing was performed as shown in Table 3.3. NR is initially masticated prior to the addition of BR to have a MV close to the one of BR. The masticated NR and BR were blended for 1 minute (min). Then half of CB and TDAE oil were added and mixed for 1 min. After that specific time, the other half of CB and TDAE oil were added and mixed for the remaining time according to the DOE parameter settings in Table 3.4. Mixer rotor speed and set temperature were also DOE parameters. Finally, the other ingredients: ZnO, stearic acid, 6PPD and TMQ were added and mixed for 2.5 mins. The compounds were discharged, sheeted off on a two-roll mill and kept overnight before incorporation of sulfur and CBS in the same internal mixer at a set mixer temperature of 70°C and initial rotor speed of 50 revolutions per minute (rpm). For this, the masterbatch was mixed for 1 min, then the rotor speed was decreased to 30 rpm and the curatives added to the compound and mixed for a final 2 mins.

Table 3.3 Two-stage mixing procedure.

Mixing procedure	Time (mins)
Step 1: Internal mixer	
Mixer set temperature and rotor speed: varied depending on the DOE factor level settings	- Mixing of masticated-NR and BR 1
	- Addition of half (CB and TDAE oil) 1
	- Addition of half (CB and TDAE oil) Remaining time setting
	- Addition of ZnO, stearic acid, 6PPD and TMQ 2.5
Step 2: Internal mixer	
Mixer set temperature: 70°C	- Masterbatch 1
Initial rotor speed: 50 rpm	- Addition of curatives (sulfur and CBS) 2

3.2.3 TESTING OF COMPOUND AND VULCANIZATE PROPERTIES

The following compound and vulcanizate properties were chosen as the defined responses for DOE:

Mooney Viscosity (MV) – The compounds were tested for their MV by using a Mooney Viscometer 2000VS (Alpha Technologies, USA) at 100°C with a large rotor for 4 mins with 1 min of pre-heating according to ASTM D1646. The value is represented as ML(1+4)100°C.

Payne Effect (PE) – The storage modulus (G') of the compounds was measured using a Rubber Processing Analyzer (RPA 2000 Alpha Technologies, USA). A strain sweep test was done in the range of 0.56 to 100% strain at 0.5 Hz and 100°C. The difference of G' at 0.56% and at 100% strain ($\Delta G'$) was taken as measure of filler-filler interaction.

Hysteresis ($\tan \delta$) – The compounds were cured to their ($t_{90}+2$) mins at 150°C in the RPA. After curing in situ, the temperature was decreased to 100°C for the hysteresis measurement. The $\tan \delta$ was then recorded in a frequency sweep of 0.5 – 33 Hz and a fixed strain of 10%.

Stress-strain properties – All compounds were vulcanized at a cure time ($t_{90}+2$) mins at 150°C in a Wickert Laboratory Press (WLP1600, Wickert Maschinenbau GmbH, Germany). The sheets having a thickness of 2 millimeters (mm) were die-cut into dumbbells type 2 for the Modulus at 300% elongation (M300%) and Tensile Strength (TS) measurements. The tests were done with a Zwick Roell Z1.0 tensile testing machine using a crosshead speed of 500 mm/min according to ISO 37.

3.2.4 DOE SCREENING

A DOE screening was employed in the first stage of experiments. The objective at this stage was to explore if factors influence the selected responses and to identify the appropriate ranges. A two-level full factorial approach comprising four factors is shown in Table 3.4. Each factor has two levels: low -1 and high +1 with an additional Center Point (CP) 0, chosen for replication, except for the BR type. Table 3.5 shows the rubber properties as defined responses.

Table 3.4 Experimental design for optimizing mixing conditions.

Parameters	-1	0	+1
A: BR type	HC BR	-	HC LCB BR
B: Mixer set temperature (°C)	50	75	100
C: Rotor speed (rpm)	60	90	120
D: Filler mixing time (min)	2	6	10

Table 3.5 Defined responses.

Responses	Rubber properties	Abbreviation
Y1	Mooney Viscosity	MV
Y2	Payne Effect	PE
Y3	$\tan \delta$ at 100°C	$\tan \delta$
Y4	Modulus 300%	M300%
Y5	Tensile Strength	TS

Figure 3.1 depicts the two-level full factorial design with four factors, denoted 2^4 , which is geometrically represented in a cube. The cube is representative for each of the two different types of BR. The three axes are dedicated to mixer set temperature, rotor speed and filler mixing time. The total number of experiments for this stage is 22 runs.

The cube represents a single type of BR
(HC BR and HC LCB BR)
DOE full factorial + 3 CP replication
No. of factors = 4
No. of levels = 2
No. of experiments = $2^4 + (2 \times 3) = 22$

Figure 3.1 Two-level full factorial DOE setup with center points.

After completion of the experimental runs, the data were analyzed by a Pareto approach to find out which factors and/or interactions significantly influence the responses. Pareto calculations comprise the following steps [19]:

$$Effect = \frac{\sum Y_+}{n_+} - \frac{\sum Y_-}{n_-} \quad \text{Equation 3.1}$$

$$Sum\ of\ Squares(SS) = \frac{(n_+ + n_-)}{4} \times (Effect)^2 \quad \text{Equation 3.2}$$

$$Mean\ of\ Squares\ (MS) = \frac{SS}{df} \quad \text{Equation 3.3}$$

$$MS_{residual} = \frac{SS_{residual}}{df_{residual}} \quad \text{Equation 3.4}$$

$$t - value = \frac{|Effect|}{\sqrt{MS_{residual} \times \left(\frac{1}{n_+} + \frac{1}{n_-}\right)}} \quad \text{Equation 3.5}$$

Y_+ : the results of observed response in level +1

Y_- : the results of observed response in level -1

n_+ : the total number of experiments in level +1

n_- : the total number of experiments in level -1

df : degrees of freedom

The effect of factors and the interaction between factors on the rubber properties (Y) were analyzed using Analysis of Variance (ANOVA) and then modeled by fitting a polynomial model to the data as described in Equation 3.6 [20]:

$$Y = \beta_o + \beta_A A + \beta_B B + \beta_C C + \beta_D D + \beta_{AB} AB + \beta_{AC} AC + \beta_{AD} AD + \beta_{BC} BC + \beta_{BD} BD + \beta_{CD} CD + \varepsilon \quad \text{Equation 3.6}$$

where A , B , C , and D are the independent factors (BR type, mixer set temperature, rotor speed, filler mixing time), β_o is a constant, β_A , β_B , β_C , β_D are linear coefficients, β_{AB} , β_{AC} , β_{AD} , β_{BC} , β_{BD} , β_{CD} are interaction regression coefficients, and ε is the residual response variation not explained by the model.

Contour and interaction plots were used to describe the effects of factors and/or interactions on responses in more detail.

3.2.5 DOE OPTIMIZATION

The two most significant factors on defined-responses: rotor speed and filler mixing time, from the DOE screening were further optimized using the Response Surface Method (RSM). A Central Composite Circumscribed (CCC) design was selected for the DOE optimization, with the level settings as shown in Figure 3.2. A total of 11 runs was performed to elucidate in more detail the effect of the two most significant factors and their interactions on the defined responses.

Figure 3.2 CCC design setup.

The assessment of the significance of the factors and their interaction in the DOE optimization was the same as in the DOE screening. The difference lies only in the model used for fitting; this permits the response to be modeled with a second order polynomial equation, allowing the analysis of main, quadratic (curvature), and interactive effects [17]. The equation used in the central composite design for fitting the effect of factors (C and D) on the response (Y) is described by Equation 3.7. The symbols are the same as mentioned in Equation 3.6, with the additional quadratic coefficients.

$$Y = \beta_o + \beta_C C + \beta_D D + \beta_{CD} CD + \beta_{CC} C^2 + \beta_{DD} D^2 + \beta_{C^2D} C^2 D + \beta_{CD^2} CD^2 + \beta_{C^2D^2} C^2 D^2 + \varepsilon \quad \text{Equation 3.7}$$

3.3 RESULTS AND DISCUSSION

3.3.1 DOE SCREENING

Table 3.6 shows the values of each response resulting from the DOE screening. The effect, Sum of Squares (SS), and Mean of Squares (MS) were calculated using Equations 3.1 - 3.4. Table 3.7 shows an example of the calculated effect, SS, MS for Mooney Viscosity (MV).

Table 3.6 Results of defined responses from DOE screening.

No.	A: BR type	B: Mixer set temperature (°C)	C: Rotor speed (rpm)	D: Filler mixing time (min)	Y1: MV (MU)	Y2: PE (kPa)	Y3: tan δ at 100°C (-)	Y4: M300% (MPa)	Y5: TS (MPa)
1	1	1	-1	1	81	494	0.120	17	25
2	-1	1	1	-1	75	479	0.127	16	30
3	-1	0	0	0	84	581	0.132	17	31
4	1	-1	-1	1	91	764	0.144	17	30
5	1	0	0	0	81	529	0.122	16	32
6	1	1	1	-1	76	578	0.121	17	25
7	1	0	0	0	78	559	0.134	17	31
8	1	-1	1	-1	86	588	0.128	16	26
9	-1	0	0	0	82	622	0.136	17	31
10	-1	0	0	0	87	686	0.138	17	29
11	1	-1	-1	-1	102	1000	0.152	13	26
12	-1	-1	-1	1	101	914	0.138	14	25
13	1	1	-1	-1	94	850	0.144	16	30
14	1	-1	1	1	66	383	0.103	18	25
15	1	1	1	1	50	278	0.110	15	24
16	-1	1	-1	1	91	544	0.133	17	29
17	-1	1	1	1	60	332	0.106	19	25
18	-1	-1	1	1	64	369	0.113	17	27
19	-1	1	-1	-1	108	966	0.143	14	25
20	-1	-1	1	-1	92	641	0.132	15	26
21	1	0	0	0	78	546	0.132	17	32
22	-1	-1	-1	-1	101	891	0.148	11	28

Table 3.7 Example of calculated effect, SS, MS, F-value for MV

Factors and two-factor interaction	Effect	Sum of Squares (SS)	Degrees of freedom (df)	Mean of Squares (MS)
Model		4379.52	10	437.95
A: BR type	-5.85	185.60	1	185.60
B: Mixer set temperature	-8.65	299.29	1	299.29
C: Rotor speed	-25.28	2555.30	1	2555.30
D: Filler mixing time	-16.50	1089.00	1	1089.00
AB	-2.30	21.16	1	21.16
AC	2.58	26.52	1	26.52
AD	-1.55	9.00	1	9.00
BC	-3.33	44.22	1	44.22
BD	-1.50	9.00	1	9.00
CD	-5.93	140.42	1	140.42
Residual		157.71	9	17.52
Total		4537.23		

Figure 3.3 shows the Pareto charts of factors for defined responses from the DOE screening. A t-test compares the observed t-value according to Equation 3.5 to a t-value limit derived from the t-distribution table for df_{residual} 9 and alpha 0.05 [19], in order to determine whether the difference between the estimated and hypothesized values of the factor or interaction is statistically significant. Alpha 0.05 means having 5% probability of incorrectly rejecting the null. The null states that there is no difference or no effect of the parameters being studied. If the t-value is higher than the t-value limit, it means that the factor/interaction is statistically significant.

The graphs show that rotor speed and filler mixing time are the most significant factors influencing MV, PE, $\tan \delta$ at 100°C, and M300%. The mixer temperature has an influence on MV and PE, but less of an effect on $\tan \delta$ and M300%. The type of BR has an effect on MV and M300%. For TS, the effect of these factors is not conclusive as seen from their t-values being below the t-value limit. Note that the colored bars without notation are the interactions that are not included in the model (examples: ABC, ABD, ABCD) because they are not two-factor interactions (examples: AB, AC, AD).

Figure 3.3 Pareto charts of factors for the properties: MV (a); PE (b); $\tan \delta$ at 100°C (c); M300% (d); TS (e).

Table 3.8 parts 1 and 2 show the coefficients of the parameters studied, obtained from ANOVA. Rotor speed (C) and filler mixing time (D) are statistically significant factors (p-value ≤ 0.05 , written in blue) for MV, PE, $\tan \delta$ at 100°C and M300%. The P-value is the probability of obtaining a sample “more extreme” than the ones observed in the data assuming that the null hypothesis is true. The Null hypothesis states that there is no difference or no effect of the parameters being studied. The effect of the studied factors on the properties is strongly related to a R-squared of 0.9 or above, except for the M300% values. R-Squared is a statistical measure of how close the data are to the fitted regression line. An increase of rotor speed increases the shear stress, thus enables a decrease of MV and a low filler-filler interaction [21, 22]. M300% correlates with the parameters studied with a R-squared value slightly below 0.9, while TS shows no linear correlation with the studied factors: The R-squared is 0.16. There are two possible explanations for this:

1. The TS of the materials might not follow a linear model as described in Equation 3.6. Indeed, during the optimization, when a quadratic model was used (Equation 3.7), the R-squared value increased to 0.93, see Table 3.9.
2. This property is influenced by a variety of other factors which are not covered in the model. TS depends not only on the degree of filler dispersion, but also on crosslink density, rubber–filler interaction, and filler loading [23], to mention only a few. At equal filler loadings, TS depends on the degree of filler dispersion and is closely related to the degree of rubber–filler interaction. Therefore, changes in any parameter that improves filler dispersion and rubber-filler interaction will also influence TS [17].

Table 3.8 Coefficients of parameters studied by DOE screening (part 1).

Responses		Constant	Variables			
			BR type A	Mixer set temperature B	Rotor speed C	Filler mixing time D
		β_o	β_A	β_B	β_C	β_D
MV, MU	HC BR	116.80	-	0.12	-0.15	0.91
	HC LCB BR	112.42	-	0.03	-0.06	0.53
	p-value	-	0.004	0.001	<0.0001	<0.0001
PE, kPa	HC BR	1633.10	-	-3.48	-8.96	-3.70
	HC LCB BR	1579.69	-	-3.70	-8.07	-12.40
	p-value	-	0.22	0.006	<0.0001	<0.0001
$\tan \delta$ at 100°C	HC BR	0.19	-	-3.2E-04	-4.6E-04	-4.6E-04
	HC LCB BR	0.20	-	-3.7E-04	-5.2E-04	-8.1E-04
	p-value	-	0.21	0.04	<0.0001	0.0002
M300%, MPa	HC BR	-0.46	-	0.13	0.12	0.94
	HC LCB BR	5.95	-	0.10	0.09	0.77
	p-value	-	0.18	0.05	0.001	0.001
TS, MPa	HC BR	23.99	-	0.62	0.02	0.03
	HC LCB BR	29.29	-	0.59	-0.03	0.02
	p-value	-	0.95	0.73	0.44	0.98

Table 3.8 Coefficients of parameters studied by DOE screening (part 2).

Responses		Variables						R-Squared
		AB	AC	AD	BC	BD	CD	
		β_{AB}	β_{AC}	β_{AD}	β_{BC}	β_{BD}	β_{CD}	
MV, MU	HC BR	-	-	-	-2.2E-03	-7.5E-03	-0.02	0.97
	HC LCB BR	-	-	-	-2.2E-03	-7.5E-03	-0.02	
	p-value	0.25	0.20	0.44	0.10	0.44	0.01	
PE, kPa	HC BR	-	-	-	0.03	-0.33	0.04	0.93
	HC LCB BR	-	-	-	0.03	-0.33	0.04	
	p-value	0.89	0.50	0.38	0.21	0.11	0.83	
tan δ at 100°C	HC BR	-	-	-	2.5E-06	-2.5E-06	1.3E-05	0.90
	HC LCB BR	-	-	-	2.5E-06	-2.5E-06	1.3E-05	
	p-value	0.67	0.56	0.74	0.22	0.87	0.32	
M300%, MPa	HC BR	-	-	-	-7.5E-04	-4.4E-03	-3.2E-03	0.86
	HC LCB BR	-	-	-	-7.5E-04	-4.4E-03	-3.2E-03	
	p-value	0.08	0.07	0.13	0.02	0.06	0.09	
TS, MPa	HC BR	-	-	-	-3.4E-03	-5.1E-03	3.9E-05	0.16
	HC LCB BR	-	-	-	-3.4E-03	-5.1E-03	3.9E-05	
	p-value	0.81	0.48	0.94	0.65	0.57	0.97	

Contour plots are used to see the effect of factors and interactions on responses more clearly. The interaction factor 'interaction between rotor speed and filler mixing time' on MV is depicted in Figure 3.4 for the two types of BR at 100°C of mixer temperature. A synergistic effect of rotor speed and filler mixing time was found at the high-level settings, in which the combination of high rotor speed and long filler mixing time decreases MV of compounds considerably, as can be seen more clearly in Figure 3.5, where the distance between the lines is not the same at low- and high-level settings of rotor speed and filler mixing time. A high rotor speed provides higher shear stresses and results in higher stock temperatures, both lowering MV.

At the same rotor speed and filler mixing time, the MV of the rubber compounds containing HC BR is higher than the one of the compounds containing HC LCB BR. The high MV values are due to the slightly higher molecular weight of HC BR, thus higher viscosity compared to HC LCB BR, which has a lower molecular weight. Branching of HC LCB BR also improves the processability resulting in lower MV compared to the linear chain HC BR compounds.

Figure 3.4 The effect of rotor speed and filler mixing time on MV.

Figure 3.5 Interaction plot between rotor speed and filler mixing time on MV.

The effect of the two most significant factors on PE is shown in Figure 3.6. The higher the rotor speed and the longer the filler mixing time, the lower the PE. High rotor speed provides high shear rate, which is necessary for dispersive mixing and enhances the fragmentation of CB agglomerates down to CB aggregates. Longer mixing times increase the inter-aggregate distance of CB, leading to reduced formation of filler networks [24]. The combination of both factors results in an even lower PE compared to using only one single factor (rotor speed or filler mixing time) at high level settings. HC LCB BR shows a lower PE compared to HC BR due to branching which enhances processability.

Figure 3.6 The effect of rotor speed and filler mixing time on PE.

Tan δ at 100°C is used as an indication of hysteresis: a lower tan δ indicates less hysteresis and lower heat generation. Figure 3.7 shows the effect of rotor speed and filler mixing time on tan δ at 100°C: high rotor speed and long filler mixing time decrease tan δ . The tan δ values correlate well with Payne effect values, as low tan δ values correspond to low filler-filler interaction.

Figure 3.7 The effect of rotor speed and filler mixing time on tan δ .

High M300% values were observed in the HC BR compounds, which were mixed at high rotor speed and long filler mixing time as shown in Figure 3.8 left. Like TS, M300% is influenced by many factors such as filler-filler interaction, filler-rubber interaction, and the type of polymers used. The linear chain of HC BR has a simple structure, and it can be packed tightly, while the branched HC LCB BR has a complex structure and is packed loosely [25]. As a result, HC BR exhibits higher mechanical properties compared to HC LCB BR. However, HC BR shows poor processability: HC BR requires more severe mixing conditions (temperature and filler mixing time) than HC LCB BR to achieve high filler dispersion and optimum M300%.

Figure 3.8 The effect of rotor speed and filler mixing time on M300%.

In contrast, M300% values of HC LCB BR are relatively independent of rotor speed and filler mixing time at a mixer set temperature of 100°C: Figure 3.8 (right). At lower mixer set temperatures of 50°C and 75°C, the rotor speed and filler mixing time do influence M300% values of HC LCB BR. Due to the branching, thus better processability, the maximum M300% value is already reached at a mixer set temperature of 50°C. Increasing mixer set temperature to 70°C decreases the maximum M300% values of HC LCB BR, see Figure 3.9 (right), and at a mixer set temperature of 100°C no difference in M300% values is observed within the investigation range of rotor speed and filler mixing time: Figure 3.8 (right).

Figure 3.9 The effect of rotor speed and filler mixing time on M300% of HC LCB BR at a mixer temperature of 50°C and 75°C.

Although the effect of rotor speed and filler mixing time on TS as depicted in the Pareto chart and ANOVA are not conclusive, there is a slight indication in the contour plot in Figure 3.10 that low rotor speed and mixer set temperature are preferable for increased TS. The decrease of TS is attributed to thermal polymer degradation, in particular for NR at high temperatures, and to shearing forces breaking the polymer chains [26].

Figure 3.10 The effect of mixer temperature and rotor speed on TS.

3.3.2 DOE OPTIMIZATION

Rotor speed and filler mixing time were further optimized, while mixer set temperature was set at 50°C since a higher setting of this parameter has a negative effect on M300% and TS based on the DOE screening: Figures 3.9 and 3.10. HC LCB BR was chosen because the properties are comparable to HC BR, but showed better processability. The RSM-CCC design was used, see Figure 3.2, in order to find the best level setting for optimizing all properties.

Table 3.9 parts 1 and 2 show the coefficient parameters of the DOE optimization. The correlation factors between the parameters rotor speed and filler mixing time, and the responses increase following a quadratic instead of a linear correlation. All responses show R-squared of above 0.9.

Table 3.9 Coefficients of parameters studied by DOE optimization (part 1).

Responses		Constant	Variables				
			C	D	CD	C ²	D ²
		β_o	β_C	β_D	β_{CD}	β_{CC}	β_{DD}
MV, MU	Coef.	157.83	-0.99	-1.14	-0.01	4.5E-03	0.01
	p-value		0.0006	0.004	0.88	0.02	0.07
PE, kPa	Coef.	3118.31	-36.32	-312.89	4.56	-0.16	20.52
	p-value		0.0001	0.0005	0.003	0.0008	0.04
tan δ at 100°C	Coef.	0.62	-8.1E-03	-0.10	-1.8E-03	6.9E-03	6.9E-03
	p-value		0.001	0.005	0.18	0.01	0.03
M300%, MPa	Coef.	-7.43	0.26	1.82	-6.0E-03	-1.3E-03	-0.01
	p-value		0.001	0.01	0.01	0.007	0.003
TS, MPa	Coef.	115.01	-2.17	-15.83	0.41	0.01	0.65
	p-value		0.005	0.04	0.03	0.52	0.06

Table 3.9 Coefficients of parameters studied by DOE optimization (part 2).

Responses		Variables			R-Squared
		C ² D	CD ²	C ² D ²	
		β_{C^2D}	β_{CD^2}	$\beta_{C^2D^2}$	
MV, MU	Coef.	-4.1E-04	-9E-04	3.5E-05	0.99
	p-value	0.71	0.30	0.85	
PE, kPa	Coef.	-0.03	-0.4	2.7E-03	0.99
	p-value	0.02	0.05	0.13	
tan δ at 100°C	Coef.	-9.1E-06	-1.3E-04	6.5E-07	0.99
	p-value	0.15	0.61	0.15	
M300%, MPa	Coef.	-1.3E-03	-0.02	9.2E-05	0.99
	p-value	0.12	0.13	0.04	
TS, MPa	Coef.	-2.6E-03	-0.02	1.2E-04	0.93
	p-value	0.02	0.05	0.12	

Figure 3.11 (a.1 and a.2) to (e.1 and e.2), shows the response surfaces and the contour plots for rotor speed and filler incorporation time derived from the DOE optimization. Similar trends as in the DOE screening were found for MV: a higher rotor speed and longer filler mixing time decrease MV. For PE, $\tan \delta$ at 100°C and M300%, an optimum filler mixing time in combination with high rotor speed is needed to improve those properties. In the case of TS, high rotor speed and long filler mixing time have an adverse effect, thus decreasing those properties.

(a.1)

(a.2)

(b.1)

(b.2)

Figure 3.11 Response surfaces and contour plots of: MV 9 (a.1, a.1); PE (b.1, b.2); $\tan \delta$ (c.1, c.2); M300% (d.1, d.2); TS (e.1, e.2).

3.3.3 DOE VALIDATION

The DOE validation was performed at the last stage of the DOE process. This is the final check on how close the predicted values from the model are to the actual values from experimental runs. The overlay plot shows the parameter settings for obtaining the target values of each of the rubber properties (responses): see the yellow area in Figure 3.12. The target value is the individual goal of each property. In this project, the goal is to get the optimum setting of each factor to balance the properties of AC tire retreads: MV for ease in processability, low PE and low $\tan \delta$ while maintaining acceptable M300% and TS values. Table 3.10 shows the target values, the predicted values, and actual values of defined responses from mixing of HC LCB BR filled with CB at 50°C, 130 rpm, and 7 mins. The predicted values from the model are close to the actual values, indicating that the predicting model from optimized DOE factors was accurate.

Figure 3.12 Overlay plot of all properties.

Table 3.10 Target values, predicted values and actual values of envisaged properties.

Properties	Target values	Predicted values (130 rpm, 7 mins)	Actual values (130 rpm, 7 mins)
MV (MU)	60 – 75	60	58
PE (kPa)	<270	270	260
TS (MPa)	min 22 [27]	25	24
M300% (MPa)	8 – 16 [27]	15	15.7
$\tan \delta$ at 100°C	0.07 – 0.17 [1]	0.099	0.098

3.4 CONCLUSIONS

A comprehensive study by means of DOE to determine the most significant factors influencing the properties of CB-filled NR/BR compounds for AC tire treads was carried out. As a general conclusion, it can be stated that DOE is a suitable tool for elaborating the optimum parameter settings to balance the properties as desired. This approach results in predictive models giving values close to the actually measured ones.

Among four factors studied in DOE, rotor speed and filler mixing time are the most significant. All required properties needed for the AC tire tread application were fulfilled by optimizing the setting conditions for these two factors. At the same time, the mixer temperature can be set at a low value, and HC LCB BR should be used since it imparts better properties.

3.5 REFERENCES

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OPTIMIZATION OF THE MIXING PARAMETERS FOR NR/BR BLENDS WITH A HYBRID CARBON BLACK/SILICA AND A SILICA FILLER SYSTEM

ABSTRACT

Two types of Butadiene Rubber (BR): High-Cis BR (HC BR) and High-Cis Long-Chain Branched BR (HC LCB BR), and two types of fillers: Silica (SI) and a combination of Carbon Black and Silica (CB/SI), as well as silanization temperature and time are investigated in order to optimize the properties of aircraft tire retreads. The silanization temperature turns out to be the most significant factor defining the properties of rubbers. A sufficient silanization time is beneficial to enhance the hydrophobation of silica by bis-(TriEthoxySilylPropyl)Tetrasulfide (TESPT) as a coupling agent. The use of HC LCB BR enhances processability by lowering the viscosity, and better silanization results in a lower Payne Effect (PE) compared to the HC BR counterpart. High filler-rubber interactions of HC LCB BR lead to higher crosslink density, lower $\tan \delta$ at 100°C, as well as higher Modulus at 300% elongation (M300%) and Tensile Strength (TS) compared to the HC BR based rubber. CB/SI-filled vulcanizates show slightly improved mechanical properties, i.e., TS and hardness. However, the $\tan \delta$ /heat-build-up values of CB/SI-filled vulcanizates are still higher compared to ones of the pure SI-filled vulcanizates, while the filler-rubber interactions are not only chemical but also physical.

4.1 INTRODUCTION

Natural rubber (NR) still is the primary ingredient in aircraft tire tread formulations. The excellent properties of NR provide superior stress-strain properties as well as low heat build-up and wear resistance as required for Aircraft (AC) tires. In the filled system, NR works best with CB since both have a relatively small difference in polarity. Therefore, it is relatively easy to disperse CB in NR. In the previous study: Chapter 3, we elaborated on optimizing rotor speed and filler mixing time for the main property required for AC tire retreads, which is low heat build-up measured as $\tan \delta$ at 100°C, without sacrificing stress-strain properties, hardness, or processability.

It is crucial to decrease the hysteresis in Aircraft (AC) tire treads to lower the temperature build-up in the tire, which finally decreases tread wear and increases service life of the tire. Silica (SI) together with a silane as coupling agent gained popularity in the rubber world since the introduction of the “green tire” by Michelin [1]. The use of SI yields a lower rolling resistance and better traction than CB filled rubber, especially for Passenger Car Tires (PCT) [2, 3]. The substitution of low levels of 5 to 10 phr of CB by SI can enhance tear, cut growth resistance, and adhesion properties [4].

Incorporation of SI in compounds containing non-polar rubbers such as NR and BR is challenging. Due to the difference in polarity between SI and these polymers, the degree of dispersion of SI is lower compared to the dispersion of CB. The interaction between the SI particles themselves is stronger than the interaction between the polar siloxane or silanol moieties on the SI surface and the rubber [5]. The SI surface comprises silanol groups, which create hydrogen bonds between other surface silanol groups, resulting in strong SI clusters causing poor dispersion of the SI in rubber compounds [6] which deteriorates the properties [6, 7]. Moreover, the viscosity of compounds will increase substantially, when a large portion of SI is added, which makes them more challenging to process [8]. Both processing properties can significantly be improved by the addition of a coupling agent like a silane.

To ensure that the silanization reaction occurs, SI in combination with the silane needs to be mixed into the rubber under optimal conditions [8, 9] using a suitable formulation. Bis-(TriEthoxySilylPropyl)Tetrasulfide (TESPT) is the most widely used bifunctional organosilane in the tire industry and was studied by many researchers [8-14]. Optimized silanization conditions will lead to a high degree of bonding of the silane onto the SI surface. Subsequently, the coupling reaction between silane and elastomer is formed during vulcanization. The filler-elastomer network in combination with elastomer crosslinks leads to low hysteresis of rubber vulcanizates [15].

To optimize the properties of AC tire retreads containing SI, four parameters are investigated comprising two types of Butadiene Rubber (BR), two types of filler, as well as time and temperature of silanization. The objective of this research is to study the effect of

these factors on the compound and vulcanizate properties, and to derive general guidelines for mixing optimization of the in-situ modification reaction between TESPT and silica.

4.2 EXPERIMENTAL

4.2.1 MATERIALS

In Chapter 3, the following ingredients were specified: NR, BR: HC BR and HC LCB BR, CB, Zinc Oxide (ZnO), stearic acid, TDAE oil, TMQ, 6PPD, CBS, and sulfur. The silica used in this study was ULTRASIL 7005, and the silane coupling agent TESPT, both supplied by Evonik, Germany. 1,3-DiPhenylGuanidine (DPG) was obtained from Flexsys, Belgium.

The compound formulation for this study is depicted in Table 4.1. A two-level Design of Experiments (DOE) was used for optimizing the mixing process of the compounds containing SI. The two types of BR were used as specified in Chapter 3. Fillers used in this study are a blend of CB/SI (level -1) and SI only (level +1).

Table 4.1 Compound formulation.

Mixing	Ingredients	Level -1	Level +1
1 st stage	NR	70	70
	HC BR	30	–
	HC LCB BR	–	30
	CB	27.5	–
	SI	27.5	55
	TESPT	2.5	5.0
	ZnO	5	5
	Stearic acid	3	3
	6PPD	2	2
	TMQ	1	1
	TDAE	7.5	7.5
2 nd stage	Sulfur	1.5	1.5
	CBS	1.5	1.5
	DPG	0.6	1.1

Amount of TESPT and DPG were calculated according to the following equations:

$$\text{TESPT (phr)} = 0.00053 \times Q \times A \text{ and } \text{DPG (phr)} = 0.00012 \times Q \times A$$

Where Q is the amount of SI (phr) and A is the CTAB surface area of the SI (171 m²/g).

4.2.2 COMPOUND PREPARATION

Mixing was performed in an internal mixer Brabender Plasticorder 350s. The mixer was operated with a fill factor of 70%. The initial temperature and rotor speed were set at 100°C and 60 rpm. Two-stage mixing was performed as shown in Table 4.2. NR was initially masticated prior to the addition of BR to have a viscosity close to the one of BR. The masticated NR and BR (level -1 or level +1) were blended for 1 min. Then, half of the filler (level -1 or +1), TESPT and TDAE oil were added and mixed for 1 min. After 1 min, the remaining filler (level -1 or +1) and all other rubber ingredients except curatives were added and mixed for 1 min. The rotor

speed was adjusted in order to reach the targeted temperature for silanization. The temperature and time of silanization were maintained depending on the level settings as shown in Table 4.3. The compounds were discharged, sheeted off on a two-roll mill and kept overnight prior to incorporation of sulfur, CBS and DPG in the internal mixer at a set temperature of 70°C and initial rotor speed of 50 rpm. After the masterbatch was mixed for 1 min, the rotor speed was decreased to 30 rpm before curatives were added and mixed for 2 mins.

Table 4.2 Two-stage mixing process conditions.

	Mixing procedure	Time (mins)
Step 1: Internal mixer	- Mixing of masticated NR and BR	1
Initial mixer set temp. 100°C	- Addition of SI and silane (level -1) or ½ (SI and silane) (level +1), ½ TDAE	1
Initial rotor speed 60 rpm	- Addition of CB (level -1) or ½ (SI and silane) (level +1), other remaining ingredients (½ TDAE, ZnO, stearic acid, TMQ, 6PPD)	1
	- Silanization temperature and time varied depending on the level settings	Varied depending on level settings
Step 2: Internal mixer	- Masterbatch	1
Mixer set temp. 70°C	- Addition of curatives (sulfur, CBS and DPG)	2
Rotor speed 50 rpm		

4.2.3 TESTING OF COMPOUND AND VULCANIZATE PROPERTIES

Mooney Viscosity (MV), Payne Effect (PE), Modulus 300% (M300%), Tensile Strength (TS), and $\tan \delta$ at 100°C of the rubber compounds and vulcanizates were measured according to the methods described in Chapter 3. Other measurements are as follows:

Hardness shore A – The vulcanizates were measured with a Zwick 3150 Shore A hardness tester according to ASTM D2240.

Apparent crosslink density – Various organic additives and impurities in vulcanizates were removed by extracting in toluene for 2 days and in acetone for another 2 days. After the extraction process, the samples were dried for 1 day at 60°C in a vacuum oven. After drying, the vulcanizates were cut into specific shapes and a weight of 60 mg. The samples were swollen in toluene at room temperature to an equilibrium swelling state and then removed from the solvent. The toluene on the surface of the sample was quickly blotted off with tissue paper. They were immediately weighed on an analytical balance and then dried in a vacuum oven. The volume fraction (V_r) of rubber in the swollen gel was calculated by Equation 4.1, and the apparent crosslink density (X_c) was calculated by using the Flory-Rehner theory [16] according to Equation 4.2:

$$V_r = \frac{m_1/\rho_1}{(m_1/\rho_1) + (m_2/\rho_2)} \quad \text{Equation 4.1}$$

where m_1 and m_2 are the weight of polymer and weight of solvent in the swollen sample at equilibrium swelling. ρ_1 is the density of un-swollen rubber vulcanizates, and ρ_2 is the density of the solvent.

$$X_c = \frac{(\ln(1-V_r) + V_r + \chi V_r^2)}{V_2(V_r^{1/3} - V_r/2)} \quad \text{Equation 4.2}$$

where χ is the polymer-solvent interaction parameter (0.36) [17], and V_2 is the molar volume of the solvent (106.3 cm³/mol). No correction of the crosslink density was applied for the fillers contained in the compounds, as the influence of the different filler combinations on the polymer-solvent interaction parameter is not known. But as in each compound formulations, the amount of filler is not varied, the swelling data can be mutually compared to provide – what will be called – apparent crosslink density.

4.2.4 DOE METHOD

The type of BR and filler, as well as the silanization temperature and time were varied following the experimental design as shown in Table 4.3.

Table 4.3 Experimental design for optimizing mixing.

Factor	Parameters	Level -1	Level 0	Level +1
Categoric	A: BR type	HC BR		HC LCB BR
Categoric	B: Filler type	CB/SI		SI
Numeric	C: Silanization temperature (°C)	130	140	150
Numeric	D: Silanization time (min)	2	6	10

A Resolution IV design with four factors (2 numerical and 2 categorical) and two levels (-1 and +1) was applied. The number of experiments for Resolution IV design is 2^{4-1} and geometrically represented in a cube as shown in Figure 4.1. The cube is representative for two different types of BR. The three main axes refer to filler type, silanization temperature and silanization time. The center point is added for replication at each categorical factor. The total number of experiments is 16 runs.

Figure 4.1 Experimental design of Resolution IV with center points.

The effects of factors and the interaction between factors on rubber properties (Y) were evaluated by Analysis of Variance (ANOVA) and then modeled by fitting a polynomial model to the data as described in Equation 4.3 [18].

$$Y = \beta_o + \beta_A A + \beta_B B + \beta_C C + \beta_D D + \beta_{AB} AB + \beta_{AC} AC + \beta_{AD} AD + \beta_{BC} BC + \beta_{BD} BD + \beta_{CD} CD + \varepsilon \quad \text{Equation 4.3}$$

where A, B, C, and D are independent factors; β_o is the Y-intercept; $\beta_A, \beta_B, \beta_C, \beta_D$ are linear coefficients; $\beta_{AB}, \beta_{AC}, \beta_{AD}, \beta_{BC}, \beta_{BD}, \beta_{CD}$ are interaction regression coefficients; and ε is the residual response variation not explained by the model. For DOE resolution IV, there will be confounding between two-factor interactions: $X_A X_C = X_B X_D$ and $X_A X_D = X_B X_C$.

Contour plots are used to visualize more in detail the effect of factors and/or interaction on responses.

4.3 RESULTS AND DISCUSSION

The coefficients of parameters obtained from ANOVA are shown in Table 4.4: parts 1 and 2. The silanization temperature and time are the most significant factors: p-value < 0.05, written in blue, influencing MV, PE, and $\tan \delta$ at 100°C. The effect of the investigated factors on all those mentioned properties shows a high correlation with R-squared above 0.9 except for PE. The type of filler and silanization temperature are the most significant factors on M300%. The effect of factors on M300% shows a correlation with R-squared of 0.86. TS

mainly depends on the type of BR and fillers used with R-squared of 0.84. Apparent crosslink density and hardness Shore A are poorly modeled by the factors, as the R-squared values are below 0.8.

Table 4.4 Coefficients of parameters (Part 1).

Responses		Constant	Variables			
			BR type A	Filler type B	Silanization temperature C	Silanization time D
		β_o	β_A	β_B	β_C	β_D
MV (MU)		89.68	-2.18	0.61	-3.66	-5.86
	p-value	-	0.002	0.23	0.0008	<0.0001
PE (kPa)		281.06	-5.24	12.74	-23.59	-24.39
	p-value	-	0.22	0.01	0.0035	0.0029
Apparent crosslink density (mol/cm ³)		2.81	0.05	0.02	0.05	0.05
	p-value	-	0.09	0.50	0.17	0.16
tan δ at 100°C		0.11	-0.0011	-0.0026	-0.0065	-0.0004
	p-value	-	0.31	0.03	0.0005	0.002
M300% (MPa)		7.83	0.24	-1.08	0.66	0.35
	p-value	-	0.24	0.0007	0.04	0.24
TS (MPa)		24.22	0.40	-0.43	-0.25	-0.03
	p-value	-	0.007	0.0045	0.14	0.85
Hardness shore A		61.84	-0.15	0.0042	-1.37	-0.79
	p-value	-	0.77	0.99	0.09	0.29

Table 4.4 Coefficients of parameters (Part 2).

Responses		Variables				R-squared
		AB	AC or BD	AD or BC	CD	
		β_{AB}	β_{AC} or β_{BD}	β_{AD} or β_{BC}	β_{CD}	
MV (MU)		0.84	-1.94	0.41	-3.7	0.96
	p-value	0.24	0.02	0.55	0.05	
PE (kPa)		-3.3	-0.81	-11.78	-6.72	0.89
	p-value	0.565	0.886	0.0684	0.414	
Apparent crosslink density (mol/cm ³)		0.02	0.02	0.02	0.08	0.74
	p-value	0.52	0.60	0.50	0.13	
tan δ at 100°C		-0.0035	-0.0035	-0.0055	-0.0034	0.93
	p-value	0.79	0.04	0.005	0.13	
M300% (MPa)		0.13	0.06	0.31	0.08	0.86
	p-value	0.65	0.83	0.28	0.84	
TS (MPa)		0.13	-0.08	-0.20	-0.20	0.84
	p-value	0.42	0.61	0.22	0.38	
Hardness shore A		-0.25	-0.35	-0.52	0.54	0.48
	p-value	0.72	0.62	0.48	0.60	

MV of the compounds decreases as silanization temperature and time increase, see Figure 4.2. A higher degree of silanization leads to more hydrophobation of silanol groups on the SI surface by the silane, thus lower filler-filler interaction resulting in lower viscosity. HC BR reinforced either by CB/SI or SI shows no significant difference in MV. The MV of HC BR compounds is independent of the silanization temperature at short silanization times below 6 mins. It can be seen from the mixing fingerprints as shown in Figure 4.3, that mixing HC BR-reinforced SI or CB/SI at 130°C and 150°C for 2 mins results in a similar final torque, thus no difference in MV. Increasing silanization time to 10 mins at 150°C requires a high energy input, thus more breakdown of the polymers, and results in reduction of the final torque, hence reduction in MV: see Figure 4.4.

Figure 4.2 MV of HC BR compounds reinforced with CB/SI (left) and SI (right) as function of silanization temperature and time.

Figure 4.3 Mixing fingerprints of CB/SI and SI reinforced HC BR compounds at 130°C (left) and 150°C (right) for 2 mins silanization time.

Figure 4.4 Mixing fingerprints of CB/SI and SI reinforced HC BR compound at 150°C for 10 mins silanization time.

In contrast, for HC LCB BR, both silanization time and temperature significantly influence the MV: Figure 4.5. Branching of HC LCB BR improves the processability of this polymer relative to HC BR. Besides, silanization of the CB/SI improves significantly as seen in the PE data: Figure 4.9 left. The better the silanization, the better the micro dispersion of the filler particles and the lower the final torque of CB/SI compounds obtained: Figure 4.6 - 4.7.

Figure 4.5 MV of HC LCB BR compounds reinforced with CB/SI (left) and SI (right) as function of silanization temperature and time.

Figure 4.6 Mixing fingerprints of CB/SI and SI reinforced HC LCB BR compounds at 130°C (left) and 150°C (right) for 2 mins.

Figure 4.7 Mixing fingerprints of CB/SI and SI reinforced HC LCB BR compounds at 150°C for 10 mins silanization time.

Figures 4.8 and 4.9 show the influence of temperature and silanization time on the PE: with increasing temperature and time, a lower PE is observed as the degree of silanization is increased. At higher silanization temperatures, the chain mobility increases, thus the polymers can easily penetrate into the cluster structure. The large filler clusters are successively broken to their ultimate size by shearing forces. Sufficient time of silanization is needed to ensure the hydrophobation of the SI, for the TESPT coupling agent to react with the silanol groups on the SI surface resulting in less filler-filler interaction. The interface between the matrix and the filler also increases and the filler particles are distributed homogenously in the rubber matrix. In line with the results of MV, HC BR reinforced with CB/SI and SI shows a lower degree of silanization, thus higher PE than HC LCB BR. The use of a hybrid CB/SI imparts lower filler-filler interaction compared to SI-filled in HC LCB BR: Figure 4.9.

Sattayanurak observed that the use of a low amount of CB up to 50 wt% relative to the total filler in NR-filled compounds increases the PE slightly compared to that of the reference pure SI-filled compound [19]. It was stated that CB N134 favors filler network formation and thus increases the PE due to the small particle size and high specific surface area with narrow filler particle-particle distances. The type of CB used in the present research is CB N234, which has a larger particle size and so a lower surface area than CB N134. Thus, CB N234 features a lower degree of filler network formation than CB N134. Combining CB N234 with SI decreases the filler network formation, hence lower PE compared to the use of SI alone.

Figure 4.8 PE of HC BR compounds reinforced with CB/SI (left) and SI (right) as function of silanization temperature and time.

Figure 4.9 PE of HC LCB BR compounds reinforced with CB/SI (left) and SI (right) as function of silanization temperature and time.

The apparent crosslink density indicates not only sulfur-crosslinks but also the contribution of filler-polymer coupling via the silane. HC BR filled-CB/SI and SI do not show a significant difference in the degree of silanization. This results in similar filler-rubber interaction and hence similar crosslink density: Figure 4.10. SI-filled HC LCB BR imparts higher crosslink density compared to CB/SI-filled HC LCB BR. This might be due to the higher covalent filler-rubber coupling in SI-filled rubber than in CB/SI filled material. A high covalent filler-rubber coupling contributes to a high crosslink density: Figure 4.11. The higher silanization degree results in a higher crosslink density of HC LCB BR than HC BR.

Figure 4.10 Apparent crosslink density of HC BR compounds reinforced with CB/SI (left) and SI (right) as function of silanization temperature and time.

Figure 4.11 Apparent crosslink density of HC LCB BR compounds reinforced with CB/SI (left) and SI (right) as function of silanization temperature and time.

Tan δ at 100°C as a function of silanization temperature and time is shown in Figures 4.12 and 4.13. Tan δ above 70°C can be used as an indication of heat build-up (HBU), for which a lower value indicates lower heat generation in the tire [20]. Tan δ is influenced by many factors such as crosslink density, filler-filler interaction, filler-polymer interaction, and type of polymer. HC BR shows that tan δ is not influenced much by the silanization temperature at short silanization times: Figure 4.12. This is in line with the results of MV: Figure 4.2, and apparent crosslink density: Figure 4.10, which show no significant difference in those properties in HC BR reinforced either with CB/SI or SI. HC LCB BR reinforced with CB/SI or SI show a significant difference in tan δ as silanization temperature and time increase: Figure 4.13. The low final torque at the end of mixing, thus low MV: Figure 4.5 and 4.7, corresponds to a high degree of silanization. PE substantially decreases due to reduced filler-filler interaction: Figure 4.9, and improved filler-rubber interaction, which contributes to high crosslink density: Figure 4.11. The branching in HC LCB BR also gives additional trapped entanglements. All those improved properties lead to a lower tan δ .

Comparing the two types of fillers, the SI-filler imparts lower tan δ than the CB/SI-combination. In pure SI-filled rubber, the extra network formations derived from silica-silane-rubber coupling, which is stronger than the network formation in CB/SI-filled vulcanizates. In CB/SI-filled vulcanizates the network stems from the combination of covalent silica-rubber coupling via the silane and the physical CB-rubber interactions. These physical CB-rubber interactions of polymer chains adsorbed onto the surface of CB particles consist of an immobilized polymer layer and the unrestricted bulk layer [21]. Filler-rubber interactions follow

the order: chemically bound layer < immobilized layer < unrestricted bulk layer. Therefore, the SI-filled compounds impart lower $\tan \delta$ /HBU than CB/SI-filled vulcanizates.

Figure 4.12 $\tan \delta$ of HC BR compounds reinforced with CB/SI (left) and SI (right) as function of silanization temperature and time.

Figure 4.13 $\tan \delta$ of HC LCB BR compounds reinforced with CB/SI (left) and SI (right) as function of silanization temperature and time.

Figures 4.14 and 4.15 show the influence of silanization temperature and time on the M300% of the rubber vulcanizates. M300% of CB/SI- and SI-filled HC BR vulcanizates are relatively independent of silanization time: Figure 4.14. The high molecular weight of HC BR decreases its processability. MV does not decrease at short silanization times even when a high silanization temperature is employed: Figure 4.2. Increasing silanization time and temperature decrease MV but the values are still higher compared to HC LCB BR. The apparent crosslink density of HC BR is not significantly affected by silanization time and temperature: Figure 4.10. The use of HC LCB BR imparts better processability. As the silanization temperature and time increase, the degree of silanization increases. The low PE: Figure 4.9, and high apparent crosslink density values: Figure 4.11, observed as the silanization improves, lead to higher M300%: Figure 4.15.

Figure 4.14 M300% of HC BR compounds reinforced with CB/SI (left) and SI (right) as function of silanization temperature and time.

Figure 4.15 M300% of HC LCB BR compounds reinforced with CB/SI (left) and SI (right) as function of silanization temperature and time.

The effect of silanization temperature and time on TS is shown in Figures 4.16 and 4.17. Within the range of silanization temperatures and times, the TS of the cured rubbers is relatively constant. HC LCB BR compounds show a slightly higher TS than HC BR-based compounds. The apparent crosslink density of HC LCB BR is higher than that of HC BR due to the high filler-rubber interactions and additional entanglements of the long-chain branched polymer which contribute to high crosslink density: Figure 4.11. CB/SI-filled vulcanizates show only slightly higher TS values compared to SI-filled vulcanizates due to slightly higher reinforcement: Figure 4.17.

Figure 4.16 TS of HC BR compounds reinforced with CB/SI (left) and SI (right) as function of silanization temperature and time.

Figure 4.17 TS of HC LCB BR compounds reinforced with CB/SI (left) and SI (right) as function of silanization temperature and time.

Figures 4.18 and 4.19 show the hardness of CB/SI- and SI-filled HC BR and HC LCB BR vulcanizates. The hardness of HC BR vulcanizates is clearly less dependent on silanization time and temperature compared to the HC LCB BR ones. It correlates well with the viscosity of the compounds. Due to the high linearity/high viscous polymer, HC BR is challenging to process, and a lower degree of silanization, hence higher PE, was achieved compared to HC LCB BR. Both characteristics make the MV of HC BR compounds less sensitive to silanization temperature and time: Figure 4.2. In HC LCB BR, branching improves processability. The PE decreases significantly as silanization temperature and time increase. A low MV of compounds was observed as the silanization degree increases, which leads to the low hardness of the vulcanizates. Overall the hardness is a property rather insensitive to intricate phenomena in the compound formulation, remotely related to the Young's modulus. Most conspicuous in the small difference in the values is the influence of the type of BR.

Figure 4.18 Hardness of HC BR compounds reinforced with CB/SI (left) and SI (right) as function of silanization temperature and time.

Figure 4.19 Hardness of HC LCB BR compounds reinforced with CB/SI (left) and SI (right) as function of silanization temperature and time.

4.4 VALIDATION RUNS

Validation runs were performed to assess the accuracy of the predicted properties from the model compared to the actual ones from the experimental run. The overlay plots are depicted in Figure 4.20. The silanization temperature and time can be set by following the yellow area of the overlay plot to achieve the target values. Both CB/SI- and SI-filled NR/HC LCB BR can be set at silanization temperatures of 140 – 155°C to achieve the target properties. In the case of silanization time, the SI-filled compounds need more time for mixing compared to CB/SI compounds. For the confirmation runs, the silanization was set at 150°C and 7 mins for CB/SI and 150°C and 9 mins for SI-filled to obtain a better balance between low Payne effect and low $\tan \delta$, while maintaining TS and M300%. Table 4.5 shows the target values and the actual values of the desired properties. The output values from the confirmation run are close to the target values except for hardness. The target hardness is in the range of 65 – 67. Therefore, adjustment of the current compound formulation of a hybrid CB/SI and SI should be made for the follow-up research in the next chapter to achieve the target hardness. Adjustment of the compound formulation can be made by increasing the filler, decreasing the oil content or adjusting the curatives.

Figure 4.20 Overlay plot for CB/SI (left) and SI-filled (right) NR/HC LCB BR compounds.

Table 4.5 Target values and actual values of desired properties from the confirmation runs.

Properties	Target value	A: HC LCB BR B: CB/SI 150-7	A: HC LCB BR B: SI 150-9
MV (MU)	75 – 90	74	75
PE (kPa)	max 280	188	231
TS (MPa)	min 22 [22]	24	23
M300% (MPa)	8 – 16 [22]	9	8
tan δ at 100°C	0.07 – 0.17 [23]	0.094	0.08
Hardness Shore A	65 – 67	61	59

4.5 CONCLUSIONS

The properties of AC tire treads containing SI alone or in combination with CB (CB/SI) show a strong dependence on the silanization temperature and time. High silanization temperatures and times enhance the silanization reaction, with the consequence of low filler-filler interaction and high silica-silane-rubber coupling. HC LCB BR instead of HC BR improves the processability as evidenced by lower MV of the compounds. Furthermore, it shows lower PE, tan δ at 100°C, and slightly higher mechanical properties than the HC BR counterpart. M300% and TS of CB/SI vulcanizates are higher than the ones of the SI vulcanizates. However, the tan δ /heat-build-up of CB/SI vulcanizates are still higher compared to the ones for SI vulcanizates, resulting from a combination of chemical and physical filler-rubber interactions. A slight further improvement to achieve the target hardness of 65 – 67 is needed. Both CB/SI and SI formulations can be used instead of CB to decrease heat build-up of AC tire retreads, while still maintaining acceptable mechanical properties.

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THE EFFECT OF ZINC OXIDE AND DIPHENYL GUANIDINE ADDITION SEQUENCE ON PROCESSING, MECHANICAL AND DYNAMIC PROPERTIES

ABSTRACT

The properties needed for aircraft tire treads/retreads are significantly different from the ones required for passenger car or truck tires, for which improvements mainly focus on a better balance of rolling, wet skid and wear resistance. Aircraft tires experience severe operation conditions during service: the temperature can reach above the critical temperature of polymers, thus accelerating tread wear. To reduce the peak temperatures of the tire tread during departure and landing, the material of the tread should have a low hysteresis. Furthermore, the tires need to be able to withstand high loads and impact during landing. Therefore, they also require outstanding strength properties.

This study focuses on the influence of the processing sequence of Zinc Oxide (ZnO) and DiPhenyl Guanidine (DPG) during tread compound mixing on the properties mentioned above. The compound is based on a blend of Natural Rubber and Butadiene Rubber (NR/BR) reinforced with a hybrid Carbon Black/Silica (CB/SI) filler system. It is revealed that the ZnO addition sequence has a strong influence on the properties of the compounds and vulcanizates, while the DPG addition sequence influences only cure properties and filler-rubber interaction. The incorporation of ZnO in the first stage of mixing (Z1D1 and Z1D2) results in low Mooney Viscosity (MV), better SI dispersion, high reversion resistance and mechanical properties, but slow cure rate. When ZnO is omitted in the first stage and added in the last stage of mixing (Z2D1 and Z2D2), it results in high filler-polymer interaction, which is beneficial for high stress-strain properties. However, the latter compounds were prone to reversion under prolonged vulcanization or aging leading to a significant reduction of the Modulus at 300% elongation (M300%) and apparent crosslink density. The addition of DPG in the last stage of mixing (Z1D2 and Z2D2) decreases scorch time, optimum cure time and increases filler-rubber interaction. The addition of ZnO in the first stage of the mixing process and DPG in the last stage of mixing (Z1D2) results in a reduction of the hysteresis as measured by the $\tan \delta$ of the vulcanizate at 100°C and 200°C, which corresponds to the temperature on the surface of an aircraft tire tread during service. Considering all properties above, the Z1D2 addition sequence applied to a hybrid CB/SI-filled NR/BR blend is the most promising one for aircraft tire retreads.

5.1 INTRODUCTION

The hysteresis of rubber, which results in energy dissipation and is thus responsible for Heat Build-Up (HBU), is an essential property of tires, especially Aircraft (AC) tires. A prominent example is the landing performance of an AC tire: During landing, the tire touches the ground with zero rotational speed under substantial load, thus creating massive friction between the tires and the ground. The combination of high speed and extreme load results in a severe temperature increase within the tires. The temperature in the contact patch of an AC tire can reach up to 300°C [1]. This temperature is high enough to degrade the tire material, which consists to a large portion of Natural Rubber (NR). High hysteresis can also have a negative impact on ultimate properties such as tread wear and failure. Another serious consequence is related to the chemical effects of temperature build-up on the properties of the final product: oxidation of polymer chains causing chain scission and a reduction of crosslink density resulting in softening in NR, or additional crosslink formation leading to hardening as seen in Butadiene Rubber (BR) and Styrene-Butadiene Rubber (SBR).

Several strategies are followed to minimize HBU and deterioration of properties of rubber articles which are subject to cyclic deformation. Concerning rubber mixing and compounding, the compound performance is not only determined by the right choice of the formulation components, but also by correct processing such as optimum parameter settings and addition sequence.

The polymer should be chosen to give low hysteresis at the temperature and frequency of operation [2]. AC tire treads are generally made of blends of NR and BR. The use of NR provides better mechanical strength such as superior tensile and tear properties, lower operating temperatures, reduced rolling resistance, excellent component-to-component adhesion, and good tire retreadability. A small portion of BR is added to improve the abrasion resistance.

Concerning the filler system, the attempts to minimize the hysteresis are:

- decreasing the filler loading;
- decreasing the surface area of fillers by using large particle size fillers; or
- in the case of using small particle size fillers, thus high surface area: increasing the dispersion of fillers by prolonged mixing or more efficient mixing techniques [3].

Carbon Black (CB), in particular High Abrasion Furnace (HAF), Intermediate Super Abrasion Furnace (ISAF) and Super Abrasion Furnace (SAF) types are commonly used in AC tire tread formulations to enhance abrasion resistance. Silica (SI) in combination with a coupling agent such as a silane has become a strong alternative to CB fillers in tires, especially in Passenger Car Tires (PCT). Several studies revealed that SI-silane provides a better balance in tire properties, in particular rolling resistance and wet grip, compared to CB [4, 5]. However, in AC tire treads, SI-silane filler systems are used in combination with CB [6]. Generally, a CB-

reinforced rubber has a higher modulus than a SI-reinforced one, while SI-silane provides a unique combination of tear strength, abrasion resistance, aging resistance and adhesion properties [7].

Up to now, SI cannot replace CB entirely in large tires such as truck and Off-The-Road (OTR) tires, for which reinforcement and abrasion resistance are essential properties. This is due to the fact that SI is less compatible with the polymers used for the treads of these tires, especially when NR is the primary polymer in the formulation. The non-rubber components of NR, in particular proteins, are reported to be the origin of the outstanding properties of NR. However, it has been demonstrated that the proteins contained in NR compete with the coupling agents for reaction with the SI during mixing, so disturb its reinforcement effect and consequently affect the final properties of the vulcanizate [8]. Besides, SI is more difficult to disperse and can reduce the effectiveness of some components of the vulcanization system, resulting in reduced reinforcement and poorer performance compared to the CB counterpart [9]. The use of SI with a high surface area can improve treadwear properties. However, a higher surface area means a higher number of silanol groups on the SI surface, which leads to an increase of filler-filler interaction. This increase as reflected in a higher so-called Payne Effect (PE), leads to a higher hysteresis loss. Additionally, it results in a higher degree of adsorption of accelerators [10], influencing the curing efficiency.

The effect of ZnO and DPG in SI-filled compounds was the subject of investigations of several researchers [11-15]. ZnO can interact with the SI surface, resulting in a reduction of the reaction efficiency between SI and silane: the silanol groups on the SI surface are acidic of nature, therefore they can react with an alkali such as ZnO [11]. Studies showed that a higher PE value was observed in SI-filled SSBR or SSBR/BR compounds when ZnO is introduced in the first mixing stage [11, 14]. DPG is known as a secondary accelerator, which is generally used in combination with sulfenamide types as primary accelerators such as N-Cyclohexyl-2-Benzothiazole Sulfenamide (CBS) in SI-filled compounds. DPG is required to accelerate the silanization reaction, when this type of amine is added to a SI-silane compound [16]. Considering the points discussed above, the present study aims at elucidating the influence of the addition sequence of ZnO and DPG in CB/SI-filled NR/BR blends on the compound and vulcanizate properties of AC tire retreads.

5.2 EXPERIMENTAL

5.2.1 MATERIALS

The ingredients used in the present study were described in Chapter 4. The compound formulations are shown in Table 5.1. The filler system used in this research was a hybrid of CB and SI. The compound formulation is the same as described in Chapter 4, with the difference that in this study only HC LCB BR was used, and that the total filler amount was increased from 55 to 70 parts per hundred rubber (phr) in order to obtain a comparable hardness to the one of the CB-filled vulcanizates. The amount of TESPT and DPG was calculated based on the CTAB specific surface area of the SI type as suggested by Guy et al. [17]. The addition sequence of ZnO (Z) and DPG (D) was divided into a first stage (1) and second stage (2) of mixing.

Table 5.1 Compound formulations.

Mixing	Ingredients	Z1D1	Z1D2	Z2D1	Z2D2
1 st stage	NR	70			
	HC LCB BR	30			
	CB	35			
	SI	35			
	TESPT	3.2			
	ZnO	5	5	0	0
	Stearic acid	3			
	6PPD	2			
	TMQ	1			
	TDAE oil	7.5			
	DPG	0.7	0	0.7	0
2 nd stage	Sulfur	1.5			
	CBS	1.5			
	DPG	0	0.7	0	0.7
	ZnO	0	0	5	5

Amount of TESPT and DPG were calculated according to the following equations:

$$\text{TESPT (phr)} = 0.00053 \times Q \times A \text{ and } \text{DPG (phr)} = 0.00012 \times Q \times A$$

where Q is the amount of silica (phr) and A is the CTAB surface area of the silica (171 m²/g)

5.2.2 COMPOUND PREPARATION

Two-stage mixing was performed as shown in Table 5.2. NR was initially masticated to have a Mooney Viscosity (MV) close to the viscosity of BR. The masticated NR and BR were mixed for 1 minute (min). Then SI, silane, half of the Treated Distillate Aromatic Extract (TDAE) oil with or without DPG depending on the settings were added and mixed for 1 min. After that, CB and other remaining ingredients with or without ZnO were added, and the rotor speed was adjusted in order to reach the targeted temperature for silanization within 1 min. The temperature was maintained at 150°C for about 7 mins to complete the silanization

reaction. The ram was opened for about 1 min after 3 mins of silanization to release the ethanol produced during the silanization reaction. The compounds were discharged, sheeted out on a two-roll mill and kept overnight prior to incorporation of sulfur, CBS with or without ZnO and DPG in an internal mixer at a set temperature of 70°C and initial rotor speed of 50 revolutions per minute (rpm). After the masterbatch was mixed for 1 min, the rotor speed was decreased to 30 rpm before curatives were added and mixed for 2 mins.

Table 5.2 Two-step mixing procedure.

	Mixing procedure	Time (mins)
Stage 1: Internal mixer Initial mixer set temp. 100°C Initial rotor speed 60 rpm	- Mixing of masticated NR and BR	1
	- Addition of silica, silane, 1/2 TDAE oil, with/without DPG	1
	- Addition of CB and other remaining ingredients with/without ZnO and adjustment of rotor speed till reaching the silanization temperature of 150°C	1
	- Silanization reaction (ram sweep after 3 min silanization)	7
Stage 2: Internal mixer Mixer set temp. 70°C Rotor speed 50 rpm	- Masterbatch	1
	- Addition of curatives (sulfur and CBS) with/without DPG, ZnO	2

5.2.3 TESTING OF COMPOUNDS AND VULCANIZATES

Payne Effect (PE) and stress-strain properties of the compounds were measured according to the methods described in Chapter 3. While apparent crosslink density was measured using the method described in Chapter 4. Additionally, the following measurement methods were used:

Mooney Viscosity (MV) – The compounds were tested for their MV by using a Mooney Viscometer 2000VS (Alpha Technologies, USA) at 125°C with a large rotor at a shear rate of 2 rpm for about 4 mins with 1 min of pre-heating. MV was measured at 125°C instead of 100°C to decrease the initial MV of compounds which cannot be measured due to the limitation of the machine. The initial MV decreases as the temperature of testing increases [18]. In terms of the final MV, the effect of temperature on the MV becomes small at higher shear rates (above 1 rpm) as shown in Figure 5.1. Therefore, it can be concluded that the differences in final MV at 100°C and 125°C at 2 rpm of the compounds in this study will not be very large.

Figure 5.1 The effect of shear rate and temperature on the final MV [19].

Cure behavior – Scorch time (t_{s2}) and optimum cure time (t_{90}) were tested using a Rubber Process Analyzer (RPA 2000) at 150°C, with a frequency of 1.67 Hz and 6.98% strain. The Cure Rate Index (CRI) was calculated according to Equation 5.1 and reversion (%) was calculated according to Equation 5.2:

$$CRI = \frac{100}{t_{90} - t_{s2}} \quad \text{Equation 5.1}$$

$$Reversion (\%) = \left(\frac{S_{max} - S_{final}}{S_{max}} \right) \times 100 \quad \text{Equation 5.2}$$

where S_{max} = Rheometer maximum torque;

S_{final} = Rheometer cure torque at final (measurement) time.

Bound rubber content – The uncured rubber compound (without curatives), approximately 0.2 grams, was cut and put into a metal cage and immersed in toluene at room temperature. The toluene was renewed every day. After three days, the sample was removed from the toluene and dried at 100°C for 24 hours. The bound rubber was calculated according to Equation 5.3:

$$Bound\ rubber\ content = \frac{m_r - m_f}{m_p} \times 100\% \quad \text{Equation 5.3}$$

where m_r is the dry weight of samples after toluene treatment under normal conditions, m_f is the weight of the filler in the sample and m_p is the weight of the rubber in the specimen.

Hysteresis – The hysteresis was measured for both, uncured compounds and vulcanizates. The hysteresis of uncured compounds was measured at 100°C in a frequency sweep of 0.5 – 33.33 Hertz (Hz) and a fixed strain of 10%. The hysteresis measurements for the vulcanizates were performed after curing the compounds first to their ($t_{90}+2$) mins. at 150°C in the RPA.

After curing in situ, the temperature was decreased or increased depending on the range of interest (100°C or 200°C). The hysteresis was then measured using the same parameters as used for the uncured compounds.

Scanning Electron Microscopy – Energy Dispersive X-ray spectroscopy (SEM-EDX) – Vulcanized samples were extracted by acetone for 24 hours to remove non-rubber ingredients. The samples were then cut into small pieces. The cross-sectional surface was covered with a thin layer of gold to avoid electrostatic charging during the examination. SEM-EDX images were taken by a JEOL-JSM-T20. The particle size distribution of the SEM-EDX images was calculated using ImageJ software. The detailed procedure is explained elsewhere [20].

5.3 RESULTS AND DISCUSSION

Figure 5.2 shows the MV of the CB/SI-filled NR/BR compounds with different addition sequences. Compounds containing ZnO from the masterbatch stage (Z1D1 and Z1D2) show a lower MV compared to compounds with ZnO added in the last stage of mixing (Z2D1 and Z2D2). Zinc stearate, which forms in a reaction of ZnO and stearic acid, can influence the mastication process when a high portion of NR is used. Zinc stearate can act as a peptizer, which is effective as a viscosity reducer in NR, especially when CB is also present in the rubber compound [21]. The compounds are filled with CB and SI, and zinc stearate can interact with the silanol groups of the SI. This reaction competes with the function of ZnO as an activator for the accelerators. The mechanism here involves zinc stearate, which can react with silanol groups as shown in Figure 5.3 [22] and cover the SI surface due to its long hydrocarbon side chains, this way reducing the SI network formation and resulting in a lower viscosity. Figure 5.4 depicts the possible interaction mechanism of zinc stearate during silanization reactions [23].

Figure 5.2 MV of rubber compounds with different addition sequences.

Figure 5.3 Reaction of zinc stearate with SI [22].

Figure 5.4 Possible mechanism of shielding the SI surface by zinc stearate and blocking it for silane [23].

Table 5.3 shows the curing characteristics of the various compounds with different ZnO and DPG addition sequences. ZnO is an inorganic compound which functions as an activator to speed up the vulcanization process. However, ZnO is difficult to disperse in the rubber matrix, therefore stearic acid is added to solubilize the zinc and set zinc ions free to form complexes with accelerators [24]. Addition of ZnO in the first stage of mixing (Z1D1 and Z1D2) allows better solubilization of the oxide by stearic acid to form zinc stearate. Zinc stearate provides accelerator activation through the formation of zinc-accelerator complexes. As explained earlier, zinc stearate also interacts with SI silanols, and this reaction competes with the role of zinc stearate as activator and leads to a reduction of the cure rate [25].

Table 5.3 Curing characteristics of compounds.

Characteristics	Z1D1	Z1D2	Z2D1	Z2D2
Scorch time, ts_2 (min)	5.5	4.3	3.2	2.6
Cure time, t_{90} (min)	14.0	11.4	8.6	7.7
Cure rate index, CRI (min^{-1})	12.2	14.1	18.5	19.6
$S_{\min}$ (dN.m)	3.2	3.3	3.6	3.8
$S_{\max}$ (dN.m)	16.9	17.5	17.9	18.6
Cure torque difference, $S_{\max} - S_{\min}$ (dN.m)	13.7	14.2	14.3	14.6
Reversion (%)	4.4	4.6	12.1	12.5

The DPG addition sequence slightly influences the curing characteristics, in which addition of DPG in the first stage of mixing (Z1D1 and Z2D1) decreases the cure rate. Many studies revealed that besides DPG acting as a secondary accelerator of the vulcanization reaction [12, 26], it can reduce the polarity of SI by being adsorbed onto the SI surface [27].

DPG is also capable of accelerating the silanization reaction [26]. A slower cure rate was observed when DPG was added in an early mixing stage of a SI-filled compound. Lim et al. [28] reported that the slower vulcanization rate is induced by the adsorption of DPG onto the SI surface.

Figure 5.5 shows that less reversion is occurring when ZnO is added in the first stage of mixing (Z1D1 and Z1D2). The presence of ZnO in the first mixing stage leads to a considerable decrease of the cure rate, which relates to the formation of a zinc-accelerator-sulfur coordination complex, resulting in scorch time (ts_2) delay and formation of a more stable crosslink structure. The complex may also have a thermo-stabilizing effect that can prevent the destruction processes in the elastomer main chain or the crosslinked network already occurring at the cure temperature [29].

Figure 5.5 Curing curves of rubber compounds with different addition sequences.

Figure 5.6 shows the PE with different ZnO and DPG addition sequences for the yet unvulcanized compounds. The storage modulus G' depends on the addition sequence of ZnO in these hybrid CB/SI-filled rubber compounds. The G' of compounds, in which ZnO is added at the earlier stage of mixing (Z1D1 and Z1D2), is much lower in comparison to compounds with ZnO added in the final stage of mixing (Z2D1 and Z2D2) for the same reason as described above: ZnO can react with stearic acid to produce soluble zinc stearate, which interacts with SI silanol moieties. Zinc stearate can have a positive effect on lowering the filler-filler interaction due to its long aliphatic chains (17 CH_2 - groups), thus improving SI dispersion and resulting in lower viscosity [25].

Figure 5.6 Storage modulus versus strain (left) and PE (right) of rubber compounds.

The PE, the difference of G' at low and at high strain ($\Delta G'$), indicates how well the filler disperses in the rubber matrix on microscale. A high PE indicates strong filler-filler interaction, and consequently a low degree of dispersion. Compounds with ZnO added in the last stage of mixing (Z2D1 and Z2D2) show high G' values at low strain, which indicates high filler-filler interaction, and also slightly higher G' at high strain. G' at high strain can be correlated with filler-polymer interaction. Figure 5.7 shows a typical example of the complex shear modulus of filled rubber versus dynamic shear deformation. There are four contribution parameters to the complex shear modulus: the hydrodynamic effect (filler type and loading), the polymer network (rubber type, vulcanization system), the polymer-filler interaction (filler and rubber type) and the filler-filler interaction. Only the filler-filler interaction is strain dependent. However, the trend of the PE in this study is different from results found by other researchers. Reuvekamp et al. [11] found that the presence of ZnO increases the risk of pre-scorch in silica-filled SSBR/BR compounds due to its catalytic effect on sulfur release from the coupling agent bis-(TriEthoxySilylPropyl)Tetrasulfide (TESPT). An increase of $G'(100\%)$ for the compound with ZnO added in an early mixing stage was observed, when the dump temperature exceeded 150°C. Jin [23] also reported the negative effect of ZnO in SI-filled SSBR/BR compounds, in which an increment of the PE value was observed with increasing ZnO concentration in the masterbatch (MB) stage until the ZnO concentration reached 1.5 phr.

Figure 5.7 Contributions to the shear modulus for a typical rubber compound [3].

The effect of DPG addition sequence on the PE is small in the CB/SI-filled compounds. This might be caused by a sufficient silanization time of 7 mins, during which a complete silanization reaction has been reached. Therefore, the effect of DPG as silanization booster cannot be seen anymore.

Next to the DPG addition sequence, silanization was performed for 3 resp. 7 mins to prove that DPG is acting as a silanization booster. Figure 5.8(a) shows that at short silanization times, thus when the silanization reaction is not complete, the addition of DPG together with SI in the first stage of mixing (Z1D1) can indeed promote the silanization reaction resulting in lower filler-filler interaction compared to the addition of DPG in the final step (Z1D2). However, when the silanization was complete, both compounds show the same PE regardless of the DPG addition, as shown in Figure 5.8(b).

Figure 5.8 Payne effect of compounds with different silanization times: 3 mins (a); 7 mins (b).

Bound rubber measurements were performed as further indication of polymer-filler interaction next to G' at high strain. The addition of ZnO in the final stage of mixing increases filler-polymer interaction, as depicted in Figure 5.9(a). On the one hand, when ZnO is added to the masterbatch, zinc stearate can lower the filler-filler interaction due to its long hydrocarbon chains. On the other hand, zinc stearate can block the access of silane molecules, thus interfering with the silane bonding to the silica surface during silanization and thus cause a lower amount of bound rubber. By adding ZnO in the final stage, the silanization efficiency increases. The interaction between alkoxy groups of TESPT and silanol groups on the silica surface during the mixing process reduces hydrophilicity of the silica surface and thus improves rubber-filler interaction [30]. Besides, the addition of DPG in the first mixing stage decreases bound rubber: the reaction sites on the SI surface are shielded by DPG, and in this way DPG blocks the access for the silane, the same as in the case of zinc stearate. This finding is contrary to the outcome of several other studies that amines, including DPG, are believed to promote the silanization when added in the masterbatch resulting in a decrease in filler-filler interaction and an increase in bound rubber content [15, 31]. The effect of DPG as a silanization booster might not apply to the full for all rubber formulations and mixing conditions. We prove in the present study that adding DPG in the first stage of mixing of a NR/BR blend at sufficient silanization time results in lower filler-rubber interaction than adding DPG in the last stage of mixing.

To show the contrast between the unvulcanized and the vulcanized states of the various compounds, Figure 5.9 compares the bound rubber before vulcanization and the apparent crosslink density after. Figure 5.9(b) shows the apparent crosslink density of the vulcanizates cured at 150°C and subsequently aged at 100°C for 10 mins, and the same

vulcanizates aged at 200°C for 10 mins in order to mimic the surface temperature variation of AC tire treads during service. There is a tentative relation between the apparent crosslink density after vulcanization and the bound rubber before in Figure 5.9(a), though the effect is much larger in the unvulcanized state. For the first condition, the vulcanizates show only a minimal increase in apparent crosslink densities. The 10 mins. aging at 100°C will not expected to cause a noticeable change in apparent crosslink density, as the compounds were vulcanized at 150°C. However, for the second condition: aging for 10 mins. at 200°C, the Z1D1 and Z1D2 rubbers show a higher apparent crosslink density compared to the Z2D1 and Z2D2 ones. The addition of ZnO in the first stage of mixing therefore improves the thermal stability of the network [29] as explained in the vulcanization part.

Figure 5.9 Bound rubber content of compounds (a); apparent crosslink density of vulcanizates (b) with different addition sequences (Tc: curing temperature).

Figure 5.10 shows the tensile strength and M300% of the vulcanizates investigated. The ZnO and DPG addition sequence has almost no effect on tensile strength. However, the ZnO and DPG addition sequence does affect M300%: Compounds containing a high bound rubber content before vulcanization show slightly higher M300% values compared to compounds with lower contents. Bound rubber is an immobilized polymer layer derived from the polymer chains adsorbed onto the filler surface, which cannot be removed easily. Other contributions of the polymer to reinforcement are entanglements and sulfur crosslinks formed during vulcanization. The addition of ZnO and DPG in the last stage of mixing (Z2D2) results in the highest M300% compared to the other addition sequences, in accordance also with the slight increase in apparent crosslink density for 100°C aging as seen in Figure 5.9(b).

Figure 5.10 Stress-strain properties of vulcanizates with different addition sequences.

Figure 5.11 shows the storage G' and loss moduli G'' as well as the phase angle $\tan \delta$ of the still unvulcanized rubber compounds in a frequency sweep from 0.1 till 33.33 Hz and at 10% fixed strain. As frequency increases, G' and G'' of the compounds increase. This increase in moduli with frequency is the common behavior, where the materials move away from the rubber plateau into the transition region towards the glassy state. Addition of ZnO and DPG in the last stage of mixing (Z2D2) results in considerably higher G' values compared to other addition sequences due to higher filler-filler interactions: Figure 5.6, and filler-rubber interactions: Figure 5.9(a). In the uncured rubbers, crosslink density is not a factor yet. As $\tan \delta$, taken as an indication for hysteresis, is the ratio of G'' to G' , the final value depends on both moduli. Low frequencies allow sufficient time for molecular segmental rearrangements of the polymers, while at high frequencies only a short period for the rubber molecules to rearrange is available. High filler-rubber interaction decreases the mobility of the chains. The Z2D1 and Z2D2 compounds contain a high bound rubber content, reducing the chain mobility and thus molecular friction, leading to less hysteresis and subsequent heat generation. Compounds with less bound rubber (Z1D1 and Z1D2) show a steeper increase in $\tan \delta$ towards low frequencies than high bound rubber compounds (Z2D1 and Z2D2), which in the ultimate case of all rubber immobilized would have resulted in a horizontal curve.

Figure 5.11 G' , G'' and $\tan \delta$ in a frequency sweep at 10% fixed strain for the uncured rubbers measured at 100°C.

Figure 5.12 shows the viscoelastic (G' , G'' , $\tan \delta$) properties for the vulcanizates cured at 150°C and measured at 100°C (left) and 200°C (right). (Note: This is different from the 10 mins. aging at 100°C and 200°C employed for the crosslink density measurements). The curvature of the $\tan \delta$ curves is opposite of what was seen in the previous Figure 5.11, because now the crosslink density plays the major role with an effect of the filler-filler interaction left as well, but the polymer-filler interaction merged into the crosslink network. Z2D2 shows a slightly higher $\tan \delta$ compared to the other addition sequences. This is due to the fact that Z2D2 shows the highest crosslink density: Figure 5.9(b), and also high filler-filler interaction: Figure 5.6. The other addition sequences show similar $\tan \delta$ values at 100°C due to balanced high crosslink density: Figure 5.9(b) and low filler-filler interaction: Figure 5.6. When the

hysteresis is measured at 200°C, which implicitly corresponds to a little after-cure, the $\tan \delta$ of Z1D2 improves more than for the other addition sequences. Similarly, Z1D2 showed the highest crosslink density when cured at 150°C and aged at 200°C: Figure 5.9(b). A high crosslink density decreases the dangling chain ends and entrapped entanglements. The presence of three-dimensional networks prevents the chains from slippage. These combinations result in the lowest $\tan \delta$ /HBU of Z1D2 at 200°C. Derived from these observations, Table 5.4 shows the various contributions of the different addition sequences on the various factors influencing $\tan \delta$.

Figure 5.12 Viscoelastic properties for vulcanizates cured at 150°C and hysteresis measured at 100°C (left) and at 200°C (right).

Table 5.4 Summary of the network contributions influencing $\tan \delta$.

Network contributions	Z1D1	Z1D2	Z2D1	Z2D2
Filler-filler interaction (PE)	++++	+++	++	+
Filler-polymer interaction (Bound rubber)	+	++	+++	++++
Apparent crosslink density @150°C (filler-polymer and polymer-polymer)	+++	+++	++++	++++
Apparent crosslink density @200°C (filler-polymer and polymer-polymer)	+++	++++	++	++

Note:

Ranking according to the four compounding sequences

++++ best, + worst

SEM-EDX pictures of SI in the polymer matrices are shown in Figure 5.13, representing the dispersion on macroscale. In this picture, SI clusters are clearly smaller in compounds to which ZnO is added in the first stage of mixing (Z1D1 and Z1D2) compared to the size of SI clusters in compounds when ZnO is added in the last stage of mixing (Z2D1 and Z2D2). Almost 50% of the SI clusters are below 2 μm in Z1D1 and Z1D2. The SI cluster sizes of Z2D1 and Z2D2 are more heterogenous than those of Z1D1 and Z1D2, with only 30% of them below 2 μm : Figure 5.14.

Figure 5.13 SEM-EDX images for SI clusters in the polymer matrix.

Figure 5.14 Size distribution of SI clusters in the polymer matrix.

Figure 5.15 shows the zinc dispersion in the polymer matrix from the SEM-EDX analysis. It is expected that zinc reacts with stearic acid to form zinc stearate when added in the first stage of mixing, resulting in better solubility of zinc and thus better dispersion in the polymer matrix. However, from Figure 5.15 and later confirmed by the size distribution in Figure 5.16 it is clear that different addition sequences of ZnO and DPG do not influence the dispersion of zinc compounds in the polymer matrix. Approximately 90% of the zinc clusters are smaller than or equal to 4 μm , which corresponds to the typical average particle size of Red-Seal ZnO.

Figure 5.15 SEM-EDX images for zinc dispersion in the polymer matrix.

Figure 5.16 Particle size distribution of zinc clusters in the polymer matrix.

5.4 CONCLUSIONS

Hybrid CB/SI-filled NR/BR compounds were investigated with focus on the effect of the ZnO and DPG addition sequence on the material properties with specific interest on hysteresis/ $\tan \delta$. Addition of ZnO in the first stage of mixing (Z1D1 and Z1D2) decreases the MV and results in lower filler-filler interaction (Payne Effect) and smaller SI clusters in the compound matrix as measured by SEM/EDX. The cure rate of the compounds decreased compared to compounds in which ZnO was added in the final stage of mixing, but compounds with ZnO added in the masterbatch are more resistant to thermal degradation, as expressed in a low reversion seen in the cure curves. Compounds with ZnO added in the last stage of mixing (Z2D1 and Z2D2) show a high bound rubber content as a result of a higher silanization efficiency. High filler-polymer interaction of Z2D1 and Z2D2 vulcanizates improves M300%. However, due to reversion, the vulcanizates experience a significant reduction of crosslink density, and consequently higher $\tan \delta$ /hysteresis at a temperature of 200°C. Compounds containing DPG in the last stage of mixing (Z1D2 and Z2D2) impart a higher cure rate and filler-rubber interaction compared to compounds with DPG added in the first stage of mixing (Z1D1 and Z2D1). In the case of dynamic properties, most notably the hysteresis, the addition of ZnO in the first stage of mixing and DPG in the last stage of mixing (Z1D2) results in a low $\tan \delta$ at 100°C and 200°C. Considering all properties discussed above, the Z1D2 addition sequence shows a better balance of high stress-strain properties and low hysteresis in a hybrid CB/SI-filled NR/BR blend, which is beneficial for AC tire retreads.

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THE INFLUENCE OF DIFFERENT TYPES OF BUTADIENE RUBBER ON PROCESSING, MECHANICAL AND DYNAMIC PROPERTIES OF AIRCRAFT TIRE RETREADS

ABSTRACT

The polymer selection plays a crucial role in the performance of rubber products, also for aircraft tire treads. Heat generation and high temperatures in aircraft tire treads have detrimental effects on most properties: it decreases the final performance and accelerates tread wear due to thermo-mechanical degradation, which shortens the service life of the treads. Butadiene Rubber (BR) is commonly added as minor component to Natural Rubber (NR) in aircraft tire treads to increase their longevity. In the present study, the influence of various types of BR is investigated: High-Cis BR (HC BR), High-Cis Long-Chain Branched BR (HC LCB BR), Low-Cis star-branched BR (LC BR), and High-Vinyl BR (HV BR), blended with NR, in a hybrid Carbon Black/Silica (CB/SI) filled compound on the properties of aircraft tire retreads. Comparing the four types of BR, HC LCB BR shows improvements in processability, filler-rubber interaction, as well as the lowest $\tan \delta$ values at 100°C and at low frequencies due to long-chain branching. However, at an average service temperature of aircraft tire treads of around 200°C, the use of the NR/HV BR blend shows the best performance in terms of $\tan \delta$ compared to the other BR types. Highly crosslinked networks are responsible for low Heat Build-Up (HBU). Therefore, the use of HV BR in the blends with NR in CB/SI-filled vulcanizates provides low heat generation materials and can act as a potential polymer in a blend with NR suitable for aircraft tire retreads.

6.1 INTRODUCTION

High temperature generation within the tread of aircraft tires is one of the vital concerns because it relates to the service life of the tire. Wear increases with tread temperature, and rises rapidly when the temperature passes 80°C, depending on the tread compound formulation [1]. Temperature build-up in a tire is determined by the hysteresis loss during deformation of the tire. The use of low hysteresis rubber can minimize tire temperature build-up without sacrificing other desirable properties.

Primarily Natural Rubber (NR) is used in compounds for aircraft tires because of its relatively low heat generation under dynamic conditions. Butadiene Rubber (BR) is commonly added in smaller quantities in order to increase the longevity of aircraft tire treads. Commonly the types of BR used in the tire industry are characterized by a very low glass transition temperature (T_g) in the region of -75 to -100°C. High-Cis BR grades have a cis-content of more than 95 wt%, which is beneficial for wear and cut growth resistance. Cut growth resistance is vital for reducing tear propagation or cracking during operation. The highest cis-content of about 99% results in the most linear chain structure, producing a polymer with the best tensile properties and low hysteresis, thus low Heat Build-Up (HBU) [2].

Developing tread formulations for an optimum balance between traction, hysteresis and abrasion is important. The introduction of vinyl units into polybutadiene alters its glass transition temperature and physical properties significantly. A higher vinyl content increases the T_g by creating a more rigid molecular chain structure [2]. Polybutadiene having a vinyl-content of 10 to 30 wt% has a T_g between -70 and -85°C and exhibits low wear and rolling resistance but poor wet traction. The high-vinyl polybutadiene grades with a vinyl content of 80 to 95 wt% and a T_g of -10 to -30°C provide excellent traction but poor wear resistance. Research has shown that the optimum balance between traction, wear and rolling resistance can be obtained using polybutadiene with a vinyl content of 70 wt% [3]. Figure 6.1 depicts the effect of polymer microstructure of BR on the physical properties, in particular as the result of the amount of 1,2-polybutadiene configurations, as the counterpart of cis- and trans-configurations, together adding up to 100%. The higher the qualitative ranking in Figure 6.1, the better, except for wear resistance.

Figure 6.1 Effect of the 1,2-polybutadiene level on physical properties related to tires [3].

The properties of vulcanizates are strongly affected by the polymer choice. The polymer architecture determines the performance of tires in terms of wear, traction, and rolling resistance. Therefore, proper selection of the polymers to be blended and the composition is crucial for the best compromise in compound properties. Table 6.1 shows that polymer architecture plays a key role in the viscoelastic properties of any tire elastomer as related to the overall tire performance. Certain polymer features such as weight average molecular weight (Mw) and molecular weight distribution (MWD) may be related to rolling resistance and processability. Similarly, tacticity displays a great effect on wear, rolling resistance, traction, and processability. Monomer composition and co-monomer sequence are stated to be related to wear, traction and rolling resistance. The degree of branching also affects traction, rolling resistance and processability [4].

Table 6.1 The effect of polymer architecture on the tire performance [4].

Feature \ Performance	MW and MWD	Tacticity	Monomer composition	Sequence distribution	Branching
Wear		important	important	critical	
Traction		critical	critical		important
Rolling resistance	important	critical	important	critical	important
Processability	critical	important			critical

important
 critical

6.2 EXPERIMENTAL

6.2.1 MATERIALS

For the present study, four types of BR were selected on basis of approximately the same viscosity as masticated NR, but grossly differing in molecular architectures and cis/trans- vs. 1,2-vinyl butadiene configurations. High-Cis essentially linear BR (HC BR), High-Cis Long-Chain Branched BR (HC LCB BR), Low-Cis star branched BR (LC BR) and High-Vinyl BR (HV-BR) are investigated in order to characterize their effect on processability, mechanical and dynamic properties such as $\tan \delta$ (hysteresis) in hybrid CB/SI-filled NR/BR compounds. All four samples were produced with proprietary polymerization technology of the respective suppliers, which precludes an all-encompassing understanding of all intricacies of the products, other than shown hereunder in Table 6.2. Other compounding ingredients are as described in Chapter 5. Buna CB 22 and Buna Nd 22 EZ are produced with a Neodymium (Nd) catalyst. Buna CB 60 and Europrene BR HV80 are produced by Lithium-based anionic polymerization.

Table 6.2 BRs used and properties as delivered by the supplier.

Properties	HC BR	HC LCB BR	LC BR	HV BR
Trade name	BUNA CB 22	BUNA Nd 22 EZ	BUNA CB60	EUROPRENE BR HV80
Company	ARLANXEO, Germany			VERSALIS ENI
Catalyst	Neodymium	Neodymium	Lithium	Lithium
Cis content, wt%	>96	>96	38	–
Vinyl content, wt%	–	–	11	77
MV (ML(1+4) 100°C, MU	63	63	60	70
Glass transition temperature, °C	–	–	–	-31

6.2.2 COMPOUND PREPARATION

The formulation used for this study is presented in Table 6.3, expressed in parts per hundred parts of rubber (phr). The compounds were prepared following a two-step mixing procedure as described in Chapter 5 with Zinc Oxide (ZnO) added in the first stage of mixing and DiPhenyl Guanidine (DPG) added in the second stage of mixing (Z1D2).

Table 6.3 Compound formulations.

Ingredients	phr
NR	70
BR	30
CB	35
SI	20
TESPT	1.8
Stearic acid	3
6PPD	2
TMQ	1
ZnO	5
Sulfur	1.5
CBS	1.5
DPG	0.4

Amount of TESPT and DPG were calculated according to the following equations:

$$\text{TESPT (phr)} = 0.00053 \times Q \times A \text{ and } \text{DPG (phr)} = 0.00012 \times Q \times A$$

where Q is the amount of silica (phr) and A is the CTAB surface area of the silica (171 m²/g)

6.2.3 TESTING OF RAW RUBBERS

Relative molecular weight determination – Gel Permeation Chromatography (GPC) was performed to analyze the weight average molecular weight (M_w), number average molecular weight (M_n), and Poly Dispersity Index (PDI) of the different types of BR used in this study. 10 mg of a sample and 5 mg of standard polystyrene were dissolved in 20 ml of TetraHydroFuran (THF) to obtain a sample solution. A Tosoh HLC-8320GPC was used, THF comprising 5 mmol/l of triethylamine was used as eluent, and 10 µl of the sample solution was injected to obtain a chromatogram by using a Refractive Index (RI) detector. The column oven temperature was 40°C, and the THF flow rate was 0.35 ml/min [5].

Branching Index – A measurement of the degree of branching was determined by Large Amplitude Oscillation Strain (LAOS) in a Rubber Process Analyzer (RPA) from TA Instruments at 160°C in a strain sweep in the range of 0.1–1300% strain at a fixed frequency of 0.5 Hz [6].

6.2.4 TESTING OF COMPOUND AND VULCANIZATE PROPERTIES

Mooney Viscosity (MV), Payne Effect (PE), cure characteristics, bound rubber content, apparent crosslink density, stress-strain properties and tan δ at 100°C of the compounds or tan δ at 100°C and 200°C in a frequency sweep of vulcanized rubber with different types of BR and filled with a hybrid CB/SI filler, were measured. The methods and equipment used were the same as described in Chapters 3 and 5.

Tan δ in temperature sweep – Samples were cut from vulcanized rubber sheets of 2 mm thickness. Measurements were performed using a Dynamic Mechanical Analyzer (DMA) GABO in two segmented conditions. The first condition employed was a temperature sweep in tension mode between -120°C and 40°C with 1°C/min rate at a dynamic strain of 0.1%, static strain of 1%, and a frequency of 10 Hz. The second condition was a temperature sweep from -40 to 120°C where the dynamic and static strain were set at 3%. The temperature increase rate, frequency and deformation mode were the same as described above. The glass transition temperature (T_g) of the compounds was taken as the temperature of the peak of the loss modulus (E'') curve and of the $\tan \delta$ curve. $\tan \delta$ at -30°C and $\tan \delta$ at 5°C were chosen as indicators of ICe Traction (ICT) and Wet Skid Resistance (WSR) of tire treads, respectively, while $\tan \delta$ at 100°C was used as indicator for hysteresis/Heat Build-Up (HBU).

6.3 RESULTS AND DISCUSSION

6.3.1 Mw, Mn, PDI AND BRANCHING INDEX

The BRs used were first characterized for their weight- and number-average molecular weights, M_w and M_n , respectively their $PDI = M_w/M_n$, by GPC. Table 6.4 shows the values of M_w , M_n and PDI of the different types of BR. It is to be noted that the calculated molecular weights of the BRs are relative to the known molecular weights of essentially linear narrow molecular weight polystyrene samples as a standard reference. The branching index of BRs was determined by the LAOS method. Figure 6.3 shows the strain rate plotted against the stress for one cycle of deformation of the different types of BR. The values of branching are depicted in Table 6.5: for rubber analysis, a negative (-) branching index value means that the polymer is mostly linear. The higher the branching index, the more branching the polymer has [7].

HC BR and HC LCB BR were both made with Neodymium catalysis. For HC BR this catalysis results in a "normal molecular weight distribution": Figure 6.2, with a $M_w/M_n \approx 2.0$ as given in Table 6.4. However, the molecules are not perfectly linear because of some side-reactions of the catalyst. There is some LCB taking place, which results in a positive branching index of 0.62. Similarly, for HC LCB BR, this LCB is extra promoted during polymerization, which increases the PDI to 2.2 and raises the branching index to a higher value of 1.2 (for the same MV). HV BR was produced with butyl-Lithium living polymerization which gives essentially linear molecules without branches and with all the same molecular weight. This would result in theoretical PDI 's of essentially 1.0, while from GPC measurement the result is 1.9, which means it was not quite as good as theoretically predicted. The secondary loop as shown in Figure 6.3 for HV BR indicates that this polymer has least branching compared to the other types of BR. The branching index from LAOS is -1.7, which means that no branching is detected. It is important to note that the molecular weight and PDI of LC BR was not properly defined by GPC. This is because of the star-branched molecular architecture of LC BR. All four-armed polymers have the same molecular weight, equal to 4 times the molecular weight of the individual arms. Some stars may have missed one arm, and others may have

only 2. This may have caused the broader PDI than 1.0. This star structure results in a lower hydrodynamic radius than the linear structure for the same molecular weight, by higher compaction of the molecular coils in solution. The GPC commonly used for molecular weight characterization separates the molecules based on hydrodynamic volume. Therefore, the GPC underestimates the real molecular weight and PDI of LC BR relative to the essentially linear polystyrene calibration samples. It is expected that LC BR has a higher number of branching index even than HC LCB BR. However, the branching index of LC BR is only 0.4. This value measured on the star-branched LC BR cannot directly be compared with the ones measured for the regular branched polymers because of its special architecture. Therefore, LAOS also has a problem to signify the branching index for this BR grade.

Table 6.4 Mw, Mn and PDI of different types of butadiene rubber.

BR type	Mw x 10 ⁵ (g/mol)	Mn x 10 ⁵ (g/mol)	PDI= Mw/Mn
HC BR	6.0	2.7	2.0
HC LCB BR	5.3	2.4	2.2
LC BR	3.1	1.9	1.6
HV BR	5.7	3.0	1.9

Figure 6.2 Molecular weight distribution of different types of BR.

Figure 6.3 Strain rate versus stress of different types of BR.

Table 6.5 Branching of BRs.

Branching index			
HC BR	HC LCB BR	LC BR	HV BR
0.62	1.2	0.4	-1.7

6.3.2 GLASS TRANSITION TEMPERATURE (T_g) OF THE RUBBERS

The glass transition temperature (T_g) of the polymers used in this study was measured with DMA. The T_g was calculated using two different methods: as the peak of the loss modulus (E'') signal (T_l), and as the peak of the $\tan \delta$ signal (T_t). Commonly the first occurs several degrees lower in temperature than the second [8]. Figure 6.4 shows E'' and $\tan \delta$ as functions of temperature. The measured T_g s are summarized in Table 6.6. T_l relates to the physical property changes attributed to transitions in materials that are associated with different localized or medium-to-long-range cooperative motions of molecular segments. T_t relates to the midpoint between the glassy and rubbery states of a polymer [9]. The T_g s of the HC BR and HC LCB BR are the lowest among the BRs: the double bonds in the cis-configuration reduce the energy barrier for the rotation of adjacent C-C bonds compared to those in the trans-structure, which reduces the glass transition temperature [10]. The T_g of HV BR is the highest compared to the other BRs, which is attributed to the vinyl groups restricting the segmental movements and decreasing the flexibility of the molecular chains [11]. The structure of NR is comparable to that of cis-BR. Both materials are unsaturated hydrocarbons. In the case of NR, the double bonds are activated by the presence of a methyl group, while in the polybutadiene molecule, it lacks this side group making it less reactive. Furthermore,

since the methyl side group tends to stiffen the polymer chain of NR, the T_g of NR is consequently higher than that of cis-BR [12].

Table 6.6 Measured glass transition temperatures.

Rubber	Loss modulus (E'') peak T_l ($^{\circ}\text{C}$)	Tan δ peak T_t ($^{\circ}\text{C}$)
HC BR	-102	-96
HC LCB BR	-101	-95
LC BR	-95	-87
HV BR	-36	-31
NR	-70	-65

Figure 6.4 Loss modulus (E'') and $\tan \delta$ of the rubbers measured in a temperature sweep.

6.3.3 DYNAMIC MECHANICAL PROPERTIES OF SINGLE RUBBERS AND THE BLEND (NR/BR)

6.3.3.1 UNVULCANIZED UNFILLED SINGLE RUBBERS

Figure 6.5 shows the storage modulus (G'), loss modulus (G'') and $\tan \delta$ of the single elastomers in the frequency range of 0.1 – 33 Hz. Figure 6.5(a) shows that a crossover of the G' and G'' curves can be observed for the high molecular weight, high vinyl linear polymer HV BR at about 0.3 Hz. HC BR and NR are high molecular weight polymers with a slight amount of branching, and for those the G' and G'' meet but do not cross-over yet at a frequency of 0.1 Hz. In Figure 6.5(b) showing the two-branched BR, the crossover point of G' and G'' is shifted to even lower frequencies, out of the measurement range [13]. The crossover point shifts towards a lower frequency as molecular weight and branching increases [14-17]. Therefore, within the frequency range of the measurement, the G' and G'' of HC LCB BR and LC BR run more or less parallel. This concurs with the work of Winter [18, 19]. Both G' and G'' of LC BR increase linearly as the frequency increases. Apparently, the star-branching of this latter BR is most pronounced, so that the cross-over point is situated very far left to lower frequencies.

$\tan \delta$ is the ratio of G'' over G' . Figure 6.5(c) shows $\tan \delta$ as a function of frequency for all types of BR. Generally speaking, for linear polymers, viscous behavior prevails over elastic at low frequencies, corresponding to a phase angle δ aiming for 90° , so that $\tan \delta$ goes to a high value. For heavily branched polymers the entanglements of the branches restrict flow, which usually demonstrates itself as “elastic” behavior, corresponding to a low phase angle δ , so a low $\tan \delta$ [20]. It should be noted though, that the actual molecular weight and the PDI's of the pertinent polymers also play a role herein. All these characteristic features of the polymers are to some extent interrelated. This is clearly visible in Figure 6.5(c). NR and HV BR show the typical behavior of non-entangled, non-branched polymers; HV BR even more so than NR. HC BR has a higher $\tan \delta$ at higher frequencies but levels off at lower frequencies at a lower $\tan \delta$ value; the same and even more so the HC LCB BR. This clearly points at a higher molecular weight combined with some long-chain branching and/or a somewhat broader PDI, as demonstrated in Table 6.4. LC BR shows a nearly horizontal behavior of the $\tan \delta$, very little dependence of $\tan \delta$ on frequency, typical for a heavily branched polymer. The branches entangle and cause a strong elastic response in the still liquid, non-vulcanized state.

Figure 6.5 G' and G'' of uncured unfilled-single rubbers: NR, HC BR, HV BR (a); HC LCB BR, LC BR (b); and $\tan \delta$ of uncured unfilled-single rubbers (c) measured at 100°C.

6.3.3.2 UNFILLED-NR/BR BLENDS

Figure 6.6 shows the viscoelastic properties of the uncured blends of NR with different types of BR. In the blends with NR, all types of BR still show similar viscoelastic behavior trends as measured for the pure polymers, only the magnitudes of the properties become smaller as NR is the major component of the blends.

Figure 6.6 G' and G'' of: NR/HC BR, NR/HV BR (a); NR/HC LCB BR, NR/LC BR (b); and $\tan \delta$ of uncured unfilled-NR/BR blends (c) measured at 100°C.

6.3.4 PROPERTIES OF CB/SI-FILLED NR/BR COMPOUNDS AND VULCANIZATES

6.3.4.1 VISCOSITIES

The MV of the compounds before vulcanization, consisting of a blend of NR with the different types of BR are shown in Figure 6.7. The MV of the compounds not only depends on the macro- and micro-structure of the polymers: molecular weight, PDI and branching, but also on the silanization efficiency of the SI-silane filler system in the different types of polymers. NR/LC BR shows the lowest MV among the other types of BR due to the fact that the NR unravels or dilutes the branches of this grade and thus enhances flow. For the same reason is the MV of NR/HC LCB BR lower than of NR/HC BR and NR/HV BR. The viscosities of the compounds are overall a little high due to the use of SI in their compound formulations. However, all compounds are still processable and can be compared on equal footing.

Figure 6.7 MV of CB/SI-filled NR/BR compounds.

Figure 6.8 shows the PE of the still unvulcanized compounds containing NR blends with the different types of BR. Branching improves the processability of HC LCB BR, as it enhances elastic over viscous behavior during mixing. This should result in less remaining filler-filler interaction and as a consequence better filler dispersion. HC LCB BR indeed shows the lowest PE as an indication for remaining filler-filler interaction: Figure 6.8. The NR/HV BR blend shows the highest PE: This might be due to a low silanization efficiency between SI and silane in this high 1,2-vinyl containing elastomer, as cis-1,4 units are more reactive than trans-1,4 and 1,2-vinyl units.

Figure 6.8 PE of CB/SI-filled NR/BR compounds.

Figure 6.9 shows the effect of BR types on filler-polymer interaction (as opposed to filler-filler interaction) measured as bound rubber. In compounds containing SI, the use of a silane coupling agent is essential to achieve a high SI dispersion resulting from reduced filler-filler interaction, and a good reinforcing effect by overcoming the low compatibility between rubber and SI. NR/HC BR and NR/HC LCB BR show a higher bound rubber content, thus better interaction with the fillers CB and SI compared to NR/HV BR. The coupling agent TESPT apparently has a higher reactivity towards a polymer having a higher content of cis-1,4-moieties than having 1,2-vinyl-moieties. NR/LC BR has the lowest bound rubber because LC BR has a high percentage of trans-1,4 moieties: The trans-1,4-unit has a lower reactivity than the cis-1,4-unit. The reason for this is that the trans-1,4 unit is thermodynamically more stable [21]. This finding is also in line with a model study from Sato, who found that a model olefin (cis-3-hexene) with cis-structure has higher reactivity with TESPT than the one with a vinyl structure (3-methyl-1-pentene) [22]. Another possible explanation is that the star-branched architecture of LC BR creates more steric hindrance for the polymer to attach to the SI surface for silanization. The results of bound rubber are in line with the results of the PE.

Figure 6.9 Bound rubber content of CB/SI-filled NR/BR compounds.

Figure 6.10 shows the vulcanization curves and Table 6.7 shows the cure characteristics of the compounds with different types of BR. The different types of BR do not show clear differences in scorch times (ts_2). With the content of 1,2-vinyl-units in the structure of BR increasing, the optimum vulcanization time (t_{90}) increases: HV BR with a vinyl-content of 77 wt%, compared to LC BR with 11 wt%, has a slightly longer optimum cure time (t_{90}). Compared to the high-cis BR counterparts, which by definition have a low vinyl content, the former two require a significantly longer vulcanization time. This indicates preferential participation of the 1,4-cis-units in the reaction with sulfur-containing systems, thus resulting in a faster vulcanization of high-cis rubber compared to high 1,2-vinyl rubber. All types of BR show the same torque difference at the end of their vulcanization period.

Table 6.7 Curing characteristics of compounds.

Characteristics	NR/HC BR	NR/HC LCB BR	NR/LC BR	NR/HV BR
Scorch time, ts_2 (min)	3.2	3.2	3.6	3.5
Cure time, t_{90} (min)	7.3	7.1	8.6	11.2
Cure rate index, CRI (min^{-1})	24.4	25.6	20.0	13.0
$S_{\min}$ (dN.m)	2.8	2.6	2.6	2.6
$S_{\max}$ (dN.m)	18.0	17.9	17.2	17.6
$S_{\max} - S_{\min}$ (dNm)	15.2	15.3	14.6	15.0

Figure 6.10 Vulcanization curves of CB/SI-filled NR/BR compounds at 150°C.

Figure 6.11 depicts the apparent crosslink densities of the blends after vulcanization. Due to the preferential reaction of sulfur with the cis-1,4-units of BR and high filler-rubber interaction, the blends of NR with the high-cis BRs (NR/HC BR and NR/HC LCB BR) show a higher apparent crosslink density compared to the other blends (NR/LC BR and NR/HV BR).

Figure 6.11 Apparent crosslink density of CB/SI-filled NR/BR vulcanizates cured at 150°C.

6.3.4.2 MECHANICAL PROPERTIES

The stress-strain properties of vulcanizates containing different types of BR are shown in Figure 6.12. The properties show small differences. The tensile strength, M300%, and elongation at break (EAB) of the vulcanized blends with high-cis BRs are slightly higher due to the slightly higher filler-polymer interactions: Figure 6.9 and apparent crosslink density: Figure 6.11.

Figure 6.12 Mechanical properties of CB/SI-filled NR/BR vulcanizates.

6.3.4.3 VISCOELASTIC PROPERTIES OF CB/SI-FILLED NR/BR BLENDS

6.3.4.3.1 CB/SI-FILLED NR/BR COMPOUNDS

Figure 6.13 shows the G' , G'' , and $\tan \delta$ of CB/SI-filled uncured NR/BR compounds measured at 100°C. The addition of filler reduces the G' differences between the types of BR. The G'' of NR/HV BR is higher at low frequencies, but becomes lower as the frequency increases compared to the other blends: $\tan \delta$ of a filled-NR/HV BR compound shows a similar behavior as its unfilled counterpart.

Figure 6.13 G' (a); G'' (b); and $\tan \delta$ (c) of CB/SI-filled NR/BR compounds measured at 100°C.

6.3.4.3.2 CB/SI-FILLED NR/BR VULCANIZATES

Figure 6.14 (left) depicts G' , G'' and $\tan \delta$ of CB/SI-filled NR/BR vulcanizates (cured at 150°C) measured at 100°C. The NR/HV BR vulcanizate shows a significantly lower G' and higher G'' as frequency increases compared to the other blends. High filler-filler interaction, low filler-rubber interaction, and more so low apparent crosslink density are responsible for high G'' and $\tan \delta$. NR/HC BR and NR/HC LCB BR show lower G'' hence a low $\tan \delta$. NR/HC LCB BR shows just a slightly lower $\tan \delta$ at low frequency than NR/HC BR due to the branching.

Figure 6.14 (right) shows the viscoelastic properties of CB/SI-filled NR/BR vulcanizates (cured at 150°C) measured at 200°C to mimic the high temperatures generated in aircraft tire treads during landing. The G' is the highest, while the G'' of NR/HV BR is the lowest among these blends. At a temperature of 200°C, the degradation of HV BR is dominated by re-crosslinking of radicals. 1,2-vinyl units undergo more rapid re-crosslinking than the cis-1,4 and trans-1,4 units, which reflect in better reversion resistance: Figure 6.15, and higher apparent crosslink density: Figure 6.16, than other BR types. The high crosslink density lowers the G'' and $\tan \delta$ of NR/HV BR at 200°C.

Figure 6.14 Dynamic properties (G' , G'' , $\tan \delta$) of CB/SI-filled NR/BR vulcanizates (cured in situ at 150°C) measured at: 100°C (left); 200°C (right).

Figure 6.15 Cure curves of CB/SI filled-NR/BR compounds at 200°C.

Figure 6.16 Apparent crosslink density of CB/SI-filled NR/BR vulcanizates at 200°C.

Figure 6.17 shows $\tan \delta$ as a function of temperature measured by a DMA for the CB/SI-filled NR/BR vulcanizates. All blends except NR/HV BR show a small shoulder and $\tan \delta$ peak more or at less the same temperature around -90°C . The small shoulders correspond to the T_g of the cis- and trans-configurations in the minor portions of BR (30 phr) [23]. The large $\tan \delta$ peaks correspond to the T_g of NR (70 phr): Table 6.8. For the NR/HV BR blend there is only one peak visible, which indicates that these two polymers are miscible. The T_g of NR is

-65°C and HV BR is -31°C. Using the Fox equation: see Equation 2.4, Chapter 2, the theoretical T_g blend is -49°C, while based on the DMA measurement, the T_g is approximate -44°C. A compatible blend would have a single T_g lying somewhere in between the T_g (s) of the two constituent polymers [24].

Table 6.9 shows that NR/HV BR has the highest $\tan \delta$ peak temperature, but still in the sub-zero region, indicative for best ICT and WSR of tire treads made thereof. At a temperature of 100°C, the $\tan \delta$ of NR/HV BR is still slightly higher which indicates a little higher HBU compared to the other types of BR.

Figure 6.17 $\tan \delta$ of CB/SI-filled NR/BR vulcanizates in a temperature sweep measured by DMA.

Table 6.8 T_g of CB/SI-filled NR blends with different types of BR.

Rubber	$\tan \delta$ of small shoulder BR (°C)	$\tan \delta$ peak NR (°C)
NR/HC BR	-96	-53
NR/HC LCB BR	-96	-53
NR/LC BR	-82	-51
NR/HV BR	-44	

Table 6.9 Loss tangent at different temperatures of CB/SI-filled NR/BR vulcanizates.

Blend	Ice grip $\tan \delta$ -30°C	Wet skid $\tan \delta$ 5°C	Heat build-up $\tan \delta$ 100°C
NR/HC BR	0.49	0.22	0.12
NR/HC LCB BR	0.48	0.21	0.11
NR/LC BR	0.51	0.24	0.13
NR/HV BR	0.76	0.29	0.14

6.4 CONCLUSIONS

Four different types of BR as single polymers and in blends with NR were studied concerning their influence on processing, mechanical and dynamic properties. In their nature, HC BR and HC LCB BR show a slight difference in G'' , hence low $\tan \delta$ at low frequencies due to branching in the HC LCB BR. LC BR having a star-branched architecture shows no difference in $\tan \delta$ in a frequency sweep due to no difference in G' as well as G'' as the frequency increases, typical for strongly branched polymers. An essentially linear HV BR in its nature shows a high $\tan \delta$ at low frequency and low $\tan \delta$ at high frequency, signaling a prevalence of viscous behavior over elastic. In the unfilled blends with NR, the BRs still inherit the viscoelastic behavior of their pure elastomers, only that the magnitudes become lower than for the pure rubber because of the dilution effect.

When fillers are introduced into the blends, not only the nature of the polymers, but also the interaction between the fillers and the polymers influence the final properties. NR/HC BR and NR/HC LCB BR reinforced with CB/SI show a fast optimum cure time (t_{90}), high reinforcement as well as high apparent crosslink density, and low $\tan \delta$ at 100°C. Cis-1,4 units have the highest reactivity towards the silane coupling agent, leading to lower filler-filler interaction, and correspondingly higher filler-rubber interactions compared to trans-1,4 and 1,2-vinyl units. However, at a temperature of 200°C, which can be reached at the surface of AC tire treads during landing, NR/HV BR shows the lowest $\tan \delta$. It can be explained by a higher reversion resistance which leads to a higher crosslink density of NR/HV BR at the service temperature compared to the other types of BR. This evidence reveals the potential use of HV BR blends with NR for AC tire retread applications, since it provides a low $\tan \delta$ at 200°C, signaling a low HBU.

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INCORPORATION OF RESINS FOR IMPROVING THE PROPERTIES OF AIRCRAFT TIRE RETREADS*

ABSTRACT

This study focuses on the use of oligomeric resins in order to benefit from their effect on improving the performance of aircraft tire retreads. The aim was to enhance the tackiness for the retreading process and their final performance in terms of superior stress-strain properties and low heat generation in order to decrease treadwear; thus increasing the tire's service life, and in terms of traction or skid resistance to improve safety during landing of an aircraft. Two types of resins are investigated: a terpene phenol and an aromatic hydrocarbon C9 resin, added to compounds with different filler systems: Carbon Black (CB), hybrid Carbon Black/Silica (CB/SI), and pure Silica (SI). The rubber compounds and vulcanizates are compared to their controls for each filler system.

The use of resins improves processing independent of the filler system, with a slight improvement of tensile strength, Modulus at 300% (M300%) and Elongation at Break (EAB). The incorporation of resins improves the tackiness for the compounds with all filler systems, which is beneficial for the retreading process. A significant improvement in Ice Traction (ICT) and Wet Skid Resistance (WSR) with a trade-off in Heat Build-Up (HBU) is observed in CB- and CB/SI-reinforced compounds when resins are added. Terpene phenol and aromatic hydrocarbon resin show comparable ICT, while the aromatic hydrocarbon C9 resin gives a better WSR performance than the terpene phenol in all compounds. However, a slight improvement in HBU with the use of both resins is only observed in the SI-filled system.

The present exploratory study into the addition of resins demonstrates the potential to significantly improve the overall performance of aircraft tire retreads, justifying more in-depth investigations into this possibility in real tires.

7.1 INTRODUCTION

Aircraft (AC) tires are used in different stages; these can be divided into taxiing, takeoff, and landing. During taxiing, the speed is relatively low, and therefore the tire temperature increases only slightly. During takeoff and landing, the temperature in the tread increases considerably due to high-speed friction between tire and runway [1]. However, the landing phase is the most burdensome and therefore defines the design specifications of the tire [2]. At the first touch between the tire and the runway, the tire has no rotational speed. Therefore, the tire heats up instantaneously, generates smoke from degraded rubber, and blackens the runway [3].

For AC tire/retreaded tire manufacturing, the demand is to increase service life without many changes in the existing formulation and processing. From a compounding point of view, the selection of polymers, fillers, and other additives is crucial to address the Heat Build-Up (HBU) problem in AC tire treads and minimize trade-offs. Additives are generally used at relatively low levels to fine-tune the tread performance.

Resins are used in the rubber industry as processing aids, tackifiers, curing agents, and reinforcing agents [4]. In the past, resins were used to lower viscosity, enhance tackiness and green strength of uncured compounds as well as to improve mechanical properties of the vulcanizates. Tack is the ability of two materials to resist separation after bringing the surfaces into contact for a short time under light pressure [5]. In order for a rubber compound to exhibit high tack, three conditions must be fulfilled:

- 1) Intimate molecular contact between the two surfaces,
- 2) Interdiffusion of polymeric chains across the interface,
- 3) The bond must be capable of resisting high stress before rupture [6].

In order to increase the contact area, the material must perform viscous flow. However, increasing contact area and interdiffusion are not enough to achieve high tack. The third condition must also be met, which requires sufficient green strength. Green strength is the ability of rubber compounds to resist deformation and fracture before vulcanization. The contact and interdiffusion might be achieved using a process oil, but it is inferior to cohesive strength and hence produces little tack. In contrast, hard brittle solids such as resins, have high cohesive strengths. Only polymeric materials above their glass transition temperature (T_g) can exhibit good tack because they provide a proper balance between molecular mobility needed to achieve bond formation and cohesive strength to resist rupture. Resins fulfill these requirements and are therefore known as tackifiers.

Today, resins are used in tire manufacturing, especially Passenger Car Tires (PCT), to enhance the viscoelastic properties. The use of resins in Silica (SI)-filled PCT results in an improvement in traction, handling, treadwear, and rolling resistance. It is crucial to understand

how the different types of resins affect the viscoelastic properties of the rubbers in order to tailor the tire properties.

Table 7.1 shows the types of resin used in the rubber industry. Reactive resins, for example resole-phenol-formaldehyde resins, react with unsaturated bonds in the polymer chains, improving heat and moisture resistance, but reducing flexibility. When a non-reactive resin is compatible with rubber, the polymer entanglement density decreases, which results in improved processability and decrease of the modulus of vulcanizates [7]. A softer rubber compound provides better surface contact with the substrate and increases tackiness.

A compatible and non-reactive hydrocarbon resin increases the T_g of a compound compared to the neat rubber [8]. The higher T_g of the compound raises the $\tan \delta$ value at 0°C by more viscoelastic damping and thus improves the wet traction characteristics of tire treads built on basis of these compounds. $\tan \delta$ measured between $35 - 75^\circ\text{C}$ is indicative of rolling resistance of tire treads: the higher, the more rolling loss, and this may slightly increase. At a temperature exceeding 100°C , the $\tan \delta$ of a resin-containing rubber is lower than the one of the control rubber without resin, which indicates low HBU: Figure 7.1. If the resin is partially compatible or if the loading of resin exceeds its miscibility level in the rubber compound, then a second peak from the resin is seen in the $\tan \delta$ curve [7].

Table 7.1 Types of resin used in the rubber industry [7].

Reactive resins		Non-reactive resins
Curing resins	Reinforcing resins	
Phenol-formaldehyde	Phenol-formaldehyde	Phenol-formaldehyde
Resole type	High styrene	Hydrocarbon resins
	Methylene donors	Terpene derivatives
	Resorcinol (formaldehyde)	Coumarone indene
	Polybutadiene	Rosin derivatives
	Styrene-acrylonitrile	Tall oil derivatives
	Polyvinyl chloride	Phenol-acetylene condensation

Figure 7.1 Effect of compatible vs. partially compatible resins on viscoelastic properties [7].

When designing rubber compounds with the use of resins, the properties of resins give valuable information about their suitability. The properties include:

- Softening point which is indicative of viscosity and controlled by the average molecular weight of the oligomeric material
- Glass transition temperature (T_g)
- Thermal stability
- Viscosity
- Solubility which depends on the resin type
- Average molecular weight
- Molecular weight distribution
- Compatibility which can be defined as having only one glass transition temperature. Compatibility depends on the resin type, molecular weight and its distribution, resin structure, and configuration. More details of the properties above are given in Chapter 2.

It is challenging to manipulate the performance balance of traction, treadwear, and rolling resistance of tires. These three properties are commonly referred to as the magic triangle for improving passenger car/truck tire performance. In AC tires, the properties of interest are low heat generation in the tread since this tire part is prone to temperature increase due to the extreme conditions. High temperatures are detrimental to tire properties: It can decrease the strength and accelerate treadwear. Therefore, it is crucial to develop a compound formulation with low hysteresis while maintaining other required properties. This chapter will explore how the use of resins helps to enhance the processing, tackiness and final properties of AC tire retreads.

7.2 EXPERIMENTAL

7.2.1 MATERIALS

The elastomers used in this study were Ribbed Smoked Sheet (RSS-1) from Weber & Schaer GmbH & Co. KG, Germany, and High-Cis Long-Chain Branched Butadiene Rubber (HC LCB BR) from ARLANXEO, Germany. The polymers as well as all other rubber ingredients are described in Chapter 3. The resins employed were SYLVATRAXXTM products from Kraton Polymers Corp.: SYLVATRAXX 6720 is a Terpene Phenol (TP) resin, SYLVATRAXX 4401 is an aromatic hydrocarbon C9 resin (C9). The characteristic properties are given in Table 7.2. The structure of the resins is depicted in Figure 7.2. The properties of the Treated Distillate Aromatic Extract (TDAE) oil are given in Table 7.3. Table 7.4 shows the solubility parameters of polymers and resins used in this study.

Table 7.2 Resins used in this research [9, 10].

Properties	TP	C9
Main designation	Terpene phenol	Aromatic hydrocarbon
Glass transition temperature, T _g (°C)	68	39
Softening point (°C)	113 – 123	82 – 88
Density (g/cm ³)	1.03	1.06
Viscosity at 150°C (mPa.s)	3400	650

Figure 7.2 Structure of terpene phenol [11] (a); aromatic C9 resin [12] (b).

Table 7.3 Properties of TDAE [13].

Properties	Standard test method	TDAE
Color	ASTM D156	8.0D
Density at 15°C (g/cm ³)	ASTM D1298	0.95
Density at 20°C (g/cm ³)	ASTM D1298	0.947
Kinematic viscosity at 40°C (mm ² /s)	ASTM D445	410
Kinematic viscosity at 100°C (mm ² /s)	ASTM D445	18.8
Sulfur (wt%)	ISO 14596	0.8
Aniline point (°C)	ASTM D611	68
Glass transition temp, T _g (°C)	IP346	-48

Table 7.4 Solubility parameters (δ) of polymers and resins.

	δ (MPa) ^{1/2}	δ^* (MPa) ^{1/2}	$ \delta^*_{\text{NR/BR}} - \delta^*_{\text{resin or oil}} $ (MPa) ^{1/2}
Natural rubber (NR)	16.3 – 17 [14]	17.8 [15]	–
Butadiene rubber (BR)	16 – 17 [14]	17.7 [15]	–
NR/BR 70/30	–	17.7 [15]	–
Terpene Phenol (TP)	16 – 23 [15]	20.2 ^a [15]	2.4
Aromatic hydrocarbon C9 (C9)	18 [16]	19.4 [15]	1.6
TDAE	–	17.2 [13]	0.5

*: calculation of the Hildebrand parameter from group contributions of the molar vaporization energy (U) and molar volume (V) at 25°C from Table 2.12, Chapter 2.

^a: two molecules of terpene and one molecule of phenol are assumed.

An example of the theoretical Hildebrand parameter δ^* of terpene phenol calculated from group contributions is shown in Table 7.5:

Table 7.5 Calculated solubility parameters (δ^*)^a of terpene phenol resin from group contributions.

Group contributions	Number	ΔU (kJ/mol)	Total ΔU (kJ/mol)	V (cm ³ /mol)	Total V (cm ³ /mol)
-CH ₃	15	4.7	70.7	33.5	502.5
-CH ₂ -	15	4.9	74.1	16.1	241.5
=CH-	8	4.3	34.5	13.5	108.0
>CH-	5	3.4	17.2	-1.0	-5.0
>C<	6	1.5	8.8	-19.2	-115.2
=C<	12	4.3	51.7	-5.5	-66.0
-OH	1	29.8	29.8	10.0	10.0
Conjugated =	10	1.7	16.7	-2.2	-22.0
6 membered rings	7	1.1	7.4	16.0	112.0
			310.8		765.8
δ^* terpene phenol					20.2 ^a

^a: two molecules of terpene and one molecule of phenol are assumed.

7.2.2 COMPOUND PREPARATION

The compound formulations are shown in Table 7.6. The filler systems used in this research are Carbon Black (CB), a hybrid system of Carbon Black and Silica (CB/SI) and pure Silica (SI). All control compounds were formulated to obtain a comparable hardness. The control (C) compounds contain TDAE oil in the CB-filled, but no TDAE oil in the CB/SI- and SI-filled systems. TP are compounds with Terpene Phenol resin, and C9 indicates addition of the aromatic hydrocarbon C9 resin. A standard carcass formulation [17] was used as countersurface for green tack measurements.

Table 7.6 Compound formulations.

Ingredients	Carcass	CB		CB/SI		SI	
		C	TP/C9	C	TP/C9	C	TP/C9
NR (RSS#1)	100	70					
BR (HC LCB BR)	0	30					
CB (N234)	25	55		35		0	
SI (ULTRASIL 7005)	0	0		20		55	
TESPT	0	0		1.7		4.8	
ZnO	5	5					
Stearic acid	1	3					
6PPD	1	2					
TMQ	1	1					
Resin	0	0	7.5	0	7.5	0	7.5
TDAE	4	7.5	0	0	0	0	0
Sulfur	2.5	1.5					
CBS	0.7	1.5		1.5		2	
DPG	0	0		0.4		1.1	

Amount of TESPT and DPG were calculated according to the following equations:

$$\text{TESPT (phr)} = 0.00053 \times Q \times A \text{ and } \text{DPG (phr)} = 0.00012 \times Q \times A$$

where Q is the amount of silica (phr) and A is the CTAB surface area of the silica (171 m²/g)

Mixing of the CB-filled compounds was performed using an internal mixer (Brabender Plasticorder 350s) with a mixer temperature initially set at 50°C, a rotor speed of 130 revolutions per minute (rpm), and a fill factor of 70%. NR was initially masticated prior to the addition of BR. The masticated NR and BR were blended for 1 minute (min). Then half of the CB and TDAE oil were added and mixed for 1 min. After 1 min, the other half of CB and TDAE oil were added and mixed for another 6 mins. Finally, all other ingredients: ZnO, stearic acid, 6PPD, and TMQ, were added and mixed for 2.5 mins. The compounds were dumped, sheeted out on a two-roll mill, and kept overnight before the incorporation of sulfur and CBS in the same internal mixer at a set temperature of 70°C and initial rotor speed of 50 rpm. For this, the masterbatch was mixed for 1 min, the rotor speed was decreased to 30 rpm before

curatives were added, and the compound was mixed for another 2 mins. The detailed procedure is described in Chapter 3.

For CB/SI- and SI-filled compounds, the mixer temperature and rotor speed were set at 100°C and 60 rpm. The masticated NR and BR were blended. In CB/SI, silica and silane were added first and mixed for 1 min. At the second addition, the CB was added with other rubber ingredients except for curatives. In SI-filled compounds, half silica and silane were added after mixing the rubber and the other half silica-silane and remaining ingredients except curatives at the second addition. The rotor speed was then adjusted/decreased to reach the temperature for silanization of 150°C. The temperature of silanization was maintained for 7 mins and 9 mins for the CB/SI- and the Si-filled compounds, respectively. After 3 mins of silanization, the ram was opened for about 1 min to release ethanol produced in the silanization reaction. Then the compounds were dumped. The second stage of admixing the curatives was done according to the same procedure as the CB-filled compounds.

7.2.3 TESTING OF COMPOUND AND VULCANIZATE PROPERTIES

Mooney Viscosity (MV), Payne Effect (PE), apparent crosslink density, and stress-strain properties after vulcanization were measured as described in Chapter 3. Cure behavior was measured using the procedure as explained in Chapter 5, and dynamic mechanical properties: $\tan \delta$, using a DMA were performed according to the method described in Chapter 6.

The tackiness of compounds with/without resin in different filler systems was tested using a universal tensile testing machine Zwick Z10. Tack measurements were performed using a custom-made device, and the procedure was adopted based on the work of Mikrut [18]. Pieces of rubber with dimensions of 20 x 20 x 2 mm were used as test samples. The sample and the counter sample (carcass compound) were pressed against orifice disks to generate a convex contact surface: Fig. 7.3(a). The sample was brought into contact with the counter surface with a pre-load of 10 N for 10 seconds prior to the test: Figure 7.3(b), and then separated with a speed of 500 mm/sec: Figure 7.3(c). The separation force versus separation distance were recorded. For each sample, five tack measurements were done, and the average was taken as the final result. The contact area was calculated from the radius of curvature. The measurements were performed at room temperature.

Figure 7.3 Tack measurement.

7.3 RESULTS AND DISCUSSION

7.3.1 MIXING PERFORMANCE

Figure 7.4 shows the mixing profiles of the compounds with resin in comparison to the respective controls for the materials with different filler systems. The torque curves of the resin compounds show no significant difference relative to the control in the CB system. The replacement of an equivalent amount of oil by resin in the CB-filled compounds, combined with the high temperature above the softening point of the resin generated during mixing, results in similar end torques. In the CB/SI- and SI-systems, the addition of resins imparts lower mixing torque than in the control. The temperature of silanization for both, the CB/SI- and SI-filled compound, was maintained at 150°C, well above the softening points of the resins. Thus, the resins easily penetrate into the rubber matrix, decrease the intermolecular forces and facilitate filler incorporation and distribution into the rubber matrix.

Figure 7.4 Mixing curves of compounds containing resins in comparison to the controls with different filler systems.

7.3.2 COMPOUND PROPERTIES

The addition of resins slightly decreases the MV of the CB/SI- and SI-filled compounds, as shown in Figure 7.5. All compounds were mixed above the softening points of the resins, so they were blended as viscous liquids into the compounds. The amount of resin is equal to the amount of oil in the CB-filled compound, hence no significant difference in MV is observed depending on the addition of oil or resin. In CB/SI- and SI-filled compounds, the controls contain no oil, therefore they impart high MV. The silanization temperature of CB/SI- and SI materials was maintained at 150°C, and at this temperature the resins were in liquid, viscous form. Therefore, they could easily penetrate between the polymer chains. The presence of low molecular weight molecules like resins pushes the polymer chains apart and reduces the intermolecular force between rubber molecules, which increases the free volume and facilitates better filler dispersion, decreasing the MV. The results of MV are in line with the results of the mixing curves: lower end torques for lower MV.

Figure 7.5 MV of compounds containing resins and different filler systems in comparison to the controls.

To characterize the tack properties of the compound surface, it was brought into contact with the countersurface, a carcass compound: Figure 7.3. The curves of force versus separation distance for all compounds with the different filler systems are depicted in Figure 7.6. The tack of the compounds containing resins in comparison with resin-free controls is shown in Figure 7.7(a) as the maximum force needed for separation, and the separation distance is given in Figure 7.7(b). Independent of the filler systems, the use of resins TP and C9 increases the force needed for separation. The incorporation of the higher molecular weight resins instead of oil increases the cohesive strength. CB-C shows a higher separation distance than CB-TP and CB-C9. This may be because both, CB-C and the carcass compound, contain CB and oil. The surface energies of these two materials will not differ much, thus readily promoting contact and inter-diffusion when brought into contact. The separation distance increases because these compounds are more sticky; however, the force needed for separation is low due to poor cohesive strength of the compound due to the oil. The separation distance of compounds containing resins in both, the CB/SI- and SI-filled systems, is the same as their respective controls. This is most probably due to the fact that all compounds containing silica with or without resins have to overcome the surface energy difference with the carcass material containing CB and oil. In order for the contact area to increase, for interdiffusion and for bonding between the two surfaces to take place, the material must overcome this surface energy barrier. Compounds which have different compositions might need more time, higher pressure or temperature to overcome the surface energy difference.

Figure 7.6 Force versus separation distance of compounds with/without resins for different filler systems.

Figure 7.7 Tack measured as maximum forces (a) and separation distances (b) of compounds containing resins and different filler systems in comparison to the controls.

7.3.3 VULCANIZATION CHARACTERISTICS

Figure 7.8 shows the cure curves of the compounds containing resins in comparison with their controls for the CB-, CB/SI-, and SI-filled materials. Compared to their controls, the C9 and TP resin compounds show a minor influence on scorch time (t_{s2}) and optimum cure time (t_{90}) for all filler systems: see Table 7.7. Compared to the controls, the use of C9 and TP decreases the rheometer minimum torque S_{min} in vulcanizates containing silica: CB/SI and SI. The rheometer minimum torque S_{min} bears a relation to the mixing torque at the end of the mixing process and the MV, as can be seen by comparison with the data presented in Figure 7.5.

The maximum rheometer torque S_{max} or better even the torque difference $S_{max}-S_{min}$ is often quoted as a measure for crosslink density. However, this is not quite right as the intrinsic viscoelastic rigidity of the compounds, determined by filler-filler and preferred filler-polymer interactions also contribute to the S_{max} . So, the lower the S_{min} to start with, the lower the S_{max} at equal crosslink density. The contributions of crosslink density and intrinsic viscoelastic rigidity cannot be separated in these curves. The $S_{max}-S_{min}$ generally increases in the series of CB < CB/SI < SI, irrespective of whether the controls are compared or the TP or C9 variants. Furthermore, the TP and C9 compounds generally show a reduced $S_{max}-S_{min}$ versus their controls. These rankings do qualitatively agree with those of the MV as presented in Figure 7.5. It is a clear indication that the differences are not necessarily a sign of reduced crosslink density but, like for the MV, the result of stronger filler-polymer bonding and a larger free volume due to the addition of resins. See also next paragraph: crosslink densities.

Figure 7.8 Cure curves of compounds containing resins and different filler systems in comparison with the respective controls.

Table 7.7 Cure characteristics of all compounds.

Characteristics/Properties	CB			CB/SI			SI		
	C	TP	C9	C	TP	C9	C	TP	C9
Scorch time, ts_2 (min)	4.1	3.9	3.8	3.2	3.9	3.3	5.7	6.3	6.6
Optimum cure time, t_{90} (min)	7.5	7.8	7.8	7.9	8.2	8.3	12.8	12.3	12.7
Cure rate index (min^{-1})	29.3	25.6	25.0	21.3	23.2	20.0	14.1	16.7	16.4
$S_{\min}$ (dN.m)	2.7	2.6	2.4	3.1	2.4	2.4	3.2	2.4	2.3
$S_{\max}$ (dN.m)	18.1	17.0	16.9	18.9	17.2	17.0	22.4	19.2	19.0
$S_{\max}-S_{\min}$ (dN.m)	15.4	14.4	14.5	15.8	14.8	14.6	19.2	16.8	16.7

The effect of resins on the apparent crosslink density is shown in Figure 7.9 as derived from swelling experiments. It is the resultant from the contribution of sulfur polymer-polymer crosslinks and from filler-rubber interaction. There is a slight increasing trend in going from CB towards SI, most likely because of the stronger chemical filler-rubber coupling for the latter, in comparison with the physical interaction in the CB case. The replacement of CB by silica and the addition of resins does not result in large crosslink density differences for all systems. The use of resins does neither negatively interfere with the network formation during vulcanization nor with the silanization reaction for systems containing CB/SI and SI; it even has a small positive effect.

Figure 7.9 Apparent crosslink density of vulcanizates containing resins and different filler systems compared to the controls.

7.3.4 DYNAMIC PROPERTIES AFTER VULCANIZATION

Figure 7.10 shows the PE as an indicator for the micro-dispersion of the fillers, in which lower values indicate better micro-dispersion. The viscosities of TP and C9 at 150°C are 3400 and 650 MPa.s respectively [9, 10]; the viscosity of TDAE oil at 100°C is 17.86 MPa.s [13]. Despite a higher viscosity of the resins compared to oil, they impart a similar PE in the CB system. The dispersion of CB in the polymer matrix is relatively easy due to the less developed filler-filler network of CB and the high compatibility of CB with the non-polar polymers. Therefore, replacing an equivalent amount of TDAE oil with resins in CB-filled compounds results in nearly the same PE as the CB-control. The addition of TP and C9 does not negatively interfere with the silanization and even shows a slight improvement of silanization. A slight decrease in PE is observed in CB/SI- and SI-filled systems by the addition of resins from their respective controls.

Figure 7.10 PE of compounds containing resins and different filler systems in comparison with the controls.

Figure 7.11 depicts the viscoelastic damping, $\tan \delta$ values, as a function of temperature for the vulcanizates containing resins in comparison to their controls. The T_g corresponds to the temperature, at which a peak in $\tan \delta$ is observed. Compatible resins and rubbers will shift or broaden the $\tan \delta$ peak region. In the case that resin and rubber are incompatible, two separate T_g -peaks are commonly visible in the $\tan \delta$ curve as a function of temperature [19], located at their original positions, at least if both are present in sufficient quantities. As can be seen from Table 7.8 and Figure 7.11, the use of resins shifts the $\tan \delta$ peak of the vulcanizates slightly to a higher temperature compared to the controls. This is clearly due to the addition of resins with high T_g and softening point, the more for TP than for C9. As the T_g 's of the NR-phase as well as of the BR-phase shift with the addition of the resins: Table 7.8, it may be taken as an indication that the resins have no particular preference for either of the two phases. However, due to the lower amount of BR versus NR in the formulation, the shift in T_g of BR is very difficult to discern, so the BR-data in Table 7.8 need to be taken with some reserve.

Table 7.8 Measured glass transition temperatures.

Rubber	T_g BR ($^{\circ}\text{C}$)	T_g NR ($^{\circ}\text{C}$)
CB-C	-97	-53
CB-TP	-92	-49
CB-C9	-94	-51
CB/SI-C	-97	-53
CB/SI-TP	-93	-49
CB/SI-C9	-94	-51
SI-C	-97	-51
SI-TP	-93	-49
SI-C9	-94	-50

Figure 7.11 $\tan \delta$ measured in a temperature sweep from -120 to -40°C for all vulcanizates.

Figure 7.12 shows $\tan \delta$ in a temperature sweep from -40 to 40°C. For the interpretation of these data, the well-known formalism of Nordsiek to simulate whole tire tread performance in laboratory-scale dynamic testing is used. The temperature region of -35 to 0°C can be employed as indicator for Ice Traction (ICT), and $\tan \delta$ in the region of 0 to 20°C is indicative for wet traction or Wet Skid Resistance (WSR) of a tire tread based on such a compound [20]. Figures 7.13(a) and (b) summarize the $\tan \delta$ values at -30°C for ICT and 5°C for WSR. The addition of resins, independent of the filler system, raises the $\tan \delta$ and so improves the ICT performance as well as WSR compared to the respective control vulcanizates. At -30°C, the use of TP resin results in only a slightly higher ICT than for C9 in all filler systems. This is related to the shift of the $\tan \delta$ peak as a consequence of using resins with a high T_g and molecular weight. At 5°C, the C9 resin provides a higher WSR than TP and the respective controls in all filler systems. This seemingly contradictory observation is visible in the cross-over of the $\tan \delta$ curves for TP and C9 around -20°C, as seen for all three filler systems in Figure 7.12. It relates to the structure of C9, which contains methyl groups on the aromatic rings from vinyltoluene and along the polymer chain from α -methylstyrene groups, providing more flexibility for rotation and movement than the bulky configuration of TP: see

Figure 7.2. Thus the mobility of the chains increases more for C9 than for TP at raising temperature, leading to relatively higher viscoelastic losses.

Figure 7.12 $\tan \delta$ in a temperature sweep from -40 to 40 $^{\circ}\text{C}$ for all vulcanizates.

Figure 7.13 $\tan \delta$ values of the resin-containing rubbers at -30°C (a) and 5°C (b) in comparison with the respective controls.

Figure 7.14 depicts the $\tan \delta$ values at 100°C as indicator for HBU. It is clearly visible that the $\tan \delta$ values decrease substantially for the SI-containing compounds relative to CB ones by about 50%. The use of resins for the CB-compounds raises the $\tan \delta$ values at 100°C, while for the pure SI-compound it even leads to a small but significant further reduction. The effect in the SI-filled compounds is clearly the result of the chemical bonding of the rubber molecules to the silica surface by the coupling agent TESPT versus far less strong physical adhesion for the CB-reinforced compounds. It restricts release/adhesion or segmental motions of polymer segments on the filler surface and thus reduces mechanical loss phenomena on a molecular scale [21]. The filler-rubber interaction present in the SI-filled compounds acts in a similar manner as multifunctional chemical crosslinkers, next to the crosslinks created by sulfur vulcanization.

An important point of consideration for this overall very promising observation for the application in aircraft tire treads is, that the $\tan \delta$ is in fact a relative quantity between the lost and stored energy during deformation. It says nothing about the absolute values of the losses versus stored energy, as reflected by HBU. Although $\tan \delta$ can be used as the first approximation of HBU, it is therefore necessary and highly valuable to verify these results with real tire tests, which were out of the scope of the present study.

Figure 7.14 Tan δ at 100°C of the rubber with resins in comparison to the respective controls for different filler systems.

7.3.5 MECHANICAL PROPERTIES OF THE VULCANIZATES

Figures 7.15(a)-(c) show the mechanical properties for all vulcanizates. Although the M300% reduces somewhat in going from CB- to SI-reinforcement, the tensile strength and elongation at break are significantly increasing. Slight increases in M300% and tensile strength with no significant difference in elongation at break by the addition of resins in CB/SI- and SI-filled are observed. All vulcanizates show comparable hardness, as was aimed for in this study.

Figure 7.15 Mechanical properties for all materials: M300% and tensile strength (a); elongation at break (b); hardness Shore A (c).

7.4 CONCLUSIONS

The addition of TP and hydrocarbon C9 resins in a NR/BR blend offers the potential to significantly improve ICT and WSR of aircraft tire tread formulations with CB-, SI- or dual CB/SI filler systems, based on dynamic mechanical laboratory-based testing. Apart from a very positive effect of the switch from CB to SI on the $\tan \delta$ at 100°C as indication for HBU as such of approximately 50%, a further positive effect from the resins on HBU is only observed in the SI-filled system. In the specific aircraft tire retread formulation used in the present study, both TP and C9 show comparable performances in the low temperature range for ICT, as well as at high temperatures for HBU indication. In the intermediate temperature range between 0°C and 20°C, the C9 resin promises a slightly better WSR in the SI-filled system. Apart from the influences from changing the filler system from CB to SI, the addition of 7.5 phr of resin to all reinforced systems has little influence on curing characteristics, and provides a slight improvement in tensile strength and M300% with no significant difference in elongation at break. The use of resins improves the processing as well as the tackiness of compounds, which is an important factor for the retreading process. The results of this study provide a basis for optimization of aircraft tire treads in many functional aspects: ICT, WSR and HBU, which deserve testing in real tires.

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AGING PROPERTIES OF AIRCRAFT TIRE RETREADS

ABSTRACT

The aging performance in terms of changing stress-strain properties, hardness and $\tan \delta$ of vulcanizates at a temperature of 200°C, close to the service conditions of aircraft tires, is investigated. The vulcanizates are based on Natural Rubber (NR) blended with different types of Butadiene Rubber (BR) and with different filler systems. In the first part of this study, four types of BR are used: High-Cis BR (HC BR), High-Cis Long Chain-Branched BR (HC LCB BR), Low-Cis BR (LC BR), and High-Vinyl BR (HV BR). In the second part, three different filler systems: Carbon Black (CB), a blend of Carbon Black and Silica (CB/SI), and pure Silica (SI) are used. Aging is performed in a hot air oven for up to twenty-five cycles, where one cycle consists of 5 minutes of aging (to mimic the duration of takeoff), 30 minutes rest at room temperature (approximate duration of cooling down of the tire), and 5 minutes of aging again (to approximate the duration of landing).

Comparing the various types of BR, CB/SI-filled NR/HV shows lower $\tan \delta$ than the vulcanizates with the other types of BR. At the service temperature of 200°C, the Modulus at 100% elongation (M100%) and hardness of vulcanizates containing the HV BR with a high content of 1,2-vinyl units change more, as the crosslink density of this polymer increases relatively the most. Although NR/HV BR exhibits low hysteresis, it becomes stiff and less ductile after aging. Thus, it cannot be recommended for use in aircraft tire retreads. Comparing the various types of fillers in NR/HC LCB BR vulcanizates, the pure SI-filled material shows better retention of tensile strength, Elongation at Break (EAB), M100% and $\tan \delta$ against aging compared to the other filler systems. The use of a silica-silane filler system in the NR/HC LCB BR blend results in covalent filler-rubber interaction by the comparatively stable coupling agent link. As the covalent bonds are thermally very stable and not prone to scission and rearrangements, this leads to better retention of tensile strength, EAB, M100% and $\tan \delta$ when compared to the pure CB-filled and CB/SI-filled vulcanizates. Based on the superior mechanical and dynamic properties after aging, pure SI-filled NR/HC LCB BR is preferentially recommended for use in aircraft tire retreads.

8.1 INTRODUCTION

Aircraft (AC) tires are exposed to high forces during takeoff and landing. During taxiing and takeoff the deflection may reach more than 30%, and on landing 45% deflection or more occur under impact conditions [1]. The most extreme conditions are present during landing due to a significant difference between the tangential velocity of the tire and the high speed of the heavy aircraft at touchdown.

The tires are forced to accelerate from zero to fully free rolling velocity in 0.1 seconds. At slipping, when the rotational velocity of the tire does not yet match the required tangential velocity in order to acquire free-rolling, the temperature of the tread can reach 190°C [2]. However, the largest amount of heat is generated when the tire is in full skidding. During skidding, the rotational velocity of the tire is zero, while it is in contact with the runway. Early research by NASA shows that the tread temperature in this case can instantaneously reach 315°C [2]. The temperature of the tread rubber is a function of friction and skidding speed [3]; there is no way to avoid either one at landing. Slipping and skidding cause a high accumulation of heat, enough to degrade the rubber locally [4].

The temperature increase causes degradation of the rubber. During degradation, double bonds break open [5]. These can lead to hardening or softening of the material, depending on the polymer. Degradation leads to a change in mechanical and dynamic properties as well as accelerated treadwear which is undesirable. As a consequence, tires need to be retreaded frequently or exchanged by new ones. Aircraft tires are in general retreaded seven or more times [6]. The tread has to be replaced with a new one after only a few hundred cycles. Less retreading and replacement of tires will reduce maintenance costs and downtime. Additionally, there is much pollution of particular matter by the degradation of the tread. Therefore, a rubber material with excellent dynamic and mechanical properties and a high stability against aging is desirable.

Commonly Natural Rubber/Butadiene Rubber (NR/BR) based blends are used in AC tire tread formulations. At high service temperatures, this type of blend undergoes rapid mechanical and dynamic property changes that can decrease the performance of the tread. In the present study of this thesis, selected rubber vulcanizates from previous chapters are aged to gain insight into the consequences of accelerated aging at temperatures close to the service conditions of AC tires.

8.2 EXPERIMENTAL

8.2.1 MATERIAL AND COMPOUND PREPARATION

Two series of rubber formulations were used for the aging study. In the first part of this investigation, blends of NR with various types of BR reinforced with a CB/SI-filled system were evaluated concerning their aging properties. The rubber ingredients used in this study were: NR: RSS#1, and four types of BR: High-Cis BR (HC BR), High-Cis Long-Chain Branched (HC LCB BR), Low-Cis star branched BR (LC BR), and High-Vinyl BR (HV BR). The different BR-types have been extensively detailed in Chapter 6. In the second part of this investigation, the NR/HC LCB BR blend was used with three different filler systems: CB, 60/40 CB/SI, and pure SI.

For the first part of this investigation, the rubber formulation is shown in Table 6.3 in Chapter 6. The CB/SI-filled NR/BR blends were prepared using the two-step mixing procedures as described in Chapter 5, with Zinc Oxide added in the first stage of mixing (Z1), and DPG added in the second stage of mixing (D2).

For the second part of the investigation, the formulations for the NR/HC LCB BR blend reinforced with different filler systems were specified in Table 7.6 in Chapter 7, for CB-C, CB/SI-C, and SI-C. The mixing procedure was also described in Chapter 7.

8.2.2 TESTING OF COMPOUND AND VULCANIZATE PROPERTIES

Thermal degradation - The raw rubbers were tested concerning thermal degradation using a Thermo Gravimetric Analyzer (TGA). About 8 to 15 mg of the sample was placed in a platinum pan. Analyses were performed under oxygen flow. The heating rate for the cycles was 7°C/min from 30 to 850°C.

Aging – The specimens were aged by making use of a hot-air oven. For stress-strain properties, specimens in the form of dumbbells type 2 were employed as described in ASTM 412, and for dynamic properties in tension the specimens used were according to DIN 53513. The specimens were placed in the hot-air oven at a temperature of 200°C for a specific time. The duration of aging was represented as the number of cycles. One cycle consisted of 5 mins of aging (representing aircraft takeoff), 30 mins of rest at room temperature, 5 mins of aging (representing landing). These conditions were chosen to mimic the actual service conditions.

Tan δ – Measurements were performed using a GABO Dynamic Mechanical Analyzer in a temperature sweep between 20°C and 120°C, with 1°C/min increase rate at a dynamic strain of 3% and a static strain of 3%, a frequency of 10 Hz, in tension mode.

All rubber vulcanizates were tested for tensile strength, Elongation at Break (EAB), Modulus at 100% elongation (M100%), apparent crosslink density and $\tan \delta$ at 100°C before and after aging. The stress-strain properties were tested using the procedure as described in Chapter 3. Apparent crosslink density measurements were performed using the method described in Chapter 4.

8.3 RESULTS AND DISCUSSION

Thermogravimetry curves are depicted in Figure 8.1. Pure NR shows the lowest thermal stability as NR starts to degrade at temperature of around 150°C. Different from NR, for which the thermal degradation is dominated by chain scission, the degradation of BR predominantly occurring by crosslinking of two radicals generated when BR is heated in the presence of oxygen. Figure 8.2 depicts the general mechanism of thermal degradation of elastomers including BR. HV BR shows higher thermal stability than the other types of BR. This is due to the fact that HV BR has many tertiary carbon atoms in addition to allylic hydrogen functionalities compared to the other three BR's. The hydrogen atom indicated with a * opposite of the 1,2-vinyl units is the easiest to be removed, and the carbon will be oxidized easily to generate more crosslinks than cis-1,4 or trans-1,4 units: Figure 8.3. Additionally, the 1,2-vinyl group itself is prone to react with oxygen radicals of all sorts, like given in Figure 8.2, to result in multiple crosslinks per radical. Altogether HV BR strongly tends to crosslinking upon aging, whereas the other three do not. The rapid weight loss of the other three BR's above 450°C is due to the increase of volatile decomposition species produced and a corresponding decrease in molecular weight of these BR's.

Figure 8.1 Thermogravimetry curves of NR and four types of BR.

Initiation

Propagation

Termination

Figure 8.2 Thermal oxidative degradation mechanism of rubber [5].

Figure 8.3 Structures of BR [7].

Figures 8.4(a)-(b) show the tensile strength and EAB of CB/SI-filled NR blends with the various types of BR. Tensile strength and EAB of the vulcanizates decrease rapidly at the beginning of aging, and as aging continues the values gradually decrease further. NR/HV BR shows a slightly higher tensile strength but lower EAB compared to the other types of BR.

Figure 8.4 Tensile strength (a); EAB (b) of CB/SI filled NR blends with different types of BR as a function of aging cycles.

NR generally has a lower thermal stability than BR: Figure 8.1. Therefore, at 200°C and in the presence of oxygen, NR degrades already at the beginning of the aging procedure. Chain scission is more dominant in NR than re-crosslinking of polymers. In the presence of oxygen and accelerated by heat, an intermediate cyclic structure is formed in NR. Subsequent breakage of labile oxygen-oxygen bonds leads to chain scission and shorter polymer chains with carbonyl end groups [8]. The mechanism of NR softening/degradation is shown in Figure 8.5. NR contributes more to the tensile strength of the blend vulcanizates compared to BR due to its strain-induced crystallization. Therefore, when the NR degrades rapidly in the beginning of aging up to 5 cycles, the tensile strength decreases rapidly. For all types of BR crosslinking is more dominant than chain-scission: Figure 8.2. Consequently, the ratio of crosslinking to chain scission for all NR/BR blends increases as aging proceeds, but new chains created are shorter than the initial chain lengths. An increase of network density and more shorter chains lead to an overall decrease of tensile strength and flexibility, hence a lower EAB.

 

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Figure 8.7 M100% versus apparent crosslink density of CB/SI filled NR blends with different types of BR.

On comparing the differences in aging for the four different BR's in this first part of the investigation, primarily on basis of decay in tensile strength and M100%-data, the High-Vinyl BR (HV BR) performs just a little better than the other three, although the differences are marginally small.

For the second part of this investigation with the High-Cis Long-Chain Branched BR (HC LCB BR) and variation in the filler systems: CB, CB/SI and pure SI, Figure 8.8 shows the stress-strain properties of vulcanizates as a function of aging. As aging proceeds, the SI-filled NR/HC LCB BR vulcanizate exhibits a slightly higher tensile strength and EAB compared to CB/SI- and CB-filled vulcanizates. The CB-filled rubber clearly performs worst. Similar to what was already seen in Figure 8.6(a), Figure 8.9(a) shows even clearer that M100% decreases in the beginning of aging, but later on increases again. As stated before, the governing principle is that the ratio of crosslinking to chain scission rises as the number of aging cycles increases: Figure 8.9(b). But the new network chains created become shorter than the initial chain length accompanying the increase in network density. The shorter network-chains lead to the decreases in tensile strength and EAB. As seen in the first part of this study, there is again a strong dependence of M100% on apparent crosslink density, with a higher apparent crosslink density going together with a higher M100%: Figure 8.10.

Figure 8.8 Tensile strength (a); EAB (b) of vulcanizates with different filler systems as a function of aging cycles.

The differences in apparent crosslink densities as shown in Figure 8.9(b) result from the contribution of polymer-polymer crosslinks and filler-polymer interactions. Although all filler systems result in comparable apparent crosslink densities, SI-vulcanizates show slightly superior stress-strain properties compared to the other filler systems. The noticeable difference between silica and CB lies in the type of interaction with the polymers. In the SI-filled material, the filler-rubber interaction is derived from covalent bonds between silica and the polymers via the silane coupling agent. In CB-filled rubber, two mechanisms of filler-rubber interaction are commonly proposed: the first mechanism is adsorption in which Van der Waals forces and chemisorption play the main roles [9]. The second mechanism states that bound rubber formation is attributed to a chemical process. It is based on the assumption that functional groups present on the CB surface can react with the rubber [10, 11], and/or by the reaction of rubber radicals formed by mechano-chemical degradation with the active sites of CB during mixing [12, 13]. In the CB/SI-filled polymer, filler-rubber interaction comes from the combination of chemical and physical bonds.

Altogether this series of experiments shows that pure SI rubber and somewhat less CB/SI material perform significantly better than pure CB-filled vulcanizates in terms of aging on basis of tensile strength and EAB. As to M100% and apparent crosslink density, no significant differences are seen as these two are mutually related.

Figure 8.9 M100% (a); apparent crosslink density (b) of vulcanizates with different filler systems as a function of aging cycles.

Figure 8.10 Apparent crosslink density versus M100% of vulcanizates with different filler systems.

Figure 8.11 shows the hardness as a function of aging cycles for both series of experiments combined: Figure 8.11(a) for the first series with variation in BR, and Figure 8.11(b) for the second series with variation in the filler system. The hardness of vulcanizates rises as aging increases. As hardness is directly related to modulus, the curves show the same trends as M100% and apparent crosslink density: the higher the extent of crosslinking, the higher the hardness. NR/HV BR shows a slightly higher hardness compared to the other types of BR: Figure 8.11(a), like for the M100% in Figure 8.6(a), due to the higher apparent crosslink density in Figure 8.6(b). Vulcanizates with different filler systems show comparable hardness as shown in Figure 8.11(b). The latter results are in line with the apparent crosslink density as depicted in Figure 8.9(b). Figures 8.12(a) and (b) show the dependences of hardness on apparent crosslink density for both series of investigations.

Figure 8.11 Hardness of CB/SI filled NR blends with different types of BR (a); hardness of NR/HC LCB BR reinforced with different filler systems (b) as a function of aging cycles.

Figure 8.12 Apparent crosslink density versus hardness of: CB/SI filled NR blends with different types of BR (a); NR/HC LCB BR reinforced with different filler systems (b).

The $\tan \delta$ at 100°C values derived from the temperature sweep by DMA of vulcanizates with different types of BR as a function of aging is shown in Figure 8.13(a). The $\tan \delta$ at 100°C was earlier used as indicator of Heat Build-Up (HBU). The values of $\tan \delta$ for the different types of BR are highly influenced by crosslink density. The $\tan \delta$ of NR/HV BR is the lowest among the other vulcanizates. This is in correspondence with the strongest crosslinking reactivity of HV BR compared to other types of BR, as seen before: Figure 8.6(b).

For the second series of experiments using the same rubber but different filler systems, the $\tan \delta$ of the vulcanizates reinforced by silica shows the lowest value compared to the two other filler systems as shown in Figure 8.13(b). As explained earlier, the interaction between filler and polymers in SI-filled rubber is mainly covalent of nature. Therefore, SI-filled compounds exhibit lower $\tan \delta$ compared to the other filler systems.

The inverse trend between $\tan \delta$ and apparent crosslink density is shown in Figures 8.14(a)-(b). When the vulcanizates have densely crosslinked networks, the rubber chain mobility becomes highly restricted, less friction between polymer chains occurs, thus resulting in low $\tan \delta$. The added covalent bonding of the SI-filler to the polymer clearly shows in the relatively low $\tan \delta$ values versus apparent crosslink density in Figure 8.14(b).

Figure 8.13 $\tan \delta$ of: CB/SI filled NR blends with different types of BR (a); NR/HC LCB BR reinforced with different filler systems (b) as a function of aging cycles.

Figure 8.14 Apparent crosslink density versus $\tan \delta$ of: CB/SI filled NR blends with different types of BR (a); NR/HC LCB BR reinforced with different filler systems (b).

8.4 CONCLUSIONS

The aging properties of aircraft tire retreads were studied in the present chapter. In the first part, CB/SI-filled vulcanizates with different types of BR in blends with NR were compared. The NR/HV BR blend filled with CB/SI shows the highest stiffness as indicated by M100% and lowest $\tan \delta$ after aging compared to other types of BR in the blend. Crosslink density was assigned as the main governing property changing significantly during aging. At the high temperature of aging of 200°C, close to the temperature of the AC tire tread during service, the 1,2 vinyl-BR becomes extra reactive, resulting in a rising crosslink density after a prior decrease of the blend with NR, which in turn leads to high M100% and otherwise low $\tan \delta$. NR/HV BR therefore does show low HBU, the opposite point is that the rubber may become too stiff and hence lose more ductility after aging than the alternative three BR's. Therefore, it is less recommended for AC tire retreads.

In the second part of this study, the aim was to improve the aging properties of the NR/HC LCB BR blend with varied filler systems. High-cis BR was chosen as this is by far the most common type of BR used in aircraft tire tread formulations. SI-filled NR/HC LCB BR turned out to be the most promising rubber formulation since it shows better aging properties with higher tensile strength and EAB compared to the other systems. The $\tan \delta$ of the SI-reinforced rubber is the best, not only due to the crosslinking density but also due to a high silanization efficiency leading to high density of chemical filler-rubber bonds. A NR/HC LCB BR blend with a SI-filler therefore is the most suitable candidate for use in AC tire retread applications.

8.5 REFERENCES

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SUMMARY

Aircraft (AC) tires are one of the primary components in an aircraft that have to undergo frequent replacement due to the harsh operating conditions. It is common practice to retread AC tires several times in order to reduce operating costs. To extend the service life of the AC tire tread, it is of utmost importance to optimize the performance. The key requirements are low hysteresis, excellent tensile and tear strength, high wear resistance, good adhesion to the reinforcing fabric, and good retreadability. The goals of the thesis are to develop an AC tire tread rubber with good processability and high tackiness for good retreadability, additionally to tailor the above-mentioned properties. A balanced performance in terms of low heat generation, which is associated with hysteresis, and high aging resistance with low loss in properties has to be achieved.

An introduction into AC tires including retreading, the background and the aim of the thesis are given in **Chapter 1**. A literature review on the development of AC tires/retreaded tires, the structure of these tires, the service conditions, the retreading process and the procedure for testing and certification as well as other topics related to AC tire treads/retreads are discussed in the following chapter. The types of rubber and fillers, vulcanization systems and resins used in the formulations, as well as a few examples of compounding of AC tire treads based on patents are also presented in **Chapter 2**.

The experimental part starts in **Chapter 3** by defining key factors of NR/BR based blends reinforced with Carbon Black (CB) to optimize the properties of AC tire treads. Four factors are selected, namely type of Butadiene Rubber (BR), mixer set temperature, rotor speed, and mixing time. A Design of Experiments (DOE) evaluation is utilized, consisting of a two-level full factorial setup for initial screening, Response Surface Method (RSM) for optimization, and validation runs for confirmation. It is revealed that rotor speed and mixing time are the most significant factors that considerably improved Mooney viscosity, modulus at 300% elongation (M300%), hysteresis/tan δ at 100°C as well as reduced Payne Effect. A high mixer set temperature has an adverse effect on tensile strength, hence a low temperature is preferable. Improvement in processability and filler dispersion are achieved by the use of High-Cis Long-Chain Branched BR (HC LCB BR) compared to High-Cis BR (HC BR), and the rubber has a low tan δ while still maintaining acceptable stress-strain properties.

Silica-silane filler systems have been employed in Passenger Car Tires (PCT) to replace CB in the tread compounds aiming at lower Rolling Resistance (RR), increased Wet Skid Resistance (WSR) and comparable abrasion resistance. Due to the excessive heat generation in AC tire treads during service, it is crucial to lower the hysteresis in order to lengthen the

service life of the treads. With the goal of further decrease in hysteresis, silica-silane is utilized in the AC tread compounds. To optimize the properties of the retreads for these tires, four factors are investigated in **Chapter 4**. These are the type of BR: HC BR and HC LCB BR, type of filler: CB/SI and SI, silanization temperature and time. The results show that there is a strong dependence of the properties on the silanization temperature and time. A high degree of silanization is important to enhance the hydrophobation of the silica by the silane, bis-(TriEthoxySilylPropyl) Tetrasulfide (TESPT), used as coupling agent. The use of HC LCB BR results in better processability by lowering the viscosity, and a more efficient silanization causes a lower Payne Effect (PE) compared to the HC BR counterpart. High filler-rubber interaction of HC LCB BR leads to a higher crosslink density, lower $\tan \delta$ at 100°C, and higher modulus at 300% elongation as well as tensile strength compared to those based on HC BR. CB/SI-filled vulcanizates show slightly better stress-strain properties, but $\tan \delta$ at 100°C is higher compared to the SI-filled vulcanizates, indicative for higher hysteresis and heat build-up of corresponding retreads..

The use of silica in combination with CB in rubber compounds shows potential to lower the hysteresis compared to compounds with CB as the only filler. When silica is incorporated in rubber compounds, the silanization reaction has to occur in order to create a covalent bond between silica and rubber through the coupling agent. Zinc Oxide (ZnO) and DiPhenyl Guanidine (DPG) are known as rubber ingredients which can influence the silanization reaction. **Chapter 5** focuses on the effect of the addition sequence of these two additives during mixing of AC tire retread compounds. The addition of ZnO in the first stage of mixing of NR/BR based blends improves the processability by lowering the Mooney Viscosity (MV) of the compounds and results in a low Payne effect as indication of a low degree of filler-filler interaction. The addition of ZnO in the last stage of mixing results in a high filler-rubber interaction, signaling a high silanization efficiency. However, due to low reversion resistance, these vulcanizates undergo a stronger reduction in crosslink density compared to the vulcanizates with early addition of ZnO. This occurs during curing, but also during service life. The addition of DPG in the last stage of mixing causes a short cure time and increases filler-rubber interaction. Low $\tan \delta$ at 100°C and 200°C is achieved, when ZnO is added in the first stage of mixing and DPG in the last step. This addition sequence turns out to be the most promising way to optimize properties in mixing NR/BR based AC tire tread/retread compounds.

High-cis BR is the most common type of BR used in tire tread compounds, including AC tire treads/retreads. BR with a cis-content of more than 95 wt% is known for superior wear and cut growth resistance. Nevertheless, the balance between traction, hysteresis and stress-strain properties is also crucial for AC tire treads. Butadiene rubbers with different molecular architectures: High-Cis BR (HC BR), High-Cis Long-Chain Branched BR (HC LCB BR), Low-Cis star branched BR (LC BR), High-Vinyl BR (HV BR) are investigated in **Chapter 6**. The objective is to investigate the effect of the macro- and micro-structures of these BRs on the performance of AC tire retreads in terms of the above-mentioned properties. The compounds are based on NR/BR blends reinforced with CB/SI. NR/HC LCB BR and NR/LC BR show better processability

due to the effect of branching. NR blends with HC BR or HC LCB BR show shorter cure time, higher strength as well as increased apparent crosslink density. $\tan \delta$ at 100°C turns out to be lower compared to NR blends with LC BR or HV BR. This is due to the fact that cis-1,4 units show a higher reactivity towards TESPT used as coupling agent, which results in a lower Payne effect and higher filler-rubber interaction compared to a BR type with a high percentage of trans-1,4 and 1,2-vinyl units. The difference between NR/HC LCB BR and NR/HC BR concerning their effect on $\tan \delta$ at 100°C is seen at low frequency, in which the former shows a slightly lower $\tan \delta$ than the latter due to branching. At a temperature of 200°C, which can occur on the surface of AC tire treads during landing, NR/HV BR has the lowest $\tan \delta$. NR/HV BR shows a higher reversion resistance which leads to a higher crosslink density at the service temperature compared to the other types of BR. HV BR blends with NR disclose their potential for use in AC tire retread applications, since they provide a low $\tan \delta$ at 200°C as an indication of low heat build-up (HBU).

Retreading of AC tires is the most effective way to reduce the operation costs. For the new tread compound to be able to adhere properly to the carcass of the tire to be retreaded, and to retain the shape before curing, the compound should have high tackiness and green strength. Oligomeric resins are known as tackifiers. **Chapter 7** investigates the effect of resins on tackiness and other properties of AC tire retreads. Two types of resin: terpene phenol and aromatic hydrocarbon C9 resin are added to compounds with three different filler systems: CB, CB/SI, and SI. The addition of these resins slightly increases tensile strength, M300% and Elongation at Break (EAB), independent of the filler system. The use of resins improves the tackiness of the compounds for each of the filler systems, which is beneficial for the retreading process. In the AC tire tread formulations used in the present project, the use of terpene phenol and aromatic C9 resin shows significant improvements in Ice Traction (ICT) and WSR for the three filler systems. Both resins result in comparable ICT, while the C9 resin provides a better WSR than the terpene phenol. A significant improvement of about 50% in $\tan \delta$ at 100°C as an indication of HBU is observed when switching from CB to the SI filler system. When resins are additionally used, only a slight improvement in HBU is observed in the SI-filled system. The use of resins not only improves processing and tackiness of the compounds, an important factor for the retreading process, but also shows promising results in terms of mechanical as well as dynamic properties of AC tire retreads.

The temperature reached on the surface of AC tire treads during service is so high that it can degrade the rubber. Degradation leads to a change in mechanical and dynamic properties as well as accelerated tread wear, which is unwanted. Accelerated aging at a temperature of 200°C, which is close to the service temperature of the AC tire tread during landing, is investigated in **Chapter 8** to see the performance of the tread rubber in terms of stress-strain properties, hardness, and $\tan \delta$ during its lifetime. In the first investigation, NR is blended with different types of BR: HC BR, HC LCB BR, LC BR and HV BR and reinforced with CB/SI. The vulcanizates of these compounds were aged in a hot air oven and underwent specific aging cycles. Crosslink density was determined as the main property change during

aging. At an aging temperature of 200°C, the 1,2 vinyl-BR becomes highly reactive, resulting in a rising crosslink density after a prior decrease, which in turn leads to higher M100% and lower $\tan \delta$. NR/HV BR, therefore, does show low HBU; the downside is that the rubber may become too stiff and hence loses ductility to a higher degree after aging than the material with the alternative three BR's. Therefore, this BR type is less recommended for AC tire retreads. Among the different filler systems investigated in the second part, silica in a NR/HC LCB BR blend is proven to be the most favorable combination since it exhibits excellent aging properties with higher tensile strength and EAB compared to the other materials. The $\tan \delta$ of the SI-reinforced rubber is the lowest, not only due to the crosslink density but also due to a high silanization efficiency leading to a high density of chemical filler-rubber bonds. An NR/HC LCB BR blend with silica as only filler, therefore, is the most promising candidate for use in AC tire retread applications.

This thesis confirms the importance of the correct selection of rubber ingredients as well as processing parameters to optimize the properties of AC tire retreads. It was revealed that the determination and optimization of the most significant factors in the mixing process can effectively enhance the properties of AC tire retreads. DOE was proven to be a useful tool to elaborate the significant parameters which influence the properties of AC tire retreads. Hence DOE was utilized not only to predict the properties, but also to optimize them effectively. The correct addition sequence of ZnO and DPG can improve the properties of rubbers containing silica. The use of HC LCB BR can significantly improve the processability and the dispersion of fillers. The combination of HC LCB BR and silica as reinforcing filler can lower the hysteresis which is of crucial importance for AC tire treads. The aging properties also improve considerably when silica is added while maintaining high stress-strain properties. Tackiness can be enhanced by the incorporation of resins which is beneficial in the retreading process. The current investigatory study on the addition of resins shows a significant improvement in the overall performance of AC tire retreads, justifying more in-depth investigations into this possibility in real tires. Overall, from a technological point of view, the outcome of the thesis will be valuable as guiding principles for the further optimization of retread rubber for AC tires.

SAMENVATTING

Banden vertegenwoordigen een van de belangrijkste componenten van een vliegtuig, die regelmatig vervangen moeten worden vanwege de uiterst zware belastingen. Het is gebruikelijk om vliegtuigbanden meerdere malen van een nieuw loopvlak te voorzien omwille van de hoge kosten van nieuwe banden. Om de levensduur van het loopvlak van vliegtuigbanden te verlengen, is het noodzakelijk om hun belangrijkste functionele eigenschappen te optimaliseren. De belangrijkste eisen zijn lage hysteresis, uitstekende trek- en scheursterkte, hoge slijtvastheid, goede hechting aan de versterkende koorden in het karkas en goede vernieuwbaarheid. De doelstelling van dit proefschrift was de ontwikkeling van rubber geschikt voor loopvlakvernieuwing van vliegtuigbanden, welke aan bovenstaande eisen voldoet, met goede verwerkbaarheid en hoge tack (spontane hechting bij het aanbrengen op het karkas voorafgaand aan vulkanisatie). Daarnaast moeten de gevolgen van veroudering beperkt blijven, zoals constante trek-rek-eigenschappen.

Een inleiding in het thema vliegtuigbanden inclusief loopvlakvernieuwing, de achtergrond en het doel van het proefschrift worden gegeven in **Hoofdstuk 1**. Een literatuuroverzicht over de ontwikkeling van vliegtuigbanden, de structuur van deze banden, de gebruiksomstandigheden, het vernieuwingsproces en de procedure voor testen en certificeren worden in **Hoofdstuk 2** besproken, naast andere onderwerpen die verband houden met vliegtuigbanden. De soorten rubber en vulstof, vulkanisatiesystemen en harsen die in de formuleringen worden gebruikt; enkele voorbeelden van compounding van loopvlakken voor vliegtuigbanden op basis van patenten worden ook beschreven in dit hoofdstuk.

Het experimentele deel begint in **Hoofdstuk 3** met het definiëren van de sleutelfactoren van mengsels gebaseerd op NR/BR en versterkt met Roet/Carbon Black (CB), om de eigenschappen voor gebruik in loopvlakken van vliegtuigbanden te optimaliseren. Er worden vier factoren gekozen, namelijk het type Butadiëen Rubber (BR), mengtemperatuur, rotorsnelheid en mengtijd. Er wordt gebruik gemaakt van Design of Experiments (DOE) bestaande uit een 'two level full factorial setup' voor initiële screening, 'Response Surface Method' (RSM) voor optimalisatie en validatieruns om de uitkomst te toetsen. In dit deel van het onderzoek wordt duidelijk, dat rotorsnelheid en mengtijd de belangrijkste factoren zijn om Mooney-viscositeit, Modulus bij 300% rek ($M_{300\%}$), en hysteresis/ $\tan \delta$ bij 100 °C aanzienlijk te kunnen verbeteren, evenals het Payne-effect. Een hoge mengtemperatuur heeft een nadelige invloed op de treksterkte en daarom verdient een lage mengtemperatuur de voorkeur. Verbetering van de verwerkbaarheid en een hogere dispersiegraad van de vulstof worden bereikt door het gebruik van High-Cis Long-Chain Branched Butadiëen Rubber (HC

LCB BR) in plaats van High-Cis BR (HC BR), waarbij het rubber een lage $\tan \delta$ heeft met behoud van goede trek-rek eigenschappen.

Silica-silaan vulstof systemen worden gebruikt voor personenwagenbanden in plaats van CB met als doel een lagere rolweerstand, verhoogde natte slipweerstand (WSR) en vergelijkbare slijtvastheid. Vanwege de overmatige warmteontwikkeling in het loopvlak van vliegtuigbanden tijdens gebruik is het van belang om de hysteresis te verlagen en zo de levensduur van het loopvlak te verlengen. Om de hysteresis te verminderen werd silica-silaan in plaats van roet als vulstof gebruikt in de vliegtuig-loopvlak compounds in **Hoofdstuk 4**. Voor verdere optimalisatie van de eigenschappen van de loopvlakken voor hernieuwing van vliegtuigbanden werden vier factoren onderzocht. Dit zijn het type BR: HC BR en HC LCB BR, het type vulstof: CB/SI en SI, de silanisatie-temperatuur en -tijd. De resultaten tonen aan dat het eigenschappenprofiel sterk afhangt van de silanisatie-omstandigheden. Een hoge silanisatiegraad is van doorslaggevend belang om hydrofobering van het silicaoppervlak door het silaan te bewerkstelligen. In het huidige onderzoek is bis-(TriEthoxySilylPropyl)Tetrasulfide (TESPT) als 'coupling agent' gebruikt. Wordt HC LCB BR als polymeer gebruikt, dan resulteert dit in een betere verwerkbaarheid door verlaging van de viscositeit. Daarnaast verloopt de silanisatie efficiënter, wat resulteert in een lager Payne Effect (PE) in vergelijking met de HC BR-tegenhanger. Hoge vulstof-rubber interacties van HC LCB BR-mengsels leiden tot een hogere netwerkdichtheid, lagere $\tan \delta$ bij 100 °C, hogere modulus bij 300% rek ($M_{300\%}$) en hogere treksterkte in vergelijking met de eigenschappen die met HC BR worden gehaald. Met CB/SI gevulde vulkanisaten vertonen iets betere trek-rek eigenschappen, maar de $\tan \delta$ bij 100 °C is hoger in vergelijking met de SI-gevulde vulkanisaten, aanwijzing voor een hogere hysteresis en warmte-ontwikkeling van desbetreffende loopvlakken gedurende de landing. Het gebruik van silica in combinatie met roet toont mogelijkheden om de hysteresis te verlagen ten opzichte van alleen roet als vulstof.

Wanneer silica als versterkende vulstof wordt gebruikt, moet een silaniserings-reactie plaatsvinden om een covalente binding te creëren tussen silica en rubber door middel van het silaan. ZinkOxide (ZnO) en DiPhenyl Guanidine (DPG) staan bekend als rubberingrediënten die de silaniserings-reactie kunnen beïnvloeden. **Hoofdstuk 5** richt zich op het onderzoeken van het effect van de volgorde van toevoeging van deze twee additieven tijdens het mengen van loopvlak-rubber mengsels. De toevoeging van ZnO in de eerste mengfase van mengsels op basis van NR/BR verbetert de verwerkbaarheid door de Mooney-viscositeit (MV) te verlagen, en resulteert in een laag Payne-effect als aanwijzing voor een lage vulstof-vulstof interactie. De toevoeging van ZnO in de laatste mengfase daarentegen resulteert in een hoge vulstof-rubber interactie, wat duidt op een hoge graad van silanisering. Door een hoge mate van reversie vertonen deze vulkanisaten echter een sterkere vermindering van de netwerkdichtheid in vergelijking met de vulkanisaten waarbij de toevoeging van ZnO in de eerste mengfase heeft plaatsgehad. Dit fenomeen zal zich ook voordoen tijdens het gebruik van de band, wanneer de temperatuur van het loopvlak stijgt bij de landing. De toevoeging van DPG in de laatste mengfase zorgt voor een korte vulkanisatietijd en verhoogt de interactie

tussen vulstof en rubber. Een lage $\tan \delta$ bij 100 °C en 200 °C wordt bereikt wanneer ZnO wordt toegevoegd in de eerste en DPG in de laatste mengfase. Deze volgorde bleek de meest veelbelovende manier om optimale op NR/BR gebaseerde mengsels voor loopvlakken van vliegtuigbanden te produceren.

BR met een hoog cis-gehalte is het meest gebruikte type BR in de rubbersamenstellingen van banden, met inbegrip van loopvlakken voor vliegtuigbanden. BR met een cis-gehalte van meer dan 95 gew.% staat bekend om zijn superieure scheursterkte en weerstand tegen slijtage. De balans tussen tractie, hysteresis en trek-rek eigenschappen is cruciaal voor het loopvlak van vliegtuigbanden. Butadiëen rubbers met verschillende moleculaire architecturen: High-Cis BR (HC BR), High-Cis Long-Chain Branched BR (HC LCB BR), Low-Cis star branched BR (LC BR), High-Vinyl BR (HV BR) zijn het onderwerp van **Hoofdstuk 6**. Het doel was om het effect te onderzoeken van de macro- en microstructuren van deze BR's op de prestaties van vernieuwde bandenloopvlakken met betrekking tot bovengenoemde eigenschappen. De mengsels zijn gebaseerd op NR/BR-blends versterkt met roet of silica. NR/HC LCB BR en NR/LC BR vertonen betere verwerkbaarheid door het effect van 'branching'/vertakking. NR-mengsels met HC BR of HC LCB BR laten een kortere vulkanisatietijd zien en een hogere treksterkte naast verhoogde netwerkdichtheid. De $\tan \delta$ bij 100 °C is lager in vergelijking met NR-mengsels met LC BR of HV BR. Dit komt door het feit dat cis-1,4-eenheden een hogere reactiviteit vertonen richting TESPT dat wordt gebruikt als koppelmiddel (coupling agent). Dit resulteert in een lager Payne-effect en een hogere vulstof-rubber interactie in vergelijking met een BR-type met een hoog percentage trans-1,4 en 1,2-vinyl-eenheden. Het verschil tussen NR/HC LCB BR en NR/HC BR betreffende hun effect op $\tan \delta$ bij 100 °C komt naar voren bij lage frequenties, waarbij de eerste een iets lagere $\tan \delta$ laat zien dan de laatste vanwege 'branching'. Bij een temperatuur van 200 °C, een temperatuur die tijdens het landen van een vliegtuig in het loopvlak van de banden kan optreden, heeft NR/HV BR de laagste $\tan \delta$. NR/HV BR vertoont een lagere reversie wat leidt tot een hogere netwerkdichtheid bij de gebruikstemperatuur in vergelijking met de andere BR typen. HV BR-mengsels met NR tonen hun potentieel voor gebruik ten behoeve van vernieuwde loopvlakken voor vliegtuigbanden, aangezien zij een lage $\tan \delta$ bij 200 °C vertonen als indicatie voor lage warmteopbouw (HBU).

Het vernieuwen van vliegtuigbanden is de meest effectieve manier om kosten te besparen. Om ervoor te zorgen dat nieuwe loopvlakrubber goed hecht aan het oude karkas en zijn vorm behoudt voordat deze is ge vulkaniseerd, moet het mengsel een hoge 'tack'/eigenkleverigheid en 'green strength' bezitten. Oligomere harsen staan bekend als kleefmiddelen. **Hoofdstuk 7** onderzoekt het effect van harsen op de eigenkleverigheid en andere eigenschappen van belang voor loopvlakken van vernieuwde vliegtuigbanden. Twee soorten harsen: een terpeenfenol en een aromatische koolwaterstof C9-hars worden toegevoegd aan mengsels met drie verschillende vulstof-systemen: CB, CB/SI en SI. De toevoeging van deze harsen verhoogt de treksterkte enigszins, resp. de modulus 300% en de rek bij breuk (EAB), onafhankelijk van de gebruikte versterkende vulstof. Het gebruik van harsen verbetert de eigenkleverigheid van de mengsels met elk van de vulstoffen, wat gunstig

is voor het vernieuwingsproces. In de formuleringen van het loopvlak voor vliegtuigbanden zoals in dit project gebezigd, laat het gebruik van terpeenfenol en aromatische C9-hars een significante verbetering zien in Ice Traction (ICT) en Wet Skid Resistance (WSR) voor de drie vulstoffen. Beide harsen resulteren in vergelijkbare Ice Traction, terwijl de C9-hars een betere WSR geeft dan de terpeenfenol. Een significante verbetering van ongeveer 50% in $\tan \delta$ bij 100 °C als aanwijzing voor verlaagde HBU wordt gemeten als roet vervangen wordt door silica. Een lichte verbetering in HBU bij gebruik van beide harsen in vergelijking met een mengsel zonder hars wordt alleen waargenomen in de SI-gevulde rubber. Het gebruik van harsen verbetert niet alleen de verwerking en eigenkleverigheid van de mengsels - belangrijke factoren voor het vernieuwingsproces - maar levert ook veelbelovende resultaten met betrekking tot zowel mechanische als dynamische eigenschappen van vernieuwingsloopvlakken voor vliegtuigbanden.

De temperatuur, die tijdens het gebruik in het loopvlak van vliegtuigbanden optreedt, is hoog genoeg om tot rubber-degradatie te leiden. Dit geeft een verandering in mechanische en dynamische eigenschappen en versnelde slijtage van het loopvlak, hetgeen ongewenst is. Versnelde veroudering bij een temperatuur van 200 °C bij landing, dicht bij de gebruikstemperatuur van het loopvlak van de vliegtuigband, wordt onderzocht in **Hoofdstuk 8**; met name om de verandering in trek-rek eigenschappen, hardheid en $\tan \delta$ te zien. In het eerste onderzoek wordt NR gemengd met verschillende soorten BR: HC BR, HC LCB BR, LC BR en HV BR; als vulstof wordt CB/SI gebruikt. De vulkanisaten worden verouderd in een hete lucht oven met specifieke verouderingscycli. De netwerkdichtheid blijkt het meest gevoelig te zijn voor veroudering. Bij een verouderingstemperatuur van 200 °C wordt 1,2 vinyl-BR zeer reactief, wat resulteert in een stijgende netwerkdichtheid na een eerdere afname, wat op zijn beurt leidt tot een hogere M100% en lagere $\tan \delta$. NR/HV BR vertoont daarom een lage HBU; het nadeel is dat het rubber te stijf kan worden en daardoor na veroudering in hogere mate z'n ductiliteit verliest dan de materialen met de andere drie BR's. Daarom wordt dit BR-type niet aanbevolen voor rubber voor vernieuwing van vliegtuigbanden. Van de verschillende vulstofsysteemen, die in het tweede deel zijn onderzocht, blijkt silica in een NR/HC LCB BR-mengsel de gunstigste combinatie te zijn, aangezien het uitstekende verouderingseigenschappen vertoont met een hogere treksterkte en EAB in vergelijking met de andere materialen. De $\tan \delta$ van het SI-versterkte rubber is het laagst, niet alleen vanwege de netwerkdichtheid maar ook vanwege een hoge silanisatie-efficiëntie die leidt tot een hoge dichtheid chemische vulstof-rubber bindingen. Een NR/HC LCB BR-blend met silica als vulstof is daarom de meest veelbelovende kandidaat voor gebruik in vernieuwingstoepassingen voor vliegtuigbanden.

Dit proefschrift bevestigt het belang van de juiste keuze van rubberingrediënten en verwerkingsparameters, om de eigenschappen van vernieuwde vliegtuigbanden te optimaliseren. Het is gebleken, dat de vaststelling en optimalisatie van de belangrijkste factoren in het mengproces de eigenschappen van vernieuwde vliegtuigbanden op effectieve wijze kan verbeteren. DOE bleek een nuttig hulpmiddel om de significante parameters uit te werken, die de eigenschappen van vernieuwings-loopvlakken van vliegtuigbanden

beïnvloeden. Daarom werd DOE niet alleen gebruikt om de eigenschappen te voorspellen, maar ook om de eigenschappen te optimaliseren. De juiste volgorde van de toevoeging van ZnO en DPG tijdens mengen beïnvloedt de eigenschappen van rubbers met silica als vulstof, en het gebruik van HC LCB BR kan de verwerkbaarheid en de dispersie van vulstoffen aanzienlijk verbeteren. De combinatie van HC LCB BR en silica kan de hysteresis verlagen, van groot belang voor de HBU van het loopvlak van vliegtuigbanden. Ook de verouderingseigenschappen verbeteren aanzienlijk wanneer silica wordt toegevoegd, terwijl de eigenschappen bij hoge spanning en rek behouden blijven. De 'tack' kan worden verbeterd door het inmengen van harsen, wat gunstig is bij het vernieuwingsproces. Het onderhavige onderzoek aan de toevoeging van harsen laat een significante verbetering zien in de algehele bruikbaarheid van vernieuwde loopvlakken voor vliegtuigbanden. Het rechtvaardigt meer verdiepend onderzoek naar de mogelijkheden voor automobiel-banden. Al met al zal vanuit technologisch oogpunt de uitkomst van het proefschrift waardevol zijn als leidraad voor de verdere optimalisatie van rubber voor vernieuwing van vliegtuigbanden.

SYMBOLS AND ABBREVIATIONS

SYMBOL	DESCRIPTION
$^{\circ}\text{C}$	degrees Celsius
E^*	complex modulus
E''	loss modulus
E'	storage modulus
E_D	atomic dispersion force
E_H	hydrogen bonding
E_P	polar cohesive energy
E	total cohesion energy
E_{coh}	cohesive energy
F	molar attraction constant
$^{\circ}\text{F}$	degrees Fahrenheit
G^*	complex modulus in shear
G''	loss shear modulus
G'	storage shear modulus
$\Delta G'$	difference in storage modulus
ΔH_{vap}	enthalpy of vaporization
m_1	weight of polymer
m_2	weight of solvent in swollen sample
m_r	dry weight of sample
m_f	weight of filler
m_p	weight of rubber in the sample
$\text{ML}(1+4)$	Mooney viscosity after 1 minute of preheating and 4 minutes of measuring, measured with a large rotor
$\text{M}100\%$	modulus at 100% elongation
$\text{M}300\%$	modulus at 300% elongation
$n+$	total number of experiments in level +1
$n-$	total number of experiments in level -1
R	ideal gas constant
S_{min}	minimum torque
S_{max}	maximum torque
$S_{\text{max}}-S_{\text{min}}$	torque difference
S_{final}	torque at final measurement time
T	temperature

$\tan \delta$	loss tangent
T_g	glass transition temperature
t_{90}	time needed to reach 90% vulcanization
ts_2	scorch time (2 dN.m above minimum modulus)
U	molar vaporization energy
V	molar volume
V_2	molar volume of solvent
V_r	volume fraction of rubber
ν	Poisson ratio
X_c	apparent crosslink density
χ	Florry-Huggins parameter
$Y+$	the results of observed response in level +1
$Y-$	the results of observed response in level -1
ρ_1	density of polymer
ρ_2	density of solvent
δ	solubility parameter
$\delta_1 - \delta_2$	the difference in solubility parameter

ABBREVIATION

DESCRIPTION

AC	Aircraft
ANOVA	Analysis of Variance
ANSYS	Analysis System
ARI	Abrasion Resistance Index
ASTM	American Society of Testing Materials
ATR	Aerei da Trasporto Regionale
BET	Brunauer-Emmet-Teller
BR	Butadiene Rubber
CAR	Civil Aviation Regulation
CASA	Civil Aviation Safety Authority
CASR	Civil Aviation Safety Regulations
CB	Carbon Black
CBS	N-Cyclohexyl-2-Benzothiazole Sulfenamide
CCC	Central Composite Circumscribed
Co	Cobalt
CO ₂	Carbon Dioxide
CP	Center Point
CRI	Cure Rate Index
CRJ	Canadair Regional Jet
CTAB	Cetyl-Trimethyl-Ammonium Bromide
CV	Conventional Vulcanization
DBP	DiButylPhthalate

df	degrees of freedom
DGCA	Directorate General Civil Aviation
DIN	Deutsches Institut für Normung
DOE	Design of Experiments
DPG	DiPhenyl Guanidine
EAB	Elongation at Break
EASA	European Aviation Safety Agency
EDX	Energy Dispersive X-ray
ESBR	Emulsion Styrene Butadiene Rubber
EV	Efficient Vulcanization
FAA	Federal Aviation Administration
GIA	Garuda Indonesia Airline
GMF	Garuda Maintenance Facility
GPC	Gel Permeation Chromatography
HAF	High Abrasion Furnace
HBU	Heat Build-Up
HC BR	High-Cis Butadiene Rubber
HC LCB BR	High-Cis Long Chain Branched Butadiene Rubber
HV BR	High-Vinyl Butadiene Rubber
ICT	Ice Traction
IP	Ingress Protection
IPPD	N-Isopropyl-N'-Phenyl-1,4-PhenylenDiamine
IRHD	International Rubber Hardness Degree
ISAF	Intermediate Super Abrasion Furnace
ISO	International Organization for Standardization
LAOS	Large Amplitude Oscillation Strain
LC BR	Low-Cis Butadiene Rubber
Li	Lithium
LPT	Landing per Tread
MBS	2-(4-Morpholinothio)-Benzothiazole
MES	Mild Extracted Solvate
mins.	minutes
Mn	number average molecular weight
MRO	Maintenance Repair and Overhaul
MS	Mean of Squares
Mw	Weight average molecular weight
MWD	Molecular Weight Distribution
MV	Mooney Viscosity
Nd	Neodymium
NDI	Non-Destructive Inspection
NG	Next Generation
Ni	Nickel

NR	Natural Rubber
NSA	Nitrogen Surface Area
OEM	Original Equipment Manufacturer
OFAT	One Factor At a Time
OTR	Off-The-Road
PCT	Passenger Car Tires
PDI	Poly Dispersity Index
PE	Payne Effect
Phr	Parts per hundred rubber
PMA	Part Manufacture Approval
6PPD	N-Phenyl-para-PhenyleneDiamine
p-value	probability value
RLT	Radial Light Truck
RMT	Radial Medium Truck
RPA	Rubber Processing Analyzer
RSS	Ribbed Smoked Sheet
SAF	Super Abrasion Furnace
SBR	Styrene Butadiene Rubber
SEM	Scanning Electron Microscopy
SI	Silica
SS	Sum of Squares
STC	Supplementary Type Certificate
STSA	Statistical Thickness Surface Area
TBS	N-Tert-Butyl-2-Benzothiazole Sulfenamide
TC	Type Certificate
TDAE	Treated Distillate Aromatic Extract
TESPT	bis-(TriEthoxySilylPropyl)Tetrasulfide
TGA	Thermo Gravimetric Analyzer
THF	TetraHydroFuran
Ti	Titanium
TMQ	2,2,4-TriMethyl-1,2-dihydroQuinoline
TP	Terpene Phenol
TS	Tensile Strength
TSO	Technical Standard Order
TSR	Technical Specified Rubber
WLP	Wickert Laboratory Press
WSR	Wet Skid Resistance
ZnO	Zinc Oxide

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Indria

CURRICULUM VITAE

Indriasari was born in Banyumas, Indonesia on April 9, 1979. She obtained her bachelor's degree in chemical engineering from Universitas Pembangunan Nasional "Veteran" Yogyakarta in 2003. Her thesis title was the manufacturing of glycerol from crude palm oil capacity 180,000 tons/year. She worked in several companies from 2003 until 2008. From 2009 until now, she works as a government staff in the Center for Material Technology, the Agency of Assessment and Application of Technology (now the National Research and Innovation Agency). In 2013, she continued her study in chemical engineering, at the University of Twente with the funding from the StuNed scholarship. She received her Master of Science (MSc) degree in 2015 with the thesis on a design of experiments Taguchi approach for studying the effect of selected factors on enhancing bonding of short aramid fibers reinforced rubber compounds at Elastomer Technology and Engineering (ETE) group under the supervision of Prof. Dr. J.W.M. Noordermeer. In 2016, she continued to pursue her PhD at the ETE group with the funding from the scholarship program for Research and Innovation in Science and Technology Project (RISET-Pro).

*Sometimes the best thing
you can do is not think,
not wonder, not imagine,
not obsess.*

*Just breathe and have faith
that everything will work out
for the best
#peacefuldiaries*