SILICA-REINFORCED NATURAL RUBBER: SHIFTING TIRE PERFORMANCE BY HYBRIDIZATION WITH SECONDARY FILLERS AND POLYMERS

Silica-reinforced Natural Rubber (NR) offers modern tires with low rolling resistance and high wet traction indicative for fuel saving and safety, but insufficient abrasion resistance or tire durability. Therefore, the main goal of this project was to further enhance the key performances of silica truck tire tread compounds, especially abrasion resistance. This thesis covers hybrid filler compounds of silica with high specific surface area Carbon Black (CB) N134 or OrganoClay (OC) as secondary fillers as well as hybrid polymer compounds of NR with Butadiene Rubber (BR) or Solution-Styrene Butadiene Rubber (SSBR) as secondary polymers. The silica/CB N134 combination gives an indication for a tire tread compound with improved ice and wet traction, respectively abrasion resistance. Whereas the silica/OC combination provides the indication of a tire tread compound with better rolling resistance and ice traction as well as a little improvement in wet traction and abrasion resistance. The combinations of silica/CB-filled NR/BR and NR/SSBR give an indication for tire tread compounds with a large improvement in ice and wet traction as well as abrasion resistance but poorer rolling resistance. The use of the silica/OC-filled NR/BR and NR/SSBR combination offers the potential to enhance ice traction and abrasion resistance. So overall, the combination of OC and BR with silica-reinforced NR shows the best performance. The mechanistic details of these optimizations are highlighted in this thesis.

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With Secondary Fillers and Polymers

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This research is a joint project between the University of Twente and Prince of Songkla University, sponsored by the Netherlands Natural Rubber Foundation, Apollo Tyres Global R&D, the Netherlands and Prince of Songkla University PhD Scholarship, Thailand.

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SILICA-REINFORCED NATURAL RUBBER:

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CHAPTER 1

Introduction

1.1 Development of silica technology for tires

Tires are built from several components that are made from different types of compounds which contain about 30% by weight of particulate reinforcing fillers such as Carbon Black (CB) and silica [1]. Replacement of CB with silica in passenger car tire tread compounds, after the patent of Michelin in 1992 [2], offers tires with higher wet traction and lower rolling resistance resulting in enhanced safety and fuel savings [3]. However, mixing of silica into rubber faces several difficulties such as incompatibility with non-polar elastomers, poor dispersion and distribution in the rubber matrix, and poor filler-rubber interaction. To overcome these problems, silane coupling agents such as bis-(3-TriEthoxySilylPropyl) Tetrasulfide (TESPT) are generally used in silica-reinforced rubber compounds resulting in higher filler-rubber interaction between the silica and rubber matrix, better silica dispersion and also to prevent accelerator adsorption on the silica surface, that mean less of a negative effect on vulcanization properties.

The mixing of silica with silane in rubber involves a chemical reaction, called silanization. The mixing temperature has a more dominant effect than mixing time on the silica-silane reaction [4]. The effect of mixing temperature for the silica-silane (TESPT) technology has been studied in different types of elastomers such as a Styrene Butadiene Rubber (SBR) blend with Butadiene Rubber (BR) [5-6], Isoprene Rubber (IR) [7] and Natural Rubber (NR) [7-8]. The silanization reaction between silica and silane coupling agent increases with increasing mixing dump temperature, as indicated by a reduction of filler-filler interactions monitored by the Payne effect, and increased filler-elastomer interactions as evidenced by higher chemically bound rubber content. The extent of silanization has a dramatic effect on the resulting compound properties [8-9]. Previous researchers tried to improve silica compounds by adding Epoxidized Natural Rubber (ENR) as a compatibilizer, where the results show an enhancement of filler-rubber interaction, silica dispersion and tensile strength by adding ENR as a compatibilizer when compared with a compound without ENR. ENR consisting of

51 mol% epoxide or ENR-51 at 7.5 phr shows the best overall properties, however still somewhat lower than silica-TESPT silane compounds [10]. The addition of Epoxidized Low Molecular Weight Natural Rubber (ELMWRN) as a compatibilizer in silica-filled NR compounds was also studied [11]. It decreases the compound viscosity and the Payne effect to levels close to those of a compound with TESPT, and also increases bound rubber content and filler dispersion resulting in improvement of mechanical properties by adding 10 phr of ELMWRN-28 mol% epoxide in the silica-filled NR compounds.

However, a question remains regarding the performance of such tires in terms of abrasion or wear resistance. High abrasion resistance is one of the key tire performance criteria in terms of economics and the environment, related to the service life of rubber products, not only tire treads but also e.g. belts, hoses, and shoe soles. The abrasion mechanism of rubber vulcanizates is very complex involving several factors, where the fillers and polymers strongly influence this property. When compared to CB, the interaction between silica and hydrocarbon rubber is weak, but with effective use of a silane coupling agent, the abrasion resistance of silica-filled compounds can be considerably promoted which enables them to be used in tire tread compounds [12]. In many studies it was tried to improve the abrasion resistance by combining the advantages of different fillers with silica or hybrid fillers such as silica/CB [13-15] and silica/nanoclay [16-18]. For example, the simplest combination in silica/CB as both types of fillers are already commonly used in tire compounds.

1.2 Background of the research in this thesis

Natural Rubber (NR) is cis-1,4-polyisoprene which is the largest single elastomer type used for truck tire tread compounds as a result of its excellent mechanical properties and low heat build-up. NR provides high tensile and tear strength due to the strain-induced crystallization of the high molecular chains, resulting in superior chipping/chunking resistance. However, NR is limited in oxygen-, and ozone-resistance due to its unsaturation in the main chain, but this can be improved by addition of antioxidants and antiozonants [19]. Carbon Black (CB) was the first reinforcing filler for rubber compounds to improve modulus, tensile and tear strength, abrasion resistance, skid resistance and other properties. The properties of the reinforced materials are influenced by the filler's particle size, surface area, structure and surface chemistry [20]. Reduction of rolling resistance, high wet grip, and high abrasion resistance are the key tire performances to develop modern tires. The use of silica with CB results in tires with lower rolling resistance and higher wet traction, so less fuel consumption and better safety, respectively [3].

Additionally, tensile strength, heat build-up, cut-, chip-, chunking-resistance and tear strength are improved [21]. As silica has high polarity silanol groups, a hydrophilic surface and therefore easily tends to re-agglomeration or high filler-filler interaction, so the compatibility with non-polar elastomers such as NR, BR and SBR commonly used in the rubber industry [22] is insufficient, resulting in poor dispersion and distribution in the rubber matrix, and poor filler-rubber interaction. Sulfur containing silane coupling agents such as TESPT are commonly applied in such compounds cured with sulfur systems to result in high filler-rubber interaction between the silica and rubber matrix, better silica dispersion and also to prevent accelerator adsorption on the silica surface, that means less negative effect on the vulcanization properties. However, TESPT has the drawback of short scorch times due to free sulfur that is released during high temperature mixing, resulting in premature crosslink reactions [8]. For better scorch safety, bis-(3-TriEthoxySilylPropyl)Disulfide (TESPD) can be used but when compared to TESPT, compounds with lower filler-rubber interactions, dispersion stability, tensile strength, and tear resistance are observed [4].

SBR is a general purpose and the largest volume synthetic rubber used in many applications, that offers better crack-initiation resistance, good flex resistance, abrasion resistance, wet grip, and weather resistance than NR [23-24], and is often used for passenger car tire tread compounds. There are basically two classes of SBR: Emulsion-SBR (ESBR) and Solution-SBR (SSBR), where the first is conventionally used in CB-filled and the second in silica-filled tire compounds. BR is the second largest volume synthetic rubber obtained from the polymerization of 1,3-butadiene, which can be polymerized in three different configurations: cis, trans and vinyl. The cis-1,4 and vinyl-1,2 contents are important factors for the properties of BR. A high cis-1,4-content BR improves the abrasion resistance of tire tread compounds, and also gives excellent resilience resulting in decreased heat build-up. With high vinyl-1,2 content with decreased cis-1,4 content, the abrasion resistance, resilience and low temperature properties become inferior. Normally, BR is blended with other rubbers, especially NR and SBR, often used in tire applications [19]. It has been well recognized that the silica-silane technology works well with special easy-dispersion silica (or so-called highly dispersible silica) in combination with synthetic SSBR and BR in tire compounds [25]. ESBR and NR contain non-rubber components; the former one from surfactants and the latter from non-rubber constituents in the original latex state, mainly proteins, fatty acids and phospholipids. Silica-reinforced tire compounds based on these elastomers exhibit inferior abrasion resistance due to their poorer filler-rubber interaction when compared to the SSBR case [12]. In addition, the vinyl-

microstructure and more linear molecular structure of SSBR plays a role in the success of silica/silane reinforcement [26]. Blends of SBR and NR are immiscible, as shown by the presence of two relaxation peaks corresponding to the respective glass transition temperatures (T_g 's) of SBR and NR [24]. When the NR concentration is increased, tensile strength and elongation at break improve, while the storage modulus of the system decreases. Based on the results from SSBR/BR compounds, the silica-silane combination still gives poorer abrasion resistance compared to CB [12].

1.3 Aim of the research in this thesis

The present project aims to investigate a synergistic effect of silica with different fillers and/or a combination of NR with synthetic rubbers in order to shift the tire performance towards better abrasion resistance for durability, while maintaining wet grip property and rolling resistance for safety and fuel savings, respectively. The objectives for this research are listed below:

1.3.1 To optimize the mixing conditions and silane coupling agent loadings for the silica/secondary filler/NR tire tread compounds;

1.3.2 To investigate the effect of types and loadings of secondary fillers on the properties of silica-based NR tire tread compounds;

1.3.3 To investigate the effect of types and loadings of secondary polymers having different molecular characteristics on the properties of silica-based NR tire tread compounds;

1.3.4 To develop silica-reinforced NR tire compounds with enhanced performance by the influence of secondary fillers and polymers.

1.4 Concept of the research in this thesis

The choices of rubbers, fillers, curatives and other compounding ingredients have, to different extents, influences on the compound properties of final vulcanizates. Therefore, this project investigates the use of secondary fillers that have different filler characteristics, in combination with silica, so called hybrid fillers which may lead to better filler dispersion, filler-rubber interaction and better balance of abrasion resistance. Furthermore, utilization of NR in combination with a secondary polymer or a hybrid polymer which has a different glass transition temperature (T_g) and/or different microstructure should also affect the properties of the compounds. The thesis is composed of the following chapters;

Chapter 1 Introduction: This first chapter starts from the development of silica technology for tire tread compounds, followed by the background, aims and concept of this research.

Chapter 2 Review of silica-reinforced rubber with secondary fillers and polymers: This chapter focuses on the use of CB and silica as reinforcing fillers, and also the use of nanoclay in rubber compounds. Hybrid fillers or the combination of silica with CB and OrganoClay (OC) as secondary fillers are reviewed. Tire elastomers such as NR, BR and SBR rubber for tire applications are covered. The rubber blends or hybrid polymers of NR in combination with BR and SBR as secondary polymers are also reviewed. The motivation and scope of the project are provided at the end of this chapter.

Chapter 3 Optimization of mixing condition for silica-reinforced natural rubber with small amounts of secondary fillers: As to silica-reinforced NR compounds, the dump/discharge temperature after mixing is a crucial parameter that needs to be controlled, as it has a strong influence on both processing and vulcanizate properties [8]. Therefore, the influence of initial mixer temperature setting on silica in combination with CB N134 and OC Dellite 67G as secondary fillers are investigated in order to determine the optimal condition for the best possible properties of the compounds.

Chapter 4 Influence of mixing procedure and TESPD loading on the properties of silica/secondary fillers-reinforced natural rubber compounds: To study the effect of a combination of silica with CB N134 and OC Dellite 67G as secondary fillers, the incorporation of fillers into the polymer is a very important factor in order to obtain a good dispersion and distribution of filler in the rubber matrix, resulting in an improvements of compound properties. The loading procedures of secondary fillers in combination with silica are interesting to study and the loading levels of TESPD as silane coupling agent in the hybrid filler systems of silica/CB- and silica/OC-filled NR are also important to investigate.

Chapter 5 Synergistic effect by high specific surface area carbon black as secondary filler in silica-reinforced natural rubber tire tread compounds: This chapter covers high specific surface area and structure CB N134 in synergy with silica in NR tire tread compounds. The hybrid filler of silica/CB-filled NR with various ratios is investigated keeping the total filler content constant at 55 phr. The effect of CB N134 on the properties of silica-reinforced NR compounds is investigated with respect to filler networking, filler-filler

interactions, filler-rubber interactions, cure characteristics, tensile properties, dynamic mechanical properties and abrasion resistance, all of importance for tire performance.

Chapter 6 Enhancing performance of silica-reinforced natural rubber tire tread compounds by applying organoclay as secondary filler: The effect of loading levels of OC on the hybrid filler system, still in combination with mixing temperature is fully explored. The cure characteristics, filler-filler interactions, filler-rubber interactions, tensile and tear properties, DIN abrasion resistance index, dynamic mechanical properties and morphology in terms of clay dispersion of such silica/OC-filled NR compounds are studied.

Chapter 7 Effect of clay-modifier on the properties of silica- and silica/nanoclay-reinforced natural rubber compounds: The modifying agent of OC is dimethyl dihydrogenated tallow ammonium chloride (2HT), a quaternary ammonium group type. The effect of loading this modifying agent independently in silica-filled NR, the hybrid filler system of silica/OC-filled NR and silica/MMT-filled NR compounds with TESPD as silane coupling agent are investigated, where MMT stands for MontMorillonite, the basic clay used for the pre-freaked OC.

Chapter 8 Influence of secondary polymers in shifting tire tread-related properties of silica-reinforced natural rubber compounds: The effect of loadings and types of secondary polymers: BR and SSBR having different levels of microstructure such as cis-content, vinyl-content, glass transition temperature (T_g) as well as styrene content in SSBR, in combination with NR on the properties of silica-reinforced truck tire tread compounds is investigated.

Chapter 9 Improvement in silica-reinforced natural rubber tire tread compounds by joint hybridization with small amounts of secondary fillers and polymers: The effect of vinyl-contents of BR and SSBR as secondary polymers in combination with NR on the properties of silica-reinforced truck tire tread compounds, together with the combination of silica with CB N134 and OC as secondary fillers in silica-filled NR is studied.

Summary: This chapter summarizes all the findings and knowledge derived from experimental studies.

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CHAPTER 2

Review of Silica-Reinforced Rubber with Secondary Fillers and Polymers

This chapter gives an introduction into tire components, functions of tire components and polymers used in passenger car tires, the reinforcing fillers like Carbon Black (CB) and silica which have been used in the tire industry especially in tire tread compounds, classification of fillers used in the rubber industry, and the effect of CB loadings on the compound properties. It also includes the introduction of nanoclay, which has a dimension in the nanometer level, and the use of nanoclay in rubber matrices. Silica-silane filler technology provides better tire performances in terms of rolling resistance and wet traction, but still poorer abrasion resistance compared to CB. To further develop silica compounds especially with respect to abrasion resistance, the use of high specific surface CB N134, which is excellent in abrasion resistance, or OrganoClay (OC) nanofiller, both in combination with silica, or alternatively called hybrid fillers, may have a positive influence on the compound and rubber vulcanizate properties. So, an explanation of hybrid fillers, overview of silica/CB and silica/OC in rubber matrices are also mentioned. An introduction of tire elastomers like Natural Rubber (NR), Styrene Butadiene Rubber (SBR) and Butadiene Rubber (BR) which are normally used in the tire industry, and rubber blends for tire applications is given. The motivation of the research is given in the last part of this chapter.

2.1 Introduction

Tires are composed of several components, made from different rubber compounds either as single or blended rubbers as detailed in Table 2.1 [1]. Different tire categories employ various rubber types and formulations, for example tire treads of passenger car tires use SBR-based blends either with BR or NR, while truck tire treads are mainly composed of NR because of its excellent mechanical properties and low heat build-up [2-3]. However, unfilled (non-reinforced) compounds or gum rubber with only vulcanizing agents are not able to reach the compound properties and tire performances such as abrasion resistance, wet traction, and rolling resistance properties of tire treads that are indicative for durability, safety and economy of tire applications. Therefore, reinforcing fillers are added to rubber compounds to improve compound properties as well as tire performances and to also reduce the cost of tire products. Carbon Black (CB) is the oldest and commonly used as reinforcing filler for tires. Replacement of CB with the non-black filler silica in tire tread compounds, after the patent of Michelin [4], offers passenger car tires with lower rolling resistance and higher wet grip [5], so less fuel consumption and better safety. Generally, tires are composed of about 30% by weight of reinforcing fillers such as CB and silica [6-7], to improve some basic requirements in properties such as modulus, hardness, tensile strength and tear resistance. Recently, there are numerous developments of reinforcing filler technology such as introduction and usage of new grades of silica, surface-modified or plasma-treated fillers, aramid fibers, carbon fibers, development of dual fillers, a new generation of nanofillers, and nanotechnology for improved tire performance [8]. The properties of the reinforcing materials are influenced by the filler's particle size, particle shape, aspect ratio, surface area, structure and surface chemistry. The application of nanofillers which have at least one dimension in the nanometer level becomes an interesting way to improve the mechanical properties of tire compounds due to the large specific surface area, so that the interfacial area of rubber to filler is also large [9-11]. One of the most widely studied nanofillers is organically-modified clay or shortly OrganoClay (OC) [12-13]. The mechanical properties, thermal stability, gas permeability and wear resistance are improved with low contents (usually 10 phr or less) of OC nanofiller [8]. To reinforce the rubber, either a single or dual filler system is utilized. A combination of two different types of fillers or hybrid fillers attracts interests so as to combine the advantages of each filler in the rubber compounds to fulfil the major development requirements for key tire performances.

Table 2.1 Tire components, functions of tire components and polymers used in passenger car tires [1].

Tire components		Functions	Rubber types
(1) Inner liner	Prevent air leakage		CIIR ^a , BIIR ^b , NR
(2) Bead	Metal fitting tire on wheel		NR
	Endure internal air pressure as pressure vessel. Tire carcass generally uses nylon, rayon or polyester		NR, SBR, BR
(3) Ply cord			
(4) Sidewall	Protecting side area and absorbing road shocks		NR, BR
	Protecting body ply at the final phase of wear and from foreign materials such as nails, stone, etc.		NR
(5) Belt			
(6) Tread	Responsible to directly contact road which is related to safety and durability of a tire		NR, SBR, BR
(7) Bead filler	Improve handling stability by raising tire vertical/horizontal rigidity		NR, SBR, BR
(8) Cap/Layer	Improve handling stability by raising tread rigidity		NR, BR

^a CIIR: chlorobutyl rubber.

^b BIIR: bromobutyl rubber.

2.2 Reinforcing fillers

Many different types of fillers are applied in rubber technology in order to improve mechanical performances, reduce the cost of rubber products as well as to improve processing. The classification of filler in rubber industry is shown in Table 2.2 [14-15].

Table 2.2 Different types of fillers in the rubber industry [14-15].

Types of filler	Application	Examples
(1) Non-reinforcing fillers (particle size 10^3 nm)	To reduce the cost but it can reduce mechanical properties of rubber compounds	Calcium carbonate (CaCO_3), talc, mica, etc.
(2) Semi-reinforcing fillers (particle size 10^2 nm)	To little improve mechanical properties of rubber compounds	Clays, precipitated CaCO_3 , Titanium dioxide (TiO_2), etc.
(3) Reinforcing fillers (particle size 10^1 nm)	To improve mechanical properties of rubber compounds	Carbon black, silica, etc.

2.1.1 Carbon black

Carbon black is a conventional reinforcing filler for rubber compounds that is still the most commonly used one in the tire industry because it can effectively improve tensile strength, modulus, tear strength, flex fatigue, abrasion resistance, skid resistance as well as other properties.

The properties of rubber compounds with CB as reinforcing filler depend on particle size (specific surface area), particle size distribution, structure (particle aggregates) and surface activity of the filler. Particle size or specific surface area of the filler is one of the key parameters strongly affecting rubber properties. Reinforcing fillers have a high surface area that provides more active contact sites to contribute to filler-rubber interactions in rubber compounds. The particle surface area of CB is generally measured based on the Brunauer-Emmett-Teller (BET) nitrogen-adsorption technique according to American Society for Testing and Materials (ASTM) D6556 to determine the Nitrogen Surface Area (NSA) or the Statistical Thickness Surface Area (STSA). Basically, the NSA or BET method measures the overall surface area of the particles including micropores.

Structure of a filler is created by aggregates/agglomerates of primary particles caused by self-association because of the active functionalities on their surface. The term “structure” of fillers includes aggregate shape, density and size. A higher structure gives a better

reinforcement efficiency [5]. The structure of fillers was conventionally measured by DiButylPhthalate (DBP) adsorption, but this method is no longer accepted because of toxicity. The current method is based on the oil-adsorption technique according to ASTM D6854.

Particle surface activity depends on the surface chemistry of the filler. Active fillers should give a strong interaction between filler and rubber matrix. The CB surface is primarily composed of carbon with a few percentages of chemical functionalities, mostly oxygen-containing groups such as carboxyl, ketone, pyrone, hydroxyl, quinone and lactone, as illustrated in Figure 2.1 [14]. However, it is known that these chemical functional groups do not play an important role in CB reinforcement in most common rubbers. The reinforcing effect is mainly derived from mechanical interlocking of the rubber onto the CB surface and the physical adsorption of the elastomers onto the filler surface.

Figure 2.1 Surface chemistry of carbon black [14].

Generally, an increase in CB aggregate size or structure will result in an improvement in resistance against cut growth and fatigue. A decrease in particle size results in an increase in abrasion resistance and tear strength, a drop in resilience, and an increase in hysteresis and heat build-up. The physical properties of the compounds are influenced by CB loading and general trends are as shown in Figure 2.2 [2]. As the loading levels increase, heat build-up, hardness, rolling resistance and wet skid properties steadily increase. However, compound processability, tensile strength, tear resistance, and tread wear increase to reach an optimum point, thereafter these properties deteriorate [2].

A general design in the production of tires utilizing CB in tire tread compounds is to have satisfactory abrasion resistance and hysteresis. Better abrasion resistance of a tire means higher durability. Hysteresis of a rubber vulcanizate is a measure of the energy dissipated under a deformation cycle. Tire tread compounds with lower hysteresis will have reduced

rolling resistance to result in less fuel consumption during use. Tire tread compounds with higher rebound, i.e. better elasticity, generally have reduced rolling resistance and lower heat build-up.

Figure 2.2 Effect of carbon black level on compound properties [2].

2.1.2 Silica

Michelin introduced the “Green tire” in 1992 in which Solution-SBR (SSBR)/BR tire tread compounds were reinforced by silica in combination with a silane coupling agent [5]. The use of silica improves tear strength, reduces heat build-up and contributes to the improvement of tire traction and rolling resistance. Figure 2.3 shows the surface chemistry of silica that is composed of silanol groups ($-\text{Si}-\text{OH}$) arranged in three different structures; isolated, geminal (two hydroxyl groups on the same silicon atom), and vicinal (on adjacent silicon atoms) [14]. Due to the presence of a large number of polar silanol groups, the silica surface is hydrophilic and not compatible with hydrophobic rubbers. Silicas may be categorized into three classes, to include standard or conventional silica, semi-Highly Dispersible (semi-HD) or easily-dispersible silica, and the latest developed Highly Dispersible Silica or HDS, as shown in Table 2.3 [2].

The advantages of silica in rubber compounds when it is used as partial replacement of CB are reduction in heat build-up, improvement in tear strength, cut-, chip-, and chunking-resistance [2]. However, a drop in abrasion resistance is usually observed. To improve the compound performance, silane coupling agents are applied to form a chemical bond between the silica and the rubber. By the use of a bifunctional silane coupling agent, silica tread wear can be improved to match the CB-filled one while still offering an improvement in rolling resistance.

Figure 2.3 Surface chemistry of silica [14].

Table 2.3 Classification of silicas and applications in tire components [2].

Class of silica	Surface area (m ² /g)		
	90-130	130-180	180-220
Conventional	Tire casing, non-tire internal and external components	Tire treads, tire casings and non-tire products external components	Tire treads and non-tire external components for abrasion resistance
Semi-highly dispersible	Tire casing, non-tire products external components	Tire treads, tire casings	Tire treads
Highly dispersible	Tire casings, tire treads	Tire treads	High performance tire treads

2.1.2.1 Silane coupling agents

There are several types of silane coupling agents commercially available such as bis-(3-TriEthoxySilylPropyl)Tetrasulfide (TESPT), bis-(3-TriEthoxySilylPropyl)Disulfide (TESPD) and MercaptoPropylTriMethoxySilane (MPTMS). TESPT is a bifunctional polysulfidic organosilane that was originally introduced as a sulfur donor but later found its use as a coupling agent to improve the reinforcement properties of silica in rubbers [2]. The utilization of coupling agents in silica-filled rubber compounds results in several advantages such as lower heat build-up and hysteresis, enhanced 300% modulus and tensile strength, improved abrasion resistance and enhanced processing properties.

The reinforcement mechanism involved in the use of silane coupling agents with silica is comprised of two major steps; the hydrophobation reaction in which the coupling agent reacts with silica and the formation of crosslinks between the modified silica and rubber. During vulcanization, reaction between the coupling agent and the elastomer takes place as the

elemental sulfur is added into the compound or generated by disproportionation of TESPT. The reaction completes the link between the silica and rubber via a silane bridge, i.e. the silica-silane-rubber coupling, to give rise to better filler-polymer interactions and enhanced reinforcement efficiency [2].

2.1.3 Nanoclay

Nanocomposites are organic-inorganic hybrid materials in which nanofillers like nanosilica, nano-Zinc Oxide (ZnO), and nanoclay are distributed on a nanometer level within the organic polymer matrix. The high surface area of nanofillers provides a large contact area between polymer and filler, and if the interfacial interaction between nanofiller-polymer is strong, an efficient stress transfer from the matrix to filler is obtained. The use of nanoclay in polymers offers a very high degree of reinforcement, high thermal stability, improved impermeability to gases, vapors and liquids, good optical clarity in comparison to conventionally filled composites, and flame retardancy with reduced smoke emission [8]. The commonly used layered silicates are 2:1 phyllosilicates including hectrite, saponite, montmorillonite, and synthetic mica. These silicates are stacks of layers of 1 nm in thickness with difference in length such as about 50 nm (hectrite), 170 nm (saponite), and 200 nm (montmorillonite). The 2:1 phyllosilicates layers are made up by fusing two silicate tetrahedral to an edge-shared octahedral sheet of aluminum hydroxide as shown in Figure 2.4 [16]. Isomorphic substitution within the layers, such as replacement of Al^{3+} by Mg^{2+} , generates negative charges defined by the Cation Exchange Capacity (CEC). Stacking of the layers leads to a gap between each layer that is called the interlayer or gallery. This gallery is pristinely filled with exchangeable hydrated alkali metal cations to counterbalance the negative charges generated. By ion exchanging of these alkali metal cations with various organic cations, such as alkyl ammonium cationic surfactants, the normally hydrophilic silicate surface will become more hydrophobic. These layered silicates, or phyllosilicates, intercalated by organic cations are called organosilicates or OrganoClay (OC).

Figure 2.4 Structure of 2:1 phyllosilicates layers [16].

Dispersion of clay platelets in polymer during mixing can result in three possible structures as shown in Figure 2.5 [17]. Conventional composites, which are considered to have the poorest dispersion state, have stacks of clay platelets dispersed in the polymer matrix. When the extended polymer chains are intercalated in the gap between the silicate layers while the stacking order is retained, an intercalated nanocomposite is obtained. If the clay layers are individually dispersed in the polymer matrix, an exfoliated nanocomposite is attained.

Figure 2.5 Schematic representation of clay platelet dispersion as (a) conventional, (b) intercalated, or (c) exfoliated structures [17].

The investigation of organophilic MontMorillonite (MMT)-filled SBR revealed that the crosslink density increased with increasing OC content due to the presence of the amine functionality of the trialkylamine intercalant used [18]. Incorporation of the nanosilicate improved the viscoelastic behavior of the SBR vulcanizates by increasing the storage and decreasing the loss moduli. The tensile strength, 300% modulus and elongation at break

increased with the nanosilicate content. The changes in these properties were related to the silicate surface area, the extent of dispersion and the increase in crosslink density. A study of NR and organomodified cloisite clay nanocomposites, prepared by blending on a two roll mill and vulcanized by efficient (EV), conventional (CV) and peroxide (DCP) vulcanizing systems, showed that the CV vulcanized nanofilled sample exhibited higher tensile strength and elongation at break compared to EV and peroxide vulcanized samples [19]. By using different modifiers, the tensile strength of the composite was increased with the length of the hydrocarbon part in the structure of the quaternary-ammonium salt modifying agent, as the longer chain could generate larger surface spacing to accommodate more rubber molecules to intercalate. The tensile properties of the NR-clay composite increased with increasing clay content to an optimum at 5 phr, in correspondence to Transmission Electron Microscopy (TEM) photographs that showed exfoliation of the cloisite 20A clay at 5 phr.

The use of nanoclay in non-polar synthetic *cis*-1,4-polyisoprene was investigated in comparison with polar Epoxidized Natural Rubber (ENR). In non-polar rubber, the organic modification of the clay facilitated the intercalation of the rubber chains into the clay galleries [20], and the modified clay reduced filler-filler interactions, improved filler dispersion, and thus efficiently increased the tensile properties of the vulcanizates. In the case of the polar ENR having 25 or 50 mol % epoxide, the mixing of pristine clay into the rubber already gave an intercalated structure which increased the active surface area of the clay, and more intercalation was achieved when organically modified clay was used. The intercalated structure increased the effective volume, and increasing the effective filler volume resulted in more filler networking, and thus led to a high storage modulus at small strains. Teh *et al.* (2004) [21] investigated nanocomposites containing NR as matrix, ENR 25 and ENR 50 at 5 and 10 phr as compatibilizer and ammonium modified MMT at 2 phr as filler. The presence of ENR in NR decreased both scorch and cure times due to the activation effects of epoxy functional groups on the crosslinking. The increase in the maximum cure torque (M_H) and minimum cure torque (M_L), and cure torque difference ($M_H - M_L$) suggested an increment in stiffness, viscosity and crosslink density, respectively. The use of ENR 50 gave higher M_H and M_L , and $M_H - M_L$ as well as better tensile and tear properties compared to ENR 25 compatibilized- and uncompatibilized-compounds, due to a good dispersion of the OC accompanied with strong interfacial adhesion between matrix and filler. Based on TEM and X-Ray Diffraction (XRD) morphological studies, the OC was mostly intercalated, and to a lesser extent exfoliated in the nanocomposites.

Sadhu and Bhowmick (2004) [22] investigated nanocomposites based on Na-MMT clay in different grades of acryloNitrile Butadiene Rubber (NBR) with ACryloNitrile (ACN) contents of 19, 34, and 50%; SBR with 23% styrene content; and BR. The clay was modified with stearyl-amine to result in an increase in the gallery gap as analyzed by XRD. The nanocomposites showed improved mechanical properties in all cases. The extent of the increase in strength varied from 38 to 166%, depending on the nature of the base rubber and its polarity. The strength improvement was higher for NBR with a higher ACN content as the polarity of the rubber affected the extent of intercalation, as revealed by the XRD data. A study on the rheological behavior of rubber based nanocomposites [23] showed that when the rubber was more polar, the incorporation of nanoclay caused a greater decrease in shear viscosity. The viscosity decreased with the filler loading up to an optimum value, depending on the nature of the rubber, and thereafter the value increased due to filler agglomeration.

2.1.4 Hybrid fillers

For polymer systems, hybrid fillers or a combination of at least two fillers are mixed in a rubber matrix. This leads to a new material that shows new properties that are not found with the individual components. Hybrid fillers must provide superior properties compared with single filler compounds [24]. In silica technology, many researchers tried to improve rubber vulcanizates properties by combining silica with the advantages of other different fillers or secondary fillers. This thesis is focused on silica/CB [25-30] and silica/clay hybrid filler systems [31-36].

2.1.4.1 Use of silica in combination with carbon black

A combination of CB and silica attracts interests so as to combine the advantages of each filler in rubber compounds and both types of fillers are already generally used in the tire industry. The presence of silica in the mixed filler system requires the silane coupling agent to still attain optimum properties. Choi (2006) [25] investigated the influence of silica (Z175) mixed with CB (N220) in the presence and absence of silane coupling agent on the retraction behavior of NR vulcanizates. The ratios of CB/silica were varied at 40/0, 30/10, 20/20, and 10/30 phr. The vulcanizates containing silane coupling agent showed faster recovery rates compared to those without, due to the polymer-filler interactions, crosslinks between the rubber and silica, and increased crosslink densities. The vulcanizates containing the silane coupling agent showed similar retraction behaviors irrespective of filler composition, but those without

the silane coupling agent showed slower retraction behaviors with increased silica content. With increasing silica proportion, the vulcanizates with and without the silane coupling agent showed a decrease in hardness and modulus. But, the vulcanizates containing the silane coupling agent had higher modulus and tensile strength due to better filler dispersion and higher crosslink density than those without the silane coupling agent. Rattanasom *et al.* (2007) [26] investigated the mechanical properties of NR reinforced with various ratios of CB (N330)/silica (Hisil 233) hybrid filler with silane coupling agent, and reported that the vulcanizates containing 20 and 30 phr of silica in a total mixed filler of 50 phr exhibited the best overall mechanical properties. A blend of SBR/*cis*-BR/NR in the presence of CB/semi-dispersible silica/silane coupling agent was studied with the help of Taguchi experimental design for the development of a passenger tire tread compound [27], taking a formulation of SBR 100 phr and N234/N330 (50/20) as reference compound. Some part of SBR was substituted by NR and *cis*-BR, and N330 was substituted by silica/silane coupling agent. The incorporation of NR and BR enhanced vulcanization and increased tear resistance. The partial substitution of CB with silica/silane coupling agent improved tear strength and crack growth but it had a negative effect on abrasion resistance. By adding BR, the abrasion resistance was improved. Based on an optimized formulation as calculated by using the software, an excellent balance between the failure and the physico-mechanical properties of a tread formulation could be obtained in which the abrasion, tear, crack growth resistance and resilience were improved by 20, 125, 26 and 30%, respectively, compared to a reference compound.

SSBR compounds filled with different ratios of silica (Tixosil 383)/CB (N234), i.e. 0/70, 20/50, 35/35, 50/20 and 70/0 phr, were also investigated with emphasis on their antistatic characteristics [28]. The SSBR/CB compound had excellent antistatic properties while the SSBR/silica showed large static accumulation. When compared to the compounds with single fillers, the composites of SSBR/SiO₂/CB showed better filler dispersion, lower Payne effect, and a synergistic effect in mechanical properties. The SiO₂/CB ratio of 20/50 gave the best overall properties in which a good balance of rolling resistance, wet skid resistance and wear resistance was obtained. With increasing silica content, the optimum curing time was prolonged and the surface and volume resistivity were increased. The use of silica to partially replace CB in SSBR compounds was studied by Feng *et al.* [29]. This work investigated the influence of filler networking that affects reinforcement and dynamic mechanical properties by using compounds without silane coupling agent. The addition of a small amount of silica (VN3) into SSBR/CB (N330) compounds, such as by the use of a CB/silica ratio of 45/5 phr, decreased filler cluster

branching and increased the reinforcement efficiency. The depressed filler networking and more homogeneous filler dispersion resulted in better abrasion resistance, lower rolling resistance and better wet skid resistance, i.e. better dynamic mechanical properties. However, when the silica proportion was high, filler cluster branching increased quickly and deteriorated the properties. In addition to tire rubbers, the effect of CB/silica hybrid filler in a polar rubber like NBR has also been investigated. The cure characteristics and physical mechanical properties of NBR filled with CB (N770 or Semi-Reinforcing Furnace (SRF) black)/silica (Hisil233) were studied [30] in which the total hybrid filler content was kept constant at 50 phr and silica content was varied at 0, 10, 20, 25, 30, 40 and 50 phr. The optimum cure time (t_{c90}), scorch time (t_{s2}), M_L , and M_H of the CB/silica hybrid-filled NBR compounds were increased as the silica content increased. The replacement of CB with silica decreased the material's stiffness, tensile strength, compressive strength, tear strength and modulus, but increased elongation at break and rebound resilience.

2.1.4.1 Use of silica in combination with clay

A combination of silica and China clay in SBR/BR rubber blend for a heavy-duty truck tire tread formulation was studied and the best balance of heat build-up and abrasion resistance was found at a silica/clay ratio of 60/20 [31]. Hybrid fillers of precipitated silica/MMT in peroxide cured silicone rubber nanocomposites resulted in the improvement of tensile strength, Young's modulus, moduli at 100% and 300% strain (M_{100} and M_{300}), elongation at break, hardness and crosslink density [32]. Use of MMT (Cloisite 20A) and silica (ULTRASIL 7000GR) with Si69 as TESPT silane coupling agent in SSBR/BR tread compounds was reported by Bao *et al.* [33]. The MMT was mixed with ESBR by a latex compounding method, and the dried master batch was later used to add into the rubber formulation together with other ingredients in the following melt compounding. The results showed that MMT could react with the coupling agent at a higher reaction rate than silica/Si69. Fully exfoliated MMT were formed when the MMT/silica ratio was 1:4 or lower, and the MMT dispersion and exfoliation were promoted by the existence of silica. Silica also exhibited a good dispersion but gave a poorer reinforcement effect compared to MMT. The coupling agent could react with MMT, silica, and rubber matrix, thus increased the torques and curing extent of the rubber compounds. Tensile strength, elongation, and traction properties were improved with low Si69 content while modulus, hardness, wear resistance, dry handling, and rolling resistance were enhanced at high Si69 content.

A SBR/silica/N, N-DimethylDodecylAmine (DDA) modified MMT nanocomposite prepared by a latex mixing method with replacement of silica by 7 phr of OC was investigated in comparison with the use of pure silica at 60 phr loading. The OC did not form filler–filler networks with silica as indicated by the Payne effect curve of silica/OC-filled SBR compound was close to the curve of the SBR/silica 53 compound. This work also reported that the silica/OC gave an indication for better skid and rolling resistance with high 100% and 300% modulus [34]. A recent study on the hybrid filler systems consisting of precipitated silica and kaolin modified with a Sodium salt of Rubber Seed Oil (SRSO) in NR and BR blends demonstrated that a substitution of 5-10 phr of silica with SRSO modified kaolin resulted in lower Mooney viscosity and higher cure rate [35]. Higher chemical crosslink density and bound rubber content of the blends containing SRSO modified kaolin indicated a higher extent of rubber-rubber and rubber-filler interactions, respectively. The lower abrasion loss and compression set and higher tensile strength, elongation at break and tear strength of the blend rubber vulcanizates containing SRSO modified kaolin indicated its potential for application in tire tread compositions. The vulcanizate containing hybrid filler showed higher storage modulus with lower loss modulus and tan delta compared to that containing SRSO modified kaolin alone, and so could lead to lower heat build-up in tire tread applications. Isoprene Rubber (IR)/SBR filled with hybrid filler compound of OC, MMT-modified with dimethyl dihydrogenatedtalloyl ammonium as modifying agent was studied with the silica amount fixed at 70 phr and varied OC loadings. The reduction of filler networking in silica-based elastomeric nanocomposites with exfoliated organo-MMT resulted in improved mechanical reinforcement and reduced energy dissipation and thus of fuel consumption and carbon footprint of tires made thereof [36].

2.2 Tire elastomers

Natural Rubber (NR) is composed of cis-1,4-polyisoprene, offers high tensile and tear strength as a result of highly regular molecular chains that can form crystallinities above a critical strain at room or service temperature. NR provides excellent tire tread chipping/chunking resistance with low heat build-up. However, as the main chain of NR contains unsaturation, it is susceptible to degradation by oxygen and ozone, and so antidegradants are needed to protect NR against these agents. SBR is the largest volume synthetic rubber used in many applications and it is the preferred type of rubber for passenger car tire treads because of its good wear resistance and traction. There are basically two classes of SBR: Emulsion-SBR (ESBR) and Solution-SBR (SSBR). ESBR was conventionally used

in CB-reinforced tire compounds, but SSBR became the preferred choice for silica-reinforced low rolling resistance passenger tire treads. BR is the second largest volume synthetic rubber obtained from the polymerization of 1,3-butadiene, which can result in three different configurations: *cis*, *trans* and vinyl. BR with high *cis*-1,4 content gives excellent wear resistance for tires. BR exhibits excellent resilience (elasticity) that results in reduced heat build-up. As the *cis*-1,4 content decreases and 1,2-vinyl content increases, the low temperature properties, resilience and abrasion resistance become inferior. BR is mostly used for tire applications in blending with other rubbers especially NR and SBR. As to NR and SBR, protection against oxygen, and ozone is needed due to the highly unsaturated structure in the main chain [3,7].

2.2.1 Rubber blends for tire applications

A rubber blend is produced by mixing at least two polymers together to create a new material with different physical properties. It is a useful method for developing materials with superior properties having not only the main properties of each blends component but also modified or specific ones. In the tire industry, rubber blends are used due to three main reasons: improving cost reduction, enhancing the processing, and modifying the final product performance. One of the examples is the NR/SBR blend in tire tread compounds in which SBR provides good wet grip and NR gives good strength [37].

Blends of SBR and NR are immiscible, as shown by the presence of two relaxation peaks corresponding to the glass transition temperatures (T_g 's) of SBR and NR, as analyzed by Dynamic Mechanical Analysis (DMA) [38]. When the NR concentration is increased, tensile strength and elongation at break increase while the storage modulus of the system decreases. The styrene and vinyl contents in SBR are known to affect its T_g and viscoelastic behavior. The influence of the vinyl-structure in the polybutadiene part and styrene groups in SBR was studied using two types of SBR (Krynol 1721 and Buna VSL 5025-1) in comparison with general purpose SBR with styrene 23.5 wt% (Krynol 1712) in blending with NR (SMR 5) [39]. 50:50 Blends of NR with Krynol 1721 (styrene 40%) and Buna VSL 5025-1 (vinyl 50%) showed markedly lower rebound resilience while other mechanical properties were considered acceptable. With increasing the ratio of the SBRs, the rebound resilience was reduced and the effect of Buna VSL 5025-1 was more pronounced than of Krynol 1721, in line with their T_g s. Increase of the SBR blend component increased the Mooney viscosity, t_{s2} and t_{c90} , but reduced tensile and tear strength slightly. The correlation of rheological properties of rubber compounds based on NR/SBR with their thermal behaviors has been investigated by

Motiee *et al.* [40]. Degradation of SBR took place at a higher temperature than NR, and as the SBR content in the blend increased, the Differential ThermoGravimetry (DTG) peak shifted to a higher temperature, indicating a higher thermal stability of the samples.

Ternary blends of NR/BR/SBR (25:25:50) reinforced with varying contents of CB N330 were investigated for their mechanical properties and thermal aging behavior by Jovanovic *et al.* [41]. The t_{s2} and t_{c90} of the blends decreased and the M_L and M_H increased with increasing CB content. Tensile strength and elongation at break decreased, but hardness values increased with increasing aging time. The change in mechanical properties was dependent on the aging temperature, time and the CB content. Higher changes in mechanical properties were observed at longer aging times and higher CB content. The phase morphology of cryogenically cracked surface of NR/BR/SBR/CB (25/25/50/80) showed a uniform fracture that indicated good interactions between the polymer matrix and CB. A series of NR blends containing various amounts of ultra high *cis*-polybutadiene rubber (UBR) (98% *cis*-units) has been investigated by Kang *et al.* in an attempt to develop a high performance tire [42]. The strain-induced crystallization in the blend was only associated with NR, and the crystallization was retarded by the UBR chains. The presence of UBR chains speeded up overall chain orientation of the blend upon stretching, but did not play a role as nucleation sites for the NR chains to crystallize. The results showed that the crystallite size became larger with the UBR content, which was attributed to a smaller a number of nuclei formation by the presence of UBR chains. The stress-strain behavior revealed a higher overall stress level with the rubbers of higher UBR content, and network chain density derived from the stress-strain curves also increased as UBR content increased.

2.3 Motivation of the research in this thesis

Although pure silica-filled rubber compounds show better key tire properties such as lower rolling resistance and wet traction, but the abrasion resistance is lower than the CB-filled compounds. However, silica technology faces several problems in term of poor dispersion and distribution in the rubber matrix, poor filler-rubber interaction or high filler-filler interaction due to a large number of hydroxyl groups or polar groups on the silica surface. Silane coupling agents are normally used to solve these problems. The aim is to further enhance the rubber properties of silica-filled rubber compounds by using secondary fillers like CB N134 or OC. The aim is that the use of a secondary filler with different filler characteristics, in combination with silica, a so-called hybrid filler, may lead to better filler dispersion, filler-rubber interaction

and a better balance of abrasion resistance. Further utilization of secondary polymers like BR and SSBR which have different T_g and/or different microstructures could also affect the properties of the compounds.

The better balance between rolling resistance, wet skid resistance and wear resistance of silica based-reinforced NR tire compounds will encourage higher use of silica in NR tire compounds. The increased use of non-fossil-based material like silica, and a renewable material like NR will lead to production of more environmental friendly products. If the use of secondary fillers leads to better processing properties while the incorporation of the secondary polymers helps to improve abrasion resistance, silica-based NR compounds will be more widely implemented in the rubber tire industry.

2.4 References

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Optimization of Mixing Condition for Silica-Reinforced Natural Rubber with Small Amounts of Secondary Fillers

Modern fuel-saving tire treads are commonly reinforced by silica due to the fact that this leads to lower rolling resistance and higher wet grip compared to Carbon Black (CB)-filled alternatives. The introduction of secondary fillers into the silica-reinforced tread compounds, often named hybrid fillers, may have the potential to improve tire performance further. In the present work, two secondary fillers: OrganoClay (OC) nanofiller and CB N134 were added to silica-based Natural Rubber (NR) compounds at a proportion of silica/secondary filler of 45/10 phr. The compounds were prepared with variable mixing temperatures based on the mixing procedure commonly in use for silica-filled NR systems. The results of Mooney viscosity, Payne effect, cure behavior and mechanical properties imply that the silica hydrophobation and coupling reaction of the silane coupling agent with silica and elastomer are significantly influenced by OC due to an effect of its modifier: an organic ammonium derivative. This has an effect on scorch safety and cure rate. The compounds where CB N134 was added as a secondary filler do not show this behavior. They give inferior filler dispersion compared to the pure silica-filled compound, attributed to an inappropriate high mixing temperature and the high specific surface area of the CB used. The dynamic mechanical properties indicate that there is a potential to improve wet traction and rolling resistance of a tire tread when using OC as secondary filler, while the combination of CB in silica-filled NR does not change these properties.

3.1 Introduction

Tire compounds generally contain about 30% by weight of active fillers like Carbon Black (CB) and silica [1]. Carbon black is conventionally used as reinforcing filler for tire tread compounds because it can effectively improve mechanical properties such as tensile strength, modulus, tear strength, flex fatigue and abrasion resistance as well as providing good skid resistance. The reinforcing effect of CB is normally controlled by particle size, structure, specific surface area and surface chemistry [2]. Replacement of CB with silica in tire tread compounds, after the patent of Michelin [3], offers tires with lower rolling resistance and higher wet grip [4], so less fuel consumption and better safety. The other compound properties also can improve by using silica such as tensile strength, tear strength, heat build-up, cut-, chip-, and chunking-resistance [5]. However, the use of silica in rubber compounds has some shortcomings such as incompatibility with non-polar tire rubbers, poor dispersion and distribution in the rubber matrix, and poor filler-rubber interaction [6]. In order to overcome those limitations, sulfur containing silane coupling agents such as bis-(3-TriEthoxySilyl-Propyl)Tetrasulfide (TESPT) are commonly applied in such compounds. The mixing of silica with silane in rubber involves a chemical reaction, so called silanization, and the extent of this reaction has a dramatic effect on the resulting compound properties [7-8]. Due to the nature of TESPT as sulfur donor, to ensure scorch safety during processing, bis-(3-TriEthoxySilyl-Propyl)Disulfide (TESPD) may be used [9]. Moreover, Epoxidized Natural Rubber (ENR) has been also used as a compatibilizer in silica-reinforced Natural Rubber (NR) tire tread compounds, resulting in a substantial improvement in the properties when compared to a compound without ENR, but somewhat less than with using a silane coupling agent [10].

A recent study on silica-reinforced NR tire tread compounds has shown that, under optimal conditions and formulation, silica can effectively reinforce NR as shown by mechanical and dynamic mechanical properties [8]. However, there remains a question regarding the performance of such tire treads in terms of abrasion or wear resistance. The abrasion mechanism of rubber vulcanizates is very complex involving multiple factors, and fillers have a major influence on this property [11]. The filler particle size, structure, surface activity and filler-rubber interaction all have an impact on the abrasion performance. Nowadays, in addition to CB and silica, there is a new generation of reinforcing fillers available, especially nano-fillers that can be also applied for tire compounds. One of the most widely studied nanofillers is organo-modified clay or shortly OrganoClay (OC) which has been modified by cation exchange with ammonium salts or phosphonium salts in order to obtain the hydrophobic

structure that is compatible with non-polar rubbers [12,13]. OC-elastomer composites with low nanofiller contents (usually 10 phr or less) show improved mechanical properties, thermal stability, gas impermeability and wear resistance [14].

To reinforce the rubber, either a single or dual filler system is utilized. A combination of silica and CB attracts interests as to combine the advantages of each filler in the rubber compounds. Investigations on silica and CB reinforced NR-based truck tread compounds demonstrated that, when CB N220 was progressively replaced by TESPT-modified silica, the complete replacement of CB by the TESPT-silica resulted in 30% improvement in the rolling resistance with little change in the treadwear index (abrasion resistance) and wet traction [15]. The retraction behavior of NR vulcanizates as influenced by silica-N220 CB mixed fillers in the presence and absence of a silane coupling agent was studied [16], in which the vulcanizates containing the silane coupling agent showed faster recovery rates compared to those without due to the polymer-filler interactions, crosslinks between the rubber and silica, and increased crosslink densities. With increasing the silica proportion, the vulcanizates with and without the silane coupling agent showed a decrease in hardness and modulus. Based on the mechanical properties of NR reinforced with various ratios of N330 CB/silica hybrid fillers with silane coupling agent, it was reported that vulcanizates containing 20 and 30 phr of silica with a total mixed filler content of 50 phr exhibited the best overall mechanical properties [17]. The partial substitution of CB with silica/silane improved tear strength and crack growth but had a negative effect on abrasion resistance [18]. Composites of Solution-Styrene Butadiene Rubber (SSBR)/silica/CB showed better filler dispersion, lower Payne effect and a synergistic effect in mechanical properties compared to the compound with single filler. In this case, the SiO₂/CB ratio of 20/50 showed the best overall properties in which a good balance of rolling resistance, wet skid resistance and wear resistance was obtained. With increasing silica content, the optimum cure time was prolonged and the surface and volume resistivity was increased [19]. The addition of small amounts of silica into SSBR/N330 CB compounds, such as by the use of a CB/silica ratio of 45/5 phr, decreased the filler cluster branching and increased the reinforcement efficiency. The depressed filler networking and more homogeneous filler dispersion resulted in better abrasion resistance, lower rolling resistance and better wet skid resistance. However, when the silica proportion was high, filler cluster branching increased quickly and deteriorated the properties [20]. The use of Semi-Reinforcing Furnace (SRF) CB/silica hybrid filler in Nitrile Rubber compounds showed that the replacement of CB with silica decreased the

material's stiffness, tensile strength, compressive strength, tear strength and modulus, but increased elongation at break and rebound resilience [21].

A combination of silica and clay has also been studied. The physico-mechanical properties of silica/China clay-filled NR for a heavy-duty truck tire tread formulation [22] showed the best balance of properties in heat build-up and abrasion resistance at a silica/clay ratio of 60/20. The use of Precipitated Silica (PS)/MontMorillonite (MMT) in peroxide cured Silicone Rubber (SR) nanocomposites resulted in the improved maximum stress compared to unreinforced Silicone Rubber [23]. The use of MMT (Cloisite 20A) and silica with Si69 (=TESPT) as silane coupling agent in SSBR/Butadiene Rubber (BR) tread compounds improved tensile strength, elongation and traction properties at low Si69 content while enhancing modulus, hardness, wear resistance, dry handling and rolling resistance at high Si69 content [24]. Hybrid filler systems consisting of precipitated silica and kaolin modified with a Sodium salt of Rubber Seed Oil (SRSO) in NR/BR blends demonstrated that a substitution of 5-10 phr of silica with SRSO modified kaolin resulted in lower Mooney viscosity, higher cure rate, increased chemical crosslink density index and bound rubber content [25], indicating a higher extent of rubber-rubber and rubber-filler interactions. This resulted in enhanced mechanical properties such as abrasion resistance, compression set, tensile- and tear strength and elongation at break of the blend vulcanizates. The vulcanizate containing silica/SRSO hybrid filler also showed enhancement of dynamic mechanical properties, beneficial for tire tread applications. The reduction of filler networking in silica based elastomeric nanocomposites with exfoliated organo-MMT resulted in improved mechanical reinforcement and reduced energy dissipation and thus fuel consumption and carbon footprint [26].

The present work aims at a synergistic effect of silica with different additional fillers in order to shift tire performance with respect to wet grip and rolling resistance for fuel savings, respectively towards a better abrasion resistance, all characterized by the dynamic mechanical properties of the vulcanized compounds. The use of a secondary filler that has different filler characteristics in combination with silica, a so-called hybrid filler system, may lead to better filler dispersion, filler-rubber interaction and consequently a better balance of performance characteristics.

As to silica-reinforced NR compounds, the dump/discharge temperature after mixing is a crucial parameter that needs to be controlled as it has a strong influence on both processing and vulcanizate properties [8]. Therefore, the influence of initial mixer temperature setting was

investigated in this work in order to determine an optimal condition for the best possible properties of the compounds.

3.2 Experimental

3.2.1 Materials

Natural rubber (Ribbed Smoked Sheet No.3, RSS3) was provided by Sri Trang Agro-Industry, Thailand. Silica ULTRASIL 7005 with a Cetyl-Trimethyl-Ammonium-Bromide (CTAB) and Brunauer-Emmet-Teller (BET) specific surface area of 171 and 190 m²/g, respectively; and TESPD silane coupling agent were obtained from Evonik, Germany. Carbon black (N134) with CTAB and BET specific surface areas of 134 and 145 m²/g, respectively, was provided by Phillips Carbon Black Limited, India. Organoclay Dellite 67G, functionalized with 47 wt% of dimethyl dihydrogenated tallow ammonium chloride (2HT), 115 meq/100 g of cation exchange capacity and interlayer distance of 34.3 Å was provided by Laviosa Chimica Mineraria S.p.A, Italy. The other ingredients: Treated Distillate Aromatic Extract oil (TDAE) (Vivatec 500) (Hansen & Rosenthal, Germany); N-Cyclohexyl-2-Benzothiazyl Sulfenamide (CBS) primary accelerator; DiPhenyl Guanidine (DPG) secondary accelerator; 2,2,4-TriMethyl-1,2-dihydroQuinoline (TMQ) (all from Flexys, Belgium); Zinc Oxide (ZnO); stearic acid and sulfur were all commercial grades for the rubber industry.

3.2.2 Compound preparation

The rubber formulations used in this study are shown in Table 3.1. The compounds were prepared using a two-step mixing procedure: the first was to prepare a masterbatch of rubber and fillers, and the second to prepare the final compounds including the curatives. For the first step, an internal mixer Brabender Plasticoder 350 ml was used, operated at a rotor speed of 60 rpm, fill factor of 70%, and varied initial temperature settings of 60, 80, 100 and 120°C.

The secondary fillers CB N134 or OC, were added together with the first half of silica, the first half of TESPD and DPG in order to obtain good dispersion. The other halves of silica and TESPD were added later on in the first mixing step, together with TDAE extender oil. The second step was for the addition and mixing of the other half of DPG, CBS, and sulfur at a rotor speed of 30 rpm, fill factor of 70%, and an initial temperature setting of the internal mixer of 70°C. The two-step mixing procedure is summarized in Scheme 3.1. Mixing data were derived from the real-time monitoring program coupled with the internal mixer.

Table 3.1 Compound formulations used in this study.

Ingredients	Amount (phr)	
	Silica Reference	Silica/Secondary fillers
Natural rubber (RSS3)	100.0	100.0
Silica (ULTRASIL 7005)	55.0	45.0
Secondary filler ^a	-	10.0
TESPD ^b	5.0	4.1
TDAE oil	8.0	8.0
ZnO	3.0	3.0
Stearic acid	1.0	1.0
TMQ	1.0	1.0
DPG ^b	1.1	0.9
CBS	1.5	1.5
Sulfur	1.5	1.5

^a Secondary fillers were CB (N134) and OC (Dellite 67G).

^b Amounts of TESP and DPG were added according to the following equations [27]:

$$\text{TESPD (phr)} = 0.00053 \times Q \times A;$$

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).

Masterbatch compound

Masterbatch compound

Final compound

Final compound

Scheme 3.1 Two-step mixing procedures for compound preparations; NR/silica (a) and NR/silica+secondary filler (b) compounds.

3.2.3 Sample characterizations

3.2.3.1 Mooney viscosity and cure characteristics

Mooney viscosity, ML(1+4)100°C of rubber compounds were tested using a Mooney viscometer (MV200VS, Alpha Technologies) according to American Society for Testing and Materials (ASTM) D1646.

Cure characteristics of the compounds were studied using the Rubber Process Analyzer (RPA2000, Alpha Technologies) at 150°C, frequency 0.83 Hz and 2.79% strain for 30 mins.

3.2.3.2 Filler-filler interaction

Payne effects or filler-filler interactions of the still unvulcanized silica-filled NR compounds with curatives were studied using the RPA at 100°C, frequency 0.5 Hz and varying strains in the range of 0.56 to 100%. The Payne effect was taken as the difference in storage shear moduli at low strain (0.56%) and high strain (100%).

3.2.3.3 Tensile properties

The compounds were vulcanized to their optimum cure times (t_{c90}) using a Wickert WLP 1600 laboratory compression press at 150°C and 100 bars into 2 mm thick sheets. Type 2 dumbbell test specimens were die-cut from the press-cured sheets and tensile tests carried out with a Zwick tensile tester (model Z1.0/TH1S) at a crosshead speed of 500 mm/min according to ASTM D412.

3.2.3.4 Dynamic mechanical properties

The loss tangent or tan delta at 60°C of the vulcanizates was determined using the RPA at strain 3.49% with varying frequency sweeps in the range of 0.05-33.00 Hz. Prior to these measurements the samples were cured in the same RPA chamber at 150°C to their optimum cure times (t_{c90}) before being cooled down to 60°C and tested. In addition, the tan delta at -20°C, 0°C and 60°C of the vulcanizates were determined using a Dynamic Mechanical Analyzer (Metravib DMA) with temperature dependence from -80°C to 80°C analysis in tension mode at a strain of 0.1% and frequency 10 Hz. Tan delta at -20°C and 0°C were taken as indicative for ice traction and wet grip of tire treads, respectively, and tan delta at 60°C is to indicate rolling resistance of a tire tread.

3.3 Results and discussion

3.3.1 Mixing profiles, Mooney viscosity and Payne effect

Figure 3.1(a) shows that the dump/discharge temperature increases with raising the initial mixer temperature setting for both secondary fillers. The final torque of silica/CB compounds mixed at various temperatures significantly increases and then levels off at 80°C temperature setting, which is attributed to a higher degree of silanization that results in a better filler-rubber interaction. On the other side, silica/OC compounds show a slight decrease in final mixing torque with increasing dump or discharge temperature. This must be due to the effect of the modifying agent, an organic ammonium derivative [26], within the OC which remarkably reduces the mutual filler-filler interaction of silica, as is also confirmed by the Mooney viscosities and Payne effect results depicted in Figure 3.1(b).

Figure 3.1 Average mixer dump/discharge temperature and torque at the final stage of mixing in the internal mixer as a function of initial mixer temperature setting (a). Influence of dump temperature on viscosity and Payne effect of silica (S)-filled NR compounds with different secondary fillers (b).

A higher mixer temperature setting and consequent dump temperature results in a lower Mooney viscosity (at 100°C) of the compounds due to increased silanization and consequent decreased filler-filler interactions. However, the higher temperature causes also breakdown of NR molecules by oxidative reactions under shear forces [28], a factor not to be overlooked for

NR. OC shows a more substantial drop in Mooney viscosity than CB, which must be attributed to influence of the modifier of the clay, as stated before.

The Payne effects of the silica/CB-filled and silica/OC-filled NR compounds decrease with increasing dump temperature due to better silanization at higher mixing temperatures. This clearly confirms the explanation for the mixing data and corresponding compound Mooney viscosities. The Payne effect of the silica/CB-filled NR is higher than for the silica-filled NR reference compound. This is due to the smaller inter-aggregate distance of the strongly reinforcing CB that gives a higher possibility for the formation of a strong filler-filler network. On the other side, the Payne effects of the silica/OC-filled NR are much lower than for the silica-filled NR reference compound, due to lower filler-filler interactions as well as the lower Mooney viscosities, which may be ascribed again to the clay-modifier.

3.3.2 Cure characteristics

Figure 3.2 Effect of secondary fillers on cure characteristics of silica-filled NR compounds: (a) carbon black (CB), and (b) organoclay (OC). Dump temperatures indicated in curve designations.

Based on cure curves in Figure 3.2, the scorch times of silica-filled NR compounds with CB and OC as secondary fillers decrease, when compared with the reference compound with silica alone. It is well known that free silanol groups on the silica surface interfere with vulcanization due to their acidic nature and their tendency to adsorb vulcanization accelerators, and so retard the vulcanization [17]. Only about 25% of the silanol groups on silica are reacting with the silane coupling agent, so 75% remains unreacted [29]. The role of the secondary accelerator, in particular the alkaline DPG, is to shield these remaining silanol groups. In the present case, the OC-containing compounds show by far the largest decrease in scorch time, again the result of the alkaline modifying agent of the OC, an organic ammonium derivative [26,30].

Interestingly, the OC containing compounds also show a considerable decrease in torque increment: Figure 3.2(b). The main reason must again be the effect of the modifying agent of the OC that might play an extra role in further modification of the silica surface over DPG, leading to a lowered extent of hydrogen bonding between the silica particles and so a reduced Payne effect or filler-filler interactions as seen in Figure 3.1(b). These results mutually confirm each other.

3.3.3 Tensile properties

Figure 3.3 Influence of dump temperature on: (a): tensile strength and elongation at break; and (b): tensile moduli of the silica-filled NR compounds containing different secondary fillers: carbon black (CB) or organoclay (OC).

Figure 3.3 shows the mechanical properties of the corresponding vulcanizates. At various dump temperature, the tensile strength, 100% modulus (M100) and 300% modulus (M300) of NR filled with silica/CB (Figure 3.3) increase until 160°C and then decrease when the dump temperature surpasses 160°C. Natural rubber degradation at higher temperatures can be the primary reason that causes that drop in tensile strength. On the other hand, the tensile strength and elongation at break of NR filled with silica/OC remain almost on the same levels. The moduli at 100% and 300% strain of NR filled with silica/OC (Figure 3.3(b)) increase with raising dump temperature until 151°C and then slightly decrease. This is again due to degradation of NR at higher temperatures. The moduli are significantly lower than for the reference silica and silica/CB compounds, which corresponds with the much lower torque differences seen in the cure curves (Figure 3.2) for these compounds. However, interestingly

the tensile strengths and elongations at break do not differ much from those for the reference silica and silica/OC compounds.

3.3.4 Dynamic mechanical properties

Figure 3.4 shows the DMA results of tan delta at -20°C and 0°C for silica-filled NR with the hybrid fillers. The tan delta at -20°C to $+20^{\circ}\text{C}$ measured on laboratory scale is often considered to predict the wet traction of a tire equipped with a tread based on the same compound, respectively the value at -20°C as a first indication of wear resistance [31-32]. The tan delta at -20°C of the silica/CB-filled NR as well as the silica/OC-filled NR rises with increasing dump temperature. This is again due to the better silanization at higher dump temperatures as also demonstrated in the lower Payne effects in Figure 3.1(b). The tan delta at -20°C and 0°C of the silica/OC-filled with NR is substantially higher than for the silica/CB as well as for the pure silica compounds. This indicates that there is a potential to improve wet traction and wear performance of a tire tread by using a small amount of OC in combination with silica.

Figure 3.4 Influence of dump temperature on: (a): tan delta at -20 and 0°C from DMA; and (b) tan delta at 60°C from DMA and RPA of silica-filled NR compounds containing different secondary fillers: carbon black (CB) or organoclay (OC).

The tan delta at 60°C of the vulcanizates indicates the energy loss by hysteresis under dynamic deformation, related to tire rolling resistance, commonly used to indicate rolling resistance on laboratory scale [31]. When comparing the results of tan delta at 60°C of the

reference silica-filled NR, silica/CB-filled NR and silica/OC-filled NR at the given mixer dump temperatures, the results for the silica/CB compounds are comparable with the reference silica-filled NR. So, the replacement of a little silica by CB would not change the level of rolling resistance of a tire. On the other hand, the OC gives a significantly lower tan delta at 60°C compared to the reference silica-compound, pointing at a large decrease/improvement of the rolling resistance for tires with some OC applied next to silica.

3.4 Conclusions

- An increased dump temperature for silica-filled NR compounds with the secondary fillers leads to a better silanization reaction between the silica and the coupling agent TESPD, but NR degradation can occur at too high mixing temperatures.
- The silica/CB-filled NR shows a higher cure rate and tensile moduli, while maintaining similar ultimate tensile properties and tan delta at 60°C compared to a pure silica-filled system.
- The silica/OC-filled NR shows a lower Payne effect, higher cure rate, lower moduli combined with similar ultimate tensile properties to silica or silica/CB, higher tan delta at -20°C and 0°C, indication of better wear and wet grip performance, respectively a lower tan delta at 60°C compared to the silica-filled system, indicative for reduced rolling resistance.
- The use of hybrid fillers, small amounts of secondary fillers as CB and in particular OC next to silica in NR, therefore offers the potential of further improvement in wear resistance, wet traction and rolling resistance of tire treads.

3.5 References

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CHAPTER 4

Influence of Mixing Procedure and TESPD Loading on the Properties of Silica/Secondary Fillers-Reinforced Natural Rubber Compounds

Reinforcement of rubber compounds can be achieved not only by use of a single filler but also by dual or hybrid fillers, in which the latter case aims for synergistic effects. One of the key factors to attain good reinforcement is the filler dispersion level in the rubber matrix. For low rolling resistance truck tire tread compounds based on Natural Rubber (NR), silica-silane technology has been applied to enhance both rolling resistance and wet traction, but it is known that abrasion resistance is still inferior compared to Carbon Black (CB)-filled compounds. This present work investigates the use of silica in combination with CB N134 and OrganoClay (OC) as secondary fillers aiming to enhance the tire compound performance in all facets. As processing conditions, especially temperature and mixing procedure, have an effect on dispersion and thus properties, by taking the recommended temperature for silica-reinforced NR compounds, this work compares three different mixing sequences. The silica/secondary filler ratio was fixed at 45/10 phr with bis-(3-TriEthoxySilylPropyl)Disulfide (TESPD) as the silane coupling agent. The loading of CB and OC together with a first half of silica shows optimum compound properties as indicated by lower Payne effect, higher total Bound Rubber Content (BRC), higher tear strength, lower tan delta at 60°C, and higher tan delta at -20°C. By varying the TESPD loading, both hybrid filler systems show a decrease of Payne effect and compound viscosities, increase of cure torque difference, apparent crosslink density, modulus and tensile strength with increasing TESPD loadings, while tear strength and dynamic mechanical properties show an optimum point. Based on the overall properties, the optimum TESPD content is 2.3 phr for silica/OC and 4.1 phr for silica/CB.

4.1 Introduction

The use of silica in non-polar rubbers requires sufficient chemical interaction and bonding between filler and rubber that can be achieved by means of silane coupling agents such as bis-(3-TriEthoxySilylPropyl)Tetrasulfide (TESPT). The use of TESPT provides lower filler-filler interactions, better dispersion stability and enhanced mechanical as well as dynamic mechanical properties, but it has a drawback of short scorch time as demonstrated by premature crosslinking during mixing [1]. To prevent this problem, bis-(3-TriEthoxySilylPropyl)Disulfide (TESPD) is an alternative. As the mixing of silica with silane coupling agent in a rubber compound involves a chemical reaction, so-called silanization, the mixing temperature has a dominant effect [2-6]. The mixing temperature needs therefore also to be optimized for hybrid fillers system of silica with CB and silica with OC [7].

To study the effect of secondary fillers like CB N134 and OC Dellite 67G in combination with silica, in order to ensure the best possible dispersion of fillers in the rubber matrix, a suitable loading procedure of secondary fillers into the silica-reinforced NR compound needs first to be verified. Then, the loading levels of TESP as coupling agent in the hybrid filler systems of silica/CB and silica/OC are investigated. The mixing behavior, cure characteristics, filler-filler interactions, filler-rubber interactions, tensile and tear properties, and dynamic mechanical properties of both hybrid filler-filled NR compounds are studied in this chapter.

4.2 Experimental

4.2.1 Materials

Natural rubber (Ribbed Smoked Sheet No.3, RSS3) was provided by Sri Trang Agro-Industry, Thailand. Silica ULTRASIL 7005 with a Cetyl-Trimethyl-Ammonium-Bromide (CTAB) and Brunauer-Emmet-Teller (BET) specific surface area of 171 and 190 m²/g, respectively; and TESP silane coupling agent were obtained from Evonik, Germany. Carbon black (N134) with CTAB and BET specific surface areas of 134 and 145 m²/g, respectively, was provided by Phillips Carbon Black Limited, India. Organoclay Dellite 67G, functionalized with 47 wt% of dimethyl dihydrogenated tallow ammonium chloride (2HT), 115 meq/100 g of cation exchange capacity and interlayer distance of 34.3 Å was provided by Laviosa Chimica Mineraria S.p.A, Italy. The other ingredients: Treated Distillate Aromatic Extract oil (TDAE) (Vivatec 500) (Hansen & Rosenthal, Germany); N-Cyclohexyl-2-Benzothiazyl Sulfenamide (CBS) primary accelerator; DiPhenyl Guanidine (DPG) secondary

accelerator; 2,2,4-TriMethyl-1,2-dihydroQuinoline (TMQ) (all from Flexys, Belgium); Zinc Oxide (ZnO); stearic acid and sulfur were all commercial grades for the rubber industry.

4.2.2 Compound preparation

Table 4.1 Formulations of silica/secondary fillers-filled NR compounds.

Ingredients	Amount (phr)	
	Silica Reference	Silica/Secondary fillers
Natural rubber (RSS3)	100.0	100.0
ULTRASIL 7005	55.0	45.0
Secondary fillers ^a	-	10.0
TESPD ^b	5.0	4.1 (or variable) ^c
TDAE oil	8.0	8.0
ZnO	3.0	3.0
Stearic acid	1.0	1.0
TMQ	1.0	1.0
DPG ^b	1.1	0.9
CBS	1.5	1.5
Sulfur	1.5	1.5

^aSecondary fillers were CB (N134) and OC (Dellite 67G).

^bAmounts of TESPd and DPG were added according to the following equations [8]:

$$\text{TESPD (phr)} = 0.00053 \times Q \times A \quad (1)$$

$$\text{DPG (phr)} = 0.00012 \times Q \times A \quad (2)$$

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

^cFor the effect of loadings of TESPd, this was varied at 0, 1.4, 2.3, 3.2, 4.1, 5.0, 5.9 and 6.8 phr or 0, 3.1, 5.1, 7.1, 9.1, 11.1, 13.1 and 15.1 wt% relative to the silica content.

The compound formulations employed are given in Table 4.1. The compounds were prepared using a two-step mixing procedure: the first was to prepare a masterbatch of rubber and fillers, and the second was to prepare the final compounds including the curatives. For the first step, an internal mixer Brabender Plasticorder 350 ml was operated at a rotor speed of 60 rpm, fill factor of 70% and initial mixer temperature setting of 100°C. The mixing conditions were based on the optimum setting parameters as determined from our previous study [5,7]. Three different loading procedures of CB and OC as secondary fillers were compared as shown in Table 4.2 and Scheme 4.1, wherein the secondary filler was added together with the first half

of silica, with the second half of silica, and after loading all silica. Halves of the TESP and DPG were added together with the first half of silica, leaving the second half of TESP to add later on together with TDAE extender oil with the second half of silica. The second step or final compound mixing was executed to incorporate the second half of DPG, CBS primary accelerator, and sulfur at a rotor speed of 30 rpm, fill factor of 70%, and an initial mixer temperature setting of 70°C. The reference compound with pure silica was also prepared using an initial mixer temperature setting of 100°C according to the previous report [5]. After the mixing procedure was optimized, the TESP content was varied at 0, 1.4, 2.3, 3.2, 4.1, 5.0, 5.9 and 6.8 phr or 0, 3.1, 5.1, 7.1, 9.1, 11.1, 13.1 and 15.1 wt% relative to the silica amount. The silica/secondary fillers ratio at 45/10 phr was used for both parts of this study.

Scheme 4.1 Two-step mixing procedures for compound preparations; NR/silica (a) and NR/silica + secondary filler (b) compounds.

Table 4.2 Loading procedures of secondary fillers into silica-filled NR compounds during the first mixing step.

First step: Internal mixer temperature setting at 100°C, rotor speed at 60 rpm and fill factor at 70%			
Ref. (S)	S+SF/M1	S+SF/M2	S+SF/M3
Masticated NR for 2 min.	Masticated NR for 2 min.	Masticated NR for 2 min.	Masticated NR for 2 min.
Added ½ silica, ½ TESP, ½ DPG and mixed for 5 min.	Added SF, ½ silica, ½ TESP, ½ DPG and mixed for 5 min.	Added ½ silica, ½ TESP, ½ DPG and mixed for 5 min.	Added ½ silica, ½ TESP, ½ DPG and mixed for 5 min.
Added ½ silica, ½ TESP, TDAE oil and mixed for 5 min.	Added ½ silica, ½ TESP, TDAE oil and mixed for 5 min.	Added SF, ½ silica, ½ TESP, TDAE oil and mixed for 5 min.	Added ½ silica, ½ TESP, TDAE oil and mixed for 5 min.
Added stearic acid, ZnO, TMQ and mixed for 3 min.	Added stearic acid, ZnO, TMQ and mixed for 3 min.	Added stearic acid, ZnO, TMQ and mixed for 3 min.	Added SF, stearic acid, ZnO, TMQ and mixed for 3 min.
Second step: Internal mixer temperature setting at 70°C, rotor speed at 30 rpm and fill factor at 70%.			
Added ½ DPG, CBS, sulfur and mixed for 3 min.	Added ½ DPG, CBS, sulfur and mixed for 3 min.	Added ½ DPG, CBS, sulfur and mixed for 3 min.	Added ½ DPG, CBS, sulfur and mixed for 3 min.

Remark: S=Silica, SF=secondary filler; M1=SF was added with the first half of silica, M2=SF was added with the second half of silica, M3 = SF was added after complete addition of all silica.

4.2.3 Sample characterizations

4.2.3.1 Testing of compound and vulcanizate properties

Mooney viscosity, Payne effect, cure characteristics, tensile properties and dynamic mechanical properties of the silica-, silica/CB, and silica/OC-filled NR compounds were investigated following the same methods and using the equipments as described in Chapter 3.

4.2.3.2 Tear properties

The compounds were vulcanized to their optimum cure times (t_{c90}) using a Wickert WLP 1600 laboratory compression press at 150°C and 100 bars into 2 mm thick sheets. The vulcanized rubber was tested at room temperature using Delft-type specimens with the same machine and crosshead speed as applied for tensile tests according to ISO 34-2.

4.2.3.3 Characterization of Bound Rubber Content (BRC)

An amount of 0.25 g of uncured compound (without curatives) was immersed in 40 ml of toluene for 7 days at room temperature in a normal atmosphere, corresponding to total bound rubber content. Then the sample was removed from the toluene, dried at 80°C in a vacuum oven for 24 h and weighed. The bound rubber content (BRC) was calculated using the following equation.

$$BRC(\%) = \frac{(m - m_s)}{m_r} \times 100 \quad (3)$$

where m is the weight of sample after extraction, m_s and m_r are the weights of filler and rubber in the original sample, respectively.

4.2.3.4 Apparent crosslink density

Vulcanized samples with a dimension of 3 x 5 x 2 mm³ were immersed in toluene at room temperature for 7 days. Thereafter, the swollen samples were taken out and blotted lightly with paper to remove excess toluene from the surface. The weights of the rubbers before and after swelling were measured and the swelling ratio (Q) was calculated according to the following equation:

$$Swelling\ ratio\ (Q) = (M_t - M_0)/M_0 \quad (4)$$

where M_0 and M_t are the weights of the samples before and after swelling, respectively. The apparent crosslink density was calculated from the reciprocal of swelling ratio (i.e. 1/ Q) [9], because the real crosslink density by for example the Flory-Rehner approach [10] is not feasible to acquire with the varying filler loadings.

4.3 Results and discussion

4.3.1 Optimizing the loading procedures of secondary fillers into silica-filled rubber compounds

4.3.1.1 Mixing behavior of masterbatch compounds

A good mixing quality to obtain fine filler dispersion in a rubber matrix is a prime requirement to attain optimal final compound properties. Mixing silica with silane coupling agent is related to two chemical reactions; first the silica-silane reaction or silanization, and second the silane-rubber coupling reaction. Proper silanization promotes good silica dispersion. For silica-silane-rubber compound mixing, the dump or discharge temperature has already been identified as the crucial parameter that affects both pure and silica-based hybrid filler compound properties [2-7]. Based on our previous results [7], a mixer temperature setting at 100°C to reach a discharge temperature in the range of 150°C was utilized in this present study. The effect of loading procedures of secondary fillers, i.e. CB N134 and OC Dellite 67G, in combination with silica was investigated for the best possible balance of compound properties. The silica/CB and silica/OC ratio was fixed at 45/10 phr, and three different loading procedures of CB and OC into the rubber compounds as detailed in Table 4.2 and Scheme 4.1 were compared. The results of mixing dump torques and temperature are shown in Figure 4.1(a) and 4.1(b), respectively. When compared with the pure silica reference, the compounds with CB N134 show a little higher dump torque and dump temperature due to its high specific surface area and high structure that contributes to a higher compound viscosity. Meanwhile, the compounds with silica/OC show totally different behavior as the dump torques and temperatures are lower than those of pure silica and silica/CB due to their lower compound viscosity affected by the modifying agent in OC that plasticizes the rubber compound. The loading of OC with the first half of silica shows the lowest dump torque and lowest compound viscosity, indicating the best dispersion of the fillers. The modifying agent in OC is known to provide a plasticizing effect in the rubber compounds [11] and also helps to reduce the silica network as it provides an additional shielding effect for the free silanol groups that are left over on the silica-surface after the silanization reaction.

Figure 4.1 Dump torques (a) and dump temperatures (b) of silica-filled NR compounds with varying loading procedures of secondary fillers, in comparison with pure silica-filled NR (S). (S= Silica, SF= secondary filler; M1= SF was added with the first half of silica, M2= SF was added with the second half of silica, M3= SF was added after complete addition of all silica)

4.3.1.2 Filler-filler and filler-rubber interactions

The non-linear viscoelastic behaviors of filled compounds can be observed in the change of storage modulus that decreases with increasing strain, as shown in Figures 4.2(a) and 4.2(b). Such decrease is attributed to breakdown of the filler network resulting in a reduction of filler-filler interactions. The difference between the storage modulus values at low strain and high strain is used to indicate the level of filler-filler interactions, called the Payne effect [12], as displayed in Figure 4.2(c). When compared to the silica-filled NR reference, the Payne effect of silica/CB-filled NR compounds are similar when CB was added with either the first or second half of silica, but clearly increased when CB was added after loading all silica. The addition of CB at the later stage leaves not enough incorporation time for CB and thus results in poorer dispersion in the rubber matrix as reflected by higher filler-filler interactions. On the other hand, the Payne effect of silica/OC-filled compounds with all three different loading procedures shows much lower values than that of the silica-filled NR reference compound as a result of the surface modifying agent contained in OC. Among silica/OC-filled mixes, the loading of OC at a later stage results in a slightly higher Payne effect as there is less time for OC to disperse and the modifying agent to take effect. The dramatic drop in storage modulus at low strain in the presence of OC in silica-filled NR compounds indicates a reduction of filler network and filler-filler interactions.

The lower filler-filler interaction or Payne effect in the silica/OC-filled NR compounds compared to the pure silica-filled one was reported before by us [7]. The reduction of filler network by the use of silica/OC hybrid fillers has also been previously reported by Galimberti *et al.* [11] based on a study using synergistic PolyIsoprene Rubber (IR)/SBR compounds with a fixed content of silica at 70 phr and varied OC loadings. It was discussed that the lipophilic ammonium cation of the modifying agent of OC acted as plasticizer that resulted in a reduction of the storage modulus of the matrix both at low and at large strains.

Figure 4.2 Storage modulus as a function of strain of silica/CB-filled NR (a), silica/OC-filled NR (b), Payne effect (c) and total bound rubber content (d) of silica/secondary fillers-filled NR compounds with varying loading procedures of secondary fillers, in comparison with pure silica-filled NR (S).

The filler-rubber interaction is determined by Bound Rubber Content (BRC) [13] in which a higher value indicates a better filler-rubber interaction. Figure 4.2(d) shows the total BRC as resulting from both chemical and physical interactions in the rubber compounds prepared by using different loading procedures of secondary fillers compared to the reference. The silica/CB-filled NR shows a higher BRC than the pure silica compound and the highest BRC is observed for loading of CB at the first half of silica. The highest filler-rubber interaction in this case is the result of good dispersion of the fillers, efficient silanization of silica with silane and additional physical absorption of rubber molecules on the high specific area CB. The loading of CB with the first half of silica that shows the highest total BRC is in correspondence with its lowest Payne effect as shown in Figure 4.2(c). The silica/OC-filled compounds display the lowest total BRC due to the effect of the modifying agent on OC that enhances filler dispersion and plasticizes the system to result in less occluded or trapped rubber and thus lower bound rubber.

4.3.1.3 Processability and cure characteristics

Figure 4.3 Mooney viscosity (a) and minimum cure torque (b) of silica/secondary fillers-filled NR compounds with varying loading procedures of secondary fillers, in comparison with pure silica-filled NR (S).

The processability of rubber compounds is assessed by their Mooney viscosities and minimum cure torques (M_L) in curing which indicate the ability of the materials to flow. The lower Mooney viscosity and M_L mean an improvement in processability. The NR compounds filled with silica/secondary fillers with different loading procedures of CB or OC in the

masterbatch mixing stage are displayed in Figures 4.3(a)-(b). In accordance with dump torque (Figure 4.1(a)) and Payne effect (Figure 4.2(c)), the silica/OC compounds have much lower compound viscosities compared to the reference compound with silica only and the silica/CB combination, in line with the previous observations [7,11] as influenced by 2HT which was used as modifying agent for the OC, that provides the plasticizing effect. The loading of CB with the first half of silica or at the early stage of mixing results in the lowest M_L and Mooney viscosity when compared among the three different filler loading procedures, as CB was mixed while the NR matrix viscosity remained high giving good shear force to disperse the filler.

The maximum cure torques (M_H) and cure torque differences ($M_H - M_L$) of NR filled with silica/secondary fillers prepared by various loading procedures of secondary fillers are shown in Figures 4.4(a)-(b) in comparison with the reference pure silica-filled NR. The stiffness of the rubber compounds can be related to M_H or $M_H - M_L$, that are influenced by chemical crosslinks, both chemical and physical interactions and the filler network. Both M_H and $M_H - M_L$ values of the pure silica-filled NR compound are higher than that of silica/CB-filled mixes and distinctly higher than that of the silica/OC-filled compounds due to the higher filler network of silica and the contribution from chemical bonding between the silica and rubber via silane coupling agent. The lowest M_H and $M_H - M_L$ values of the silica/OC-filled compounds again may be attributed to the effect of surface modifying agent on the clay. With regard to different loading procedures of secondary fillers into the silica-filled compounds, there is only a small variation.

Figure 4.4 Maximum cure torque (a) and cure torque difference (b) of silica/secondary fillers-filled NR compounds with varying loading procedures of secondary fillers, in comparison with pure silica-filled NR (S).

The use of secondary fillers, both CB and OC in silica-filled NR compounds reduces the scorch time (t_{s2}) and increases the Cure Rate Index (CRI) substantially, in which the silica/OC-filled system changes to a greater extent as displayed in Figure 4.5. The compound with silica only shows longer t_{s2} and lower CRI due to the retardation effect on the vulcanization reaction by acidic silanol groups [15] and adsorption of polar cure accelerators on the polar silica surface via hydrogen bonding. For the silica/CB hybrid filler system, silica was partially replaced by CB N134, so there are less silanol groups available and moreover the furnace black with high specific surface area helps to promote the cure reaction. For the silica/OC system, as the OC contains 47 wt% of modifying agent 2HT, these compounds experience an additional effect from the ammonium-based modifying agent. The amine groups of the organic modifying agent on OC promote a faster curing reaction [7,16-21], i.e. higher CRI. For cure characteristics, there is not much effect derived from the different loading procedures of CB and OC. The presence of CB and OC raises the CRI and shortens the curing cycles, that benefits productivity and the energy required for vulcanization.

Figure 4.5 Scorch time (a) and cure rate index (b) of silica/secondary fillers-filled NR compounds with varying loading procedures of secondary fillers, in comparison with pure silica-filled NR (S). The CRI was calculated to equal $[100/(\text{optimum cure time } (t_{c90}) - \text{scorch time } (t_{s2}))]$.

4.3.1.4 Mechanical properties

The tensile properties, 300% modulus (M300), reinforcement index (M300/M100), tensile strength and elongation at break, of the silica/CB- and silica/OC-filled NR compounds prepared by using different loading procedures of CB and OC compared to the pure silica-filled

NR compounds are displayed in Figures 4.6-4.7. The different loading procedures show almost no influence on tensile properties. The materials with different fillers show differences in modulus and reinforcement index, but similar ultimate tensile properties, i.e. tensile strength and elongation at break. The modulus at 300% strain of silica/OC-filled NR is much lower compared to the values of pure silica- and silica/CB-filled NR vulcanizates, in line with the results of maximum cure torques and cure torque differences in Figure 4.4. The use of silica only and silica/CB in NR results in similar 300% modulus, but the reinforcement index of silica/CB-filled NR shows much higher levels than for the silica-filled one, due to the high specific surface area and high structure of CB N134. The loading of CB N134 at the first half of silica shows slightly better reinforcement index compared to other methods.

Figure 4.6 300% modulus (a) and reinforcement index (b) of silica/secondary fillers-filled NR compounds with varying loading procedures of secondary fillers, in comparison with pure silica-filled NR (S).

Tear strengths of the NR vulcanizates filled with silica and silica/OC with different loading procedures are practically the same, but the use of silica/CB enhances the tear strength as shown in Figure 4.8(a), corresponding with the total bound rubber content in Figure 4.2(d) and the reinforcement index in Figure 4.6(b). The apparent crosslink density of NR filled with silica and secondary fillers using different loading procedures as shown in Figure 4.8(b) show the same trends as observed for the maximum cure torque, cure torque difference and 300% modulus. By comparing the different loading sequences of secondary filler, the loading of CB at the first half of silica results in slightly higher tear strength and apparent crosslink density, due to the better filler

dispersion, as seen previously in the Payne effects (Figure 4.2(c)) and total bound rubber contents (Figure 4.2(d)). The higher apparent crosslink density of the silica-filled NR compared to the hybrid filler system can be ascribed to the combination of rubber-rubber and rubber-filler crosslinks, filler network of silica, and filler-rubber interactions enhanced by the silane coupling agent.

Figure 4.7 Tensile strength (a) and elongation at break (b) of silica/secondary fillers-filled NR compounds with varying loading procedures of secondary fillers, in comparison with pure silica-filled NR (S).

Figure 4.8 Tear strength (a) and apparent crosslink density (b) of silica/secondary fillers-filled NR compounds with varying loading procedures of secondary fillers, in comparison with pure silica-filled NR (S).

4.3.1.5 Dynamic mechanical properties

Figure 4.9 Tan delta at -20°C (a) and tan delta at 60°C (b) of silica/secondary fillers-filled NR compounds with varying loading procedures of secondary fillers, in comparison with pure silica-filled NR (S).

The dynamic mechanical properties as a function of temperature of the materials were analyzed by Dynamic Mechanical Analyzer (DMA) and their loss tangent or tan delta values are used to predict tire performance, i.e. tan delta at -20°C for ice/wet traction and tan delta at 60°C for rolling resistance [22]. A higher value of tan delta at -20°C is required for better tire breaking ability and lower tan delta at 60°C is needed for low rolling resistance and thus energy saving. Figure 4.9(a) shows that the tan delta values at -20°C of NR filled with silica in combination with CB and OC are higher than for the pure silica compound. Additionally, the loading of secondary filler with the first half of silica shows a higher tan delta at -20°C than the other loading procedures. The results are in agreement with the lower filler-filler interaction or Payne effect (Figure 4.2(c)), higher total bound rubber content (Figure 4.2(d)) and better mechanical properties as shown by the reinforcement index (Figure 4.6(b)) and tear strength (Figure 4.8(a)). With regard to the tan delta at 60°C, the silica/CB- and silica/OC-filled NR prepared by using the loading procedure of secondary fillers with the first half of silica shows a similar value as that of pure silica-filled NR and better than for the other loading procedures.

Overall, based on the compound properties both before and after vulcanization, the optimum mixing sequence of the hybrid fillers filled NR compound is to add the secondary

filler at an early stage of mixing with the first half of silica in order to obtain the best possible dispersion, lowest Payne effect, highest bound rubber content and best dynamic responses.

4.3.2 Effect of loadings of TESPD on the properties of silica/secondary fillers-filled natural rubber compounds

To further optimize the properties of the NR filled with hybrid fillers, in addition to the optimized mixing procedure, this work investigates the effect of TESPD silane coupling agent loadings for silica/CB- and silica/OC-filled NR compounds, in comparison with the pure silica-silane reference.

4.3.2.1 Mixing behavior of masterbatch compounds

Figure 4.10 Dump torques (a) and dump temperatures (b) of silica/secondary fillers-filled NR compounds with varying loadings of TESPD, in comparison with pure silica-filled NR (S55).

The dump torques and temperatures of masterbatch compounds of NR filled with 45/10 phr silica/CB and silica/OC hybrid fillers with different loadings of TESPD are shown in Figures 4.10(a)-(b). With increasing loading levels of TESPD, dump torques and temperatures gradually decrease for both silica/CB and silica/OC compounds indicating lower compound viscosities and less shearing heat generated. Increased TESPD loading can effectively modify the silica surface from hydrophilic to hydrophobic and facilitate the silica dispersion. Moreover, the silane coupling agent also provides a lubrication effect resulting in lower compound viscosity. The silica/OC-filled compounds show lower dump torques and temperatures compared to silica/CB system as influenced by the modifying agent in OC. When compared to

the pure silica system, at the same TESP loading, the silica/CB-filled compound shows similar dump torque and temperature levels which are higher than those of the silica/OC-filled mix. The dump torques level off at loading levels of TESP 5.0 phr for silica/CB and silica/OC. The one point for silica/OC in Figure 4.10 may be considered as an outlier.

4.3.2.2 Filler-filler and filler-rubber interactions

Figure 4.11 Storage modulus as a function of strain of silica/CB-filled NR (a), silica/OC-filled NR (b), Payne effect (c) and total bound rubber content (d) of silica/secondary fillers-filled NR compounds with varying loadings of TESP, in comparison with pure silica-filled NR (S55).

The storage moduli as functions of strains of silica/CB-filled NR and silica/OC-filled NR are shown in Figures 4.11(a) and (b), respectively. The silica/CB-filled NR compounds clearly have higher storage moduli at low strain compared to the silica/OC systems. By calculating the difference between storage moduli at low and high strains, the Payne effect of both hybrid filler systems are displayed in Figure 4.11(c). The increasing loadings of TESPD decrease the Payne effect or filler-filler interaction especially in the case of silica/CB-filled compounds. The Payne effect of the silica/OC-filled NR compounds is much lower than that of silica/CB and shows less dependence on TESPD loading, as the systems already experience an additional effect from the OC surface modifying agent. When compared to the pure silica reference compound at the same content of TESPD, both hybrid filler systems give lower Payne effects, especially the silica/OC combination that results in remarkably low filler-filler interaction or a low filler network due to the additional shielding effect on the filler surface by the modifying agent present in OC. The Payne effect results correspond well with the compound dump torques as displayed in Figure 4.10(a).

Figure 4.11(d) shows the total bound rubber contents (BRC) for silica/secondary fillers with different loadings of TESPD. The silica only-filled NR compound with optimum content of silane at 5 phr shows a similar total BRC as that of silica/CB without TESPD. In spite of no TESPD added, the latter compound has a lower amount of silica and the presence of CB somehow improves the dispersion so that this results in similar levels of total BRC that reflects filler-rubber interaction. By introducing TESPD into silica/CB-filled NR, the total BRC increases to reach an optimum at 2.3 phr, and thereafter decreases with increasing loadings of TESPD. The silica/OC compounds show similar trends as silica/CB but at much lower level of total BRC throughout the range of TESPD loadings studied. The higher BRC of silica/CB-filled NR than for silica/OC-filled can be ascribed to various factors, including higher filler-elastomer interaction promoted by the high specific surface area of N134, and good compatibility between CB and rubber. In addition, more filler network which introduces more trapped or occluded rubber also plays a role as this silica/CB hybrid filler-filled NR has a higher Payne effect (Figure 4.11(c)).

4.3.2.3 Processability and cure characteristics

The Mooney viscosities and M_L of the NR compounds filled with silica/CB and silica/OC with different loadings of TESPD show similar trends, as seen in Figures 4.12(a)-(b). Both Mooney viscosities and M_L decrease with increasing TESPD loadings due to better silanization resulting in better filler dispersion. The decrease of compound viscosities with

increasing TESPd contents for pure silica-filled NR compounds has been reported before [1]. The reduction of both Mooney viscosities and M_L with increasing TESPd loadings is more pronounced in the case of silica/CB compared to silica/OC in which the latter clearly has lower compound viscosities. The incorporation of CB N134 with high specific surface area and high structure and small inter-aggregate distance leads to a higher possibility for the formation of a strong filler-filler network, whereas the addition of OC also introduces the surface modifying agent that can plasticize the rubber compound and reduce filler-filler interaction. Both properties correspond with the dump torques (Figure 4.10(a)) confirming that the presence of secondary fillers enhances flowability of the rubber compounds and hence improves processability.

The maximum cure torques (M_H) and cure torque differences ($M_H - M_L$) for both silica/CB- and silica/OC-filled NR compounds continuously rise with increasing amounts of TESPd as shown in Figures 4.13(a)-(b), in which the levels of both properties of silica/CB-filled NR compounds are higher than those of silica/OC-filled NR compounds due to the higher filler-filler interaction as discussed previously for the Payne effect (Figure 4.11(c)). Both M_H and $M_H - M_L$ of the rubber compounds are influenced by several parameters including chemical and physical crosslinks, chemical and physical filler-rubber interactions and the filler network. The increased loading of TESPd silane coupling agent promotes chemical bonds between the rubber and fillers as well as chemical filler-rubber interactions so that the cure torques increase.

Figure 4.12 Mooney viscosity (a) and minimum cure torque (b) of silica/secondary fillers-filled NR compounds with varying loadings of TESPd, in comparison with pure silica-filled NR (S55).

Figure 4.13 Maximum cure torque (a) and cure torque difference (b) of silica/secondary fillers-filled NR compounds with varying loadings of TESPD, in comparison with pure silica-filled NR (S55).

Figure 4.14 Scorch time, optimum cure time (a) and cure rate index (b) of silica/secondary fillers-filled NR compounds with varying loadings of TESPD, in comparison with pure silica-filled NR (S55).

With increasing TESPD contents, the silica/CB- and silica/OC-reinforced NR compounds show totally different cure behaviors, as demonstrated by their t_{s2} , optimum cure times (t_{c90}) and CRI in Figure 4.14(a)-(b). Both hybrid filler systems give much shorter t_{s2} and t_{c90} with much higher CRI compared with the pure silica reference compound as a result of less

silanol groups and the presence of either high specific surface area CB or OC with the ammonium salt-based modifying agent. Therefore, in terms of productivity, the hybrid filler is beneficial as the cycle time can drastically be reduced. For the silica/OC system, t_{s2} and CRI decrease with increasing amount of TESPd while the t_{c90} marginally increases till the TESPd amount reaches 5.0 phr, and thereafter raises dramatically. So, an excess of TESPd in the presence of the modifying agent from OC interferes with the vulcanization. On the other hand, the silica/CB-filled compounds show a maximum t_{s2} and CRI at the TESPd loading of 4.1 phr and thereafter decrease while the t_{c90} shows no clear trend. This indicates that the silica/CB hybrid filler combination requires less TESPd loading compared to the use of pure silica.

4.3.2.4 Mechanical properties

The tensile properties, i.e. tensile strength, elongation at break, 300% modulus (M300) and reinforcement index (M300/M100) of the NR vulcanizates filled with silica/secondary fillers with varied TESPd loadings are presented in Figures 4.15-4.16 in comparison with that of the silica reference compound. The tensile strength of both hybrid filler systems increases with increasing content of TESPd, while the elongation at break tends to decrease slightly. The tensile strength of silica/CB-filled NR compounds is much lower than for the silica reference at low TESPd content, but increases to match the same level for equal loading of TESPd (i.e. 5 phr) used, and then continues to increase slightly. For the silica/OC system, the tensile strength shows less dependence on TESPd loading as the property first increases but soon levels off when the TESPd loading exceeds 3 phr. The increase of TESPd loading raises the moduli at 300% strain for both hybrid filler systems in accordance with the maximum cure torque and cure torque difference (Figure 4.13) which can be ascribed to the improved dispersion and enhanced filler-rubber interaction. Again it is clear that the silica/CB-filled NR gives higher moduli than silica/OC-filled NR compounds, as previously seen in Figure 4.6. Despite the increase in 300% modulus, the reinforcement index (M300/M100) of both compound types shows no clear positive effect by the increase of TESPd loading. The values of silica/OC-filled NR compounds decrease slightly with increasing loadings of TESPd and that of silica/CB-filled NR compounds clearly decrease when TESPd loading reaches 5 phr. The change of reinforcement index of the materials is in line with their total bound rubber contents as shown in Figure 4.11(d).

Figure 4.15 Tensile strength (a) and elongation at break (b) of silica/secondary fillers-filled NR compounds with varying loadings of TESPD, in comparison with pure silica-filled NR (S55).

Figure 4.16 300% modulus (a) and reinforcement index (b) of silica/secondary fillers-filled NR compounds with varying loadings of TESPD, in comparison with pure silica-filled NR (S55).

Figure 4.17 Tear strength (a) and apparent crosslink density (b) of silica/secondary fillers-filled NR compounds with varying loadings of TESPd, in comparison with pure silica-filled NR (S55).

Tear strength shows similar trends as tensile strength with regard to the dependence on the TESPd silane coupling agent loading, but a larger difference in values between the two hybrid filler systems are observed at optimum as seen in Figure 4.17(a). The tear strength of silica/OC-filled NR improves sharply when TESPd is added, at a small amount of 1.4 phr, and then levels off. While the tear strength of silica/CB-reinforced NR shows a dramatic rise with increasing loading of TESPd to reach an optimum at 4.1 phr and thereafter decreases. At the optimum point, the silica/CB hybrid filler gives a higher tear strength than the pure silica reference compound, derived from the synergistic effect of CB N134. The use of OC as secondary filler that contains modifying agent helps to improve filler dispersion and requires less silane surface modifier. However, as this surface modifying agent also plasticizes the system, the vulcanizates therefore have a lower tear strength at high TESPd loadings compared to the silica/CB-filled rubbers. For the apparent crosslink density as shown in Figure 4.17(b), the values for both hybrid filler systems gradually increase with TESPd loading, in agreement with the 300% modulus (Figure 4.16(a)) and cure torque difference (Figure 4.13(b)).

4.3.2.5 Dynamic mechanical properties

Figure 4.18 shows the results of tan delta at 60°C of the rubber vulcanizates as tested with the Rubber Process Analyzer (RPA) and DMA, which may be used as indicative for tire rolling resistance. The tan delta at 60°C values obtained from the two different instruments show different trends when the TESPd loading is increased, probably due to the different

testing conditions, i.e. 3.49% strain for the RPA and 0.1% strain for the DMA. It is well known that the Payne effect, as indicative for filler-filler networking, occurs primarily around 1% strain for CB filled rubber compounds, whereas around 10% strain for silica-filled. The reason is the lower rubber-filler and filler-filler bond strengths for CB: physical of nature, vs silica: chemical of nature. This 1% strain is just between the two strains employed in the DMA vs. the RPA. So the present results as to the effect of the secondary fillers need to be viewed as that the filler-filler interaction for the CB-part is still present for the DMA-results, but practically gone for the RPA-results. The OC is also considered to react with the coupling agent TESPD and therefore also behaves more or less as silica, with the filler-filler network still intact for either dynamic mechanical analysis methods. The results obtained from both tests clearly show that the tan delta values at 60°C for NR filled with silica/CB are higher than those of silica/OC containing an optimum TESPD loading. In the silica/CB case, tan delta at 60°C decreases with increasing loadings of TESPD due to better silanization of the silica-part, more filler-rubber interaction and filler dispersion. However, the tan delta at 60°C for NR filled with silica/OC decreases when 2.3 phr (i.e. 4.2 wt% relative to total filler content or 5.1 wt% relative to the silica content) of TESPD was added. A further increase of TESPD increases the tan delta at 60°C and so has a negative effect on tire rolling resistance. It should be noted though that the use of the silica/OC hybrid system at optimum condition results in a lower tan delta at 60°C when compared to the use of silica only, at least in the RPA.

Figure 4.18 Tan delta at 60°C from RPA (a) and from DMA (b) of silica/secondary fillers-filled NR compounds with varying loadings of TESPD, in comparison with pure silica-filled NR (S55).

Figure 4.19 Tan delta at -20°C (a) and tan delta at 0°C (b) of silica/secondary fillers-filled NR compounds with varying loadings of TESPd, in comparison with pure silica-filled NR (S55).

Figure 4.19 shows the tan delta values at -20°C and 0°C used to indicate ice traction and wet traction, respectively. Higher values mean better properties. The silica/CB-filled NR compounds show an optimum point at TESPd loading of 2.3 phr, while the tan delta values at -20°C and 0°C of the silica/OC-filled NR compounds steadily decrease with increasing loadings of TESPd. When comparing the values at the same TESPd loading as that of the pure silica reference compound, the hybrid fillers now show positive effects on tire traction ad wet grip. But by using the optimum TESPd content for each hybrid filler system, i.e. 2.3 phr for silica/OC and 4.1 phr for silica/CB as determined based on the overall properties, clear improvements in tan delta values at -20°C and 0°C can be achieved.

4.4 Conclusions

The properties of silica/CB- and silica/OC-filled NR compounds at the ratio of 45/10 phr are affected by the loading procedures of CB and OC as secondary fillers into the mixes. By loading the CB and OC together with the first half of silica results in the best overall properties as determined by lower Payne effects, higher total bound rubber contents, higher tear strengths, lower tan deltas at 60°C but higher tan deltas at -20°C. This is caused by the addition of the secondary fillers in an early stage while the matrix viscosity is still high and there is long enough mixing time left. By applying this optimum loading procedure for CB and OC, the effect of TESPd loading varying from 0-6.8 phr was studied. The compounds with both hybrid filler systems show decreases of Payne effect and compound viscosities; increases

of cure torque difference, apparent crosslink density, modulus and tensile strength with increasing TESPd loadings; while tear strength and dynamic mechanical properties show optimum points. Based on the overall properties, the optimum TESPd contents are 2.3 phr for silica/OC and 4.1 phr for silica/CB. The presence of the modifying agent in the OC reduces the amount of TESPd needed for the rubber compounds.

These conclusions are summarized in the radar charts hereunder. Figure 4.20 and Figure 4.22 show radar charts covering the cure properties and Payne effects of the compounds (Figure 4.20(a) and Figure 4.22(a)), as well as the mechanical properties of the vulcanizates (Figure 4.20(b) and Figure 4.22(b)). These two charts are based on relative values versus the reference S55. The charts concerning tire performance as shown in Figure 4.21 and Figure 4.23 are based on index-values: the higher the better.

Optimized adding sequence of secondary fillers for silica-filled NR compounds

Figure 4.20 Radar charts comparing cure properties, Payne effect (a), and mechanical properties (b) of the silica-filled NR reference compound with silica only (S), and with carbon black N134 or organoclay as secondary filler. These compounds were prepared with an optimized sequence of the mixing (S+CB/M1 and S+OC/M1, respectively).

Figure 4.21 Radar chart comparing key tire performances indicated by lab-indicators of the silica-filled NR reference compound with silica only (S), and with carbon black N134 or organoclay as secondary filler. These compounds were prepared with an optimized sequence of the mixing (S+CB/M1 and S+OC/M1, respectively).

Optimized TESPd amounts for silica-filled NR compounds with secondary fillers

Figure 4.22 Radar charts comparing cure properties, Payne effect (a), and mechanical properties (b) of the silica-filled NR reference compound with silica only with an optimum amount of TESPd (S), and the silica-filled NR compounds with carbon black N134 or organoclay as secondary filler plus an optimum amount of TESPd at 4.1 and 2.3 phr (S+CB/TESPD 4.1 and S+OC/TESPD 2.3), respectively.

Figure 4.23 Radar chart comparing the key tire performances indicated by lab-indicators of the silica-filled NR reference compound with silica only with an optimum amount of TESPD (S), and the silica-filled NR compounds with carbon black N134 or organoclay as secondary filler plus an optimum amount of TESPD at 4.1 and 2.3 phr (S+CB/TESPD 4.1 and S+OC/TESPD 2.3), respectively.

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Synergistic Effects by High Specific Surface Area Carbon Black as Secondary Filler in Silica-Reinforced Natural Rubber Tire Tread Compounds

The partial replacement of silica by high specific surface area and high structure Carbon Black (CB) N134 as secondary filler, keeping the same total filler content at 55 phr, shows a clear synergistic effect on overall performance. At low content of CB, i.e. in the range of 0-36 wt% of CB relative to total filler amount, the Payne effect and tan delta at both 0°C and 60°C change marginally, but thereafter gradually increase. Optimum cure times are shortened in the presence of CB, facilitating an increase of productivity. Bound rubber content and mechanical properties show an optimum at 18 wt% of CB relative to total filler amount or at a ratio of silica/CB 45/10 phr. With regard to tire performance as indicated by the laboratory test results, the abrasion resistance, wet grip and ice traction can therefore be enhanced while maintaining the tire rolling resistance at the optimum level for this silica/CB ratio.

5.1 Introduction

Natural Rubber (NR) is widely used in all types of tires especially for heavy truck and aircraft tires in order to obtain a low heat build-up level and good mechanical strength. Moreover, many components of passenger car tires are also composed of NR such as bead filler, sidewall and tread compounds, making use of its low heat build-up, good flex-fatigue resistance as well as mechanical properties. Tires are built from several components that are made from different type of compounds which contain about 30% by weight of particulate reinforcing fillers such as CB and silica [1]. Carbon Black (CB) was the first reinforcing filler for rubber compounds to improve modulus, tensile and tear strength, abrasion resistance, skid resistance and other properties. The properties of the reinforced materials are influenced by the filler's particle size, surface area, structure and surface chemistry [2]. Replacement of CB with silica in passenger car tire tread compounds, after the patent of Michelin in 1992 [3], offers tire compounds with lower rolling resistance and higher wet grip [4], so less fuel consumption and better driving safety. However, the successful use of silica in rubber compounds requires sufficient bonding and/or interaction between the silica and elastomer interphases because of differences in polarity of silica and rubbers. The silica surface has a large number of silanol groups that are highly polar and can form hydrogen bonding with polar materials, especially amine-based accelerators causing an adsorption of the curing agents on the silica surface and retardation of the vulcanization reaction [5]. Moreover, these polar silanol groups cause strong filler-filler interactions and so it is difficult to disperse silica well in the non-polar tire rubbers and to obtain sufficient interfacial compatibility. However, these difficulties can be overcome by the use of silica in combination with silane coupling agents.

Mixing of silica with silane in rubber involves a chemical reaction, the so-called silanization [1,6] which takes place between the alkoxy groups of the silane and the silanol groups of the silica. The main governing parameter is the discharge mixing temperature [7,8], where the reaction can be catalyzed by the presence of DiPhenyl Guanidine (DPG) or alternative amines [9-10]. Sulfur containing silane coupling agents such as bis-(3-TriEthoxySilylPropyl)Tetrasulfide (TESPT) are commonly applied in such compounds vulcanized with a sulfur system, as TESPT has the drawback of short scorch times due to free sulfur that is released during high temperature mixing by creating premature crosslink reactions [7], a silane with smaller sulfur rank such as bis-(3-TriEthoxySilylPropyl)Disulfide (TESPD) can be used and is applied in present study.

Recently, a new generation of reinforcing fillers for rubber products have been introduced, especially nanofillers [11-12] such as nanoclay, carbon nanotubes and graphene. There is a growing interest to use a filler combination or hybrid fillers making use of the benefits provided by the individual components aiming for a synergistic effect on the rubber properties. The most simple combination should be silica/CB as both types of fillers are already commonly used in tire compounds. The use of a silica and CB combination in NR-based truck tread compounds was investigated before and the results indicated that when CB N220 was completely replaced by TESPT-modified silica, the rolling resistance was improved by about 30% while there was little change in the tread wear index (abrasion resistance) and wet traction [13]. An investigation of the influence of silica mixed with CB N220 in the presence and absence of a silane coupling agent on retraction behavior of NR vulcanizates [14] showed that the vulcanizates containing the silane coupling agent provided faster recovery rates compared to those without, due to the polymer-filler interactions, crosslinks between the rubber and silica, and increased crosslink densities. With increasing silica proportion in the silica/CB mixes, the vulcanizates with and without the silane coupling agent showed a decrease in hardness and modulus, but the ones with the silane coupling agent had higher values due to better filler dispersion and higher crosslink density than those without the silane coupling agent. A study on mechanical properties of NR reinforced with various ratios of CB N330/silica hybrid fillers with silane coupling agent showed that vulcanizates containing 20 and 30 phr of silica in a total of mixed filler of 50 phr exhibited the best overall mechanical properties [15]. The addition of a small amount of silica (VN3) into Solution-Styrene Butadiene Rubber (SSBR)/CB (N330) compounds, such as by the use of a CB/silica ratio of 45/5 phr, decreased the filler cluster branching and increased the reinforcement efficiency [16]. This decreased filler networking and more homogeneous filler dispersion subsequently resulted in better abrasion resistance, lower rolling resistance and better wet skid resistance, i.e. better dynamic mechanical properties. However, when the silica proportion was raised, filler cluster branching increased quickly and deteriorated the properties.

In addition to tire rubbers, the effect of CB/silica hybrid fillers in a polar rubber like acrylonitrile Butadiene Rubber (NBR) has also been investigated [17]. The cure characteristics and physico-mechanical properties of NBR filled with Semi-Reinforcing Furnace (SRF) black (N770)/silica (Hisil233) were studied, in which the total filler content was kept constant at 50 phr and the silica content was varied at 0, 10, 20, 25, 30, 40 and 50 phr. The optimum cure time (t_{c90}), scorch time (t_{s2}), minimum cure torque (M_L), and maximum cure torque (M_H) of CB/silica-filled NBR compounds increased as the silica content was raised. The replacement

of CB with silica decreased the material's stiffness, tensile strength, compressive strength, tear strength and modulus, but increased elongation at break and rebound resilience.

Although the use of CB in combination with silica has been widely studied and previously reported, the use of CB as secondary filler in silica-reinforced NR compounds aiming to enhance tire performance has not been considered. Our previous report on the effect of addition of small amounts of organoclay and CB as secondary fillers to silica-reinforced NR tire tread compounds [18] shows that the properties of compounds are affected by the mixing dump temperature. An increased dump temperature leads to a better silanization reaction between the silica and the coupling agent TESPD, but at too high mixing temperatures NR degradation can occur. The present study employs high specific surface area and structure CB N134 in synergy with silica in NR tire tread compounds. In the present work, the hybrid filler of silica/CB-filled NR with various ratios is investigated keeping the total filler content constant at 55 phr. The effect of CB N134 on the properties of silica-reinforced NR compounds is investigated with respect to filler networking, filler-filler interactions, filler-rubber interactions, cure characteristics, tensile properties, dynamic mechanical properties and abrasion resistance, all of importance for tire performance.

5.2 Experimental

5.2.1 Materials

Natural Rubber (Ribbed Smoked Sheet No.3, RSS3) was provided by Sri Trang Agro-Industry, Thailand. Silica ULTRASIL 7005 with a Cetyl-Trimethyl-Ammonium-Bromide (CTAB) and Brunauer-Emmet-Teller (BET) specific surface area of 171 and 190 m²/g, respectively, and silane coupling agent TESPD were obtained from Evonik, Germany. Carbon black (N134) with a CTAB and BET specific surface areas of 134 and 145 m²/g, respectively, was provided by Phillips Carbon Black Limited, India. The other ingredients: Treated Distillate Aromatic Extract oil (TDAE oil) (Vivatec 500) (Hansen & Rosenthal, Germany); DiPhenyl Guanidine (DPG), N-Cyclohexyl-2-Benzothiazyl Sulfenamide (CBS), 2,2,4-TriMethyl-1,2-dihydroQuinoline (TMQ) (all from Flexys, Belgium); Zinc Oxide (ZnO), stearic acid and sulfur are commercial grades for the rubber industry.

5.2.2 Compound preparation

The rubber compounds were prepared using a two-step mixing procedure following the formulation as shown in Table 5.1. The first step was to prepare a masterbatch of rubber and

fillers, and the second one was to prepare the final compounds including the curatives. For the first step, an internal mixer Brabender Plasticorder 350 ml was used and the mixing conditions were at a rotor speed of 60 rpm, fill factor of 70% and initial mixer temperature setting of 100°C. The CB N134 was added together with the first half of silica, TESP and DPG secondary accelerator. The other halves of silica and TESP were added later on in the first mixing step, together with treated distillate aromatic extract (TDAE) extender oil. The CB amounts were varied at 0, 5, 10, 20, 30, 40, 50 and 55 phr or 0, 9, 18, 36, 55, 73, 91 and 100 wt% relative to total filler content. The second step involved the addition of the second half of DPG, CBS and sulfur at a rotor speed of 30 rpm, fill factor of 70%, and an initial temperature setting of the internal mixer of 70°C. The two-step mixing procedure is summarized in Scheme 5.1.

Scheme 5.1 Two-step mixing procedures for compound preparations; masterbatch compound of NR/silica (a), NR/silica+CB N134 (b), NR/CB N134 (c), and final compounds (d).

Table 5.1 Formulations of silica-filled NR compounds with CB N134 as a secondary filler.

Ingredients	Amount (phr)							
	Reference	1	2	3	4	5	6	7
RSS3	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
ULTRASIL7005	55.0	50.0	45.0	35.0	25.0	15.0	5.0	-
CB N134	-	5.0	10.0	20.0	30.0	40.0	50.0	55.0
TESPD ^a	5.0	4.5	4.1	3.2	2.3	1.4	0.5	-
TDAE oil	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0
ZnO	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Stearic acid	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
TMQ	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
DPG ^a	1.1	1.0	0.9	0.7	0.5	0.3	0.1	-
CBS	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
CB amounts in								
wt% relative to								
total fillers								
content ^b								
	0	9	18	36	55	73	91	100

^aAmount of TESPD and DPG were calculated according to the following equations [19].

$$\text{TESPD (phr)} = 0.00053 \times Q \times A \quad (1)$$

$$\text{DPG (phr)} = 0.00012 \times Q \times A \quad (2)$$

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

^bDesignation of the compounds: CB-0%, CB-9%, CB-18%, CB-36%, CB-55%, CB-73%, CB-91% and CB-100%

5.2.3 Sample characterizations

5.2.3.1 Testing of compound and vulcanizate properties

Mooney viscosity, Payne effect, cure characteristics, tensile properties and dynamic mechanical properties of the silica- and silica/CB-filled NR compounds were investigated following the methods and using the equipments as described in Chapter 3. Where the methods and equipments for tear strength was explained in Chapter 4.

5.2.3.2 Characterization of Bound Rubber Content (BRC)

An amount of 0.25 g of uncured compound (without curatives) was immersed in 40 ml of toluene for 7 days at room temperature in a normal or an ammonia atmosphere. The ammonia atmosphere was used in order to cleave the physical linkages between silica and rubber but leave the chemical links intact. Then the sample was removed from the toluene, dried at 80°C in a vacuum oven for 24 h and weighed. The bound rubber content (BRC) was calculated using the following equation.

$$BRC(\%) = \frac{(m - m_s)}{m_r} \times 100 \quad (3)$$

where m is the weight of sample after extraction, m_s and m_r are the weights of filler and rubber in the original sample, respectively. Normal atmosphere corresponds to Total Bound Rubber Content; ammonia atmosphere to Chemically Bound Rubber Content.

5.2.3.3 DIN abrasion resistance index and its abraded surface

DIN abrasion resistance index (ARI) was tested using a DIN abrader (Abrasion tester 564C, Karl Frank GmbH, Germany) according to method A of DIN 53516. The test specimen has a diameter of 16 ± 2 mm with a minimum thickness of 6 mm. The pure silica-filled NR was used as reference rubber. The ARI was calculated according to the following equation:

$$ARI = \left(\frac{\Delta m_r \cdot d_t}{\Delta m_t \cdot d_r} \right) \cdot 100 \quad (4)$$

where Δm_r is mass loss of the reference rubber (g), d_r is density of the reference rubber (g/cm^3), Δm_t is mass loss of the test rubber (g), and d_t is density of the test rubber (g/cm^3).

The DIN abraded surface was characterized by scanning electron microscopy (SEM, Quanta 400, FEI Company, the Netherlands). The surface was coated with gold prior to being analyzed.

5.2.3.4 Hardness

The dumb-bell test samples of tensile properties were measured by Zwick Shore A Durometer according to DIN 5350.

5.3 Results and discussion

5.3.1 Mixing behavior, processability and cure properties

The mixing footprints, showing both mixing torques and temperatures curves, of the silica/CB-filled NR compounds with various contents of CB N134 are presented in comparison with silica-filled NR are shown in Figure 5.1.

Figure 5.1 Masterbatch mixing profiles of silica/CB-filled NR compounds with various contents of CB N134.

The changes of mixing torque, indicative for viscosity, with mixing time depend on the types and ratio of silica/CB that were incorporated into the rubber matrix. The mastication of NR first decreases the torque due to a breakdown of high molecular weight rubber components under shearing force. Then the addition of solid fillers raises the torque or viscosity according to the hydrodynamic effect [12,20]. The addition of the second half of the fillers further increases the torques, while the addition of ZnO, stearic acid and TMQ at the later stage results in a decrease of torque due to stearic acid that also acts as processing aid. Later on, filler incorporation and dispersion result in a viscosity decrease. The pure silica-filled rubber compound shows the lowest mixing torque, while the inclusion of CB increases the torques and the pure CB-filled compound displays the highest torque. The changes of the final torques with the amount of CB are shown in Figure 5.2(a) together with their respective discharge or dump temperatures.

Figure 5.2 Effect of CB N134 contents on dump torque, dump temperature (a), Mooney viscosity and minimum cure torques (b) of silica/CB-filled NR compounds.

The incorporation of high specific surface area and high structure CB N134 that has better compatibility with NR compared to polar silica, causes an increased interfacial contact and consequently higher viscosity of the masterbatch. The higher viscosity creates more shearing heat during mixing, as reflected in the continuous increase of the dump temperature with increasing the ratio of CB in the hybrid fillers. For the pure silica-filled compound with the use of TESPD silane coupling agent, the lowest dump temperature is observed corresponding to its lowest dump torque. The latter is in accordance with the Mooney viscosity and minimum cure torques (M_L) as shown in Figure 5.2(b). An interesting trend in the compound viscosities with the change of silica/CB ratio can be noticed; the viscosity rises sharply when CB is added in the range of 5-10 phr, i.e. 9-18 wt% relative to total filler content, thereafter slightly decreases before an abrupt increase again when the CB content exceeds 50 wt%. This phenomenon may be related to filler networking. The silanized silica has less filler networking after the silanization reaction, but the addition of a small amount of high structure CB may lead to a silica-CB filler network formation. However, once the CB amount is high enough in the mixture with silica and the viscosity is increased enough to create higher shearing forces, the filler network is reduced to balance the rise in viscosity. But due to the high specific surface area of CB and high filler-rubber interaction, the compounds that contain more CB than silica show again a rapid increase in viscosity. This is also due to the filler network of

CB. Moreover, it is well established that the dump temperature is a key parameter affecting the silanization reaction for silica-silane compounds [7-8,18]. The higher dump temperature promotes a greater extent of the silanization and filler-rubber interactions and thus increases the viscosity. There is a slightly different trend in the change of viscosities in the compounds with high content of CB, as determined by Mooney viscosity versus M_L and mixing torque. The higher temperature during cure measurement (at 150°C) and during mixing promotes the mobility of both fillers and polymer chains and then facilitates filler flocculation [21-23] which also has an influence on the viscosity. So, as a whole this is a complex phenomenon which involves several parameters that can either increase or decrease the compound viscosity.

Figure 5.3 Effect of CB N134 contents on scorch time, optimum cure time and cure rate index of silica/CB-filled NR compounds.

The addition of CB in combination with silica into the NR compounds affects the cure properties, i.e. scorch time (t_{s2}), optimum cure time (t_{c90}) and cure rate index (CRI), as displayed in Figure 5.3. The polar silanol groups on the silica surface are known to have a negative effect on the vulcanization caused by accelerator adsorption and the acidic nature of silica [5]. Even though a silane coupling agent is used and the silanization reaction is optimized by controlling the dump temperature, it has been reported earlier based on model compound studies that only approximately 25% of the silanol groups on the silica can react with silanes due to limited accessibility of these silanol groups for incoming silane molecules [24]. The presence of small molecules like amine-based substance such as aliphatic amines and DPG in this work

has been reported to help shielding off those left-over silanol groups and reduce the cure retardation [9-10]. Nevertheless, the pure silica-filled compound still shows longer t_{s2} and t_{c90} with lower CRI compared to the systems with silica/CB mixed fillers as correspond to the previous works for silica/CB [18,25], silica/bentonite [26] and silica/nanoclay [18,27]. The addition of CB reduces both t_{s2} and t_{c90} especially in the range of 0-40 wt% relative to total filler amount, thereafter the values decrease slightly with increasing amount of CB. The addition of CB into the compounds raises the mixing temperature (Figures 5.1 and 5.2(a)) that promotes the silanization, so there should be less free silanol groups left in such compounds. Moreover, as the thermal conductivity of CB is higher than for silica and the addition of CB particles into the rubber increases therefore the thermal conductivity [28-29], so by increasing the ratio of CB in the silica/CB-filled compounds, the vulcanization rate is enhanced. Thus, from the perspective of industrial processing, this increased CRI is beneficial as it can promote the productivity and saves energy in the production of rubber products.

5.3.2 Filler-filler interaction and filler-rubber interaction

Filler-filler and filler-elastomer interactions are important parameters that affect the reinforcement in elastomers. Non-linear viscoelastic behaviors of the filled rubber compounds can be observed in a change of storage modulus with strain as displayed in Figure 5.4(a). To determine the level of filler-filler interactions, a change of storage modulus with strain is normally measured as Payne effect, and expressed by the difference between storage moduli at low and high strains [30]. A larger difference, i.e. higher Payne effect, means a higher degree of filler-filler interactions. The results in Figure 5.4(b) show that the Payne effect of silica/CB-filled NR compounds increases in the presence of CB N134. The use of CB at 18 wt% relative to total filler amount or at 10 phr still keeps the Payne effect similar to that of the reference pure silica-filled compound. At low amount of CB below approximately 50 wt% of CB relative to total filler amount, the Payne effect tends to increase slightly, but there is a sharp rise at higher amounts indicating a large increase in filler network formation. The small particle size and high specific surface area of CB N134 with narrow filler particle-particle distances favor filler network formation and thus increase the Payne effect. In addition to the characteristics of N134 itself, based on the mixing temperatures shown in Figures 5.1 and 5.2(a), the increasing temperature at higher loading of CB causes a lower viscosity of the compounds during mixing and this can also have an effect on the shearing force applied on the filler agglomerates during the dispersion process. The *in situ* low viscosity during the mixing generates less shearing

forces to break down the filler agglomerates/aggregates as well as facilitates particle flocculation. So, the final compounds show high viscosity as well as high filler-filler interaction.

Figure 5.4 Effect of CB N134 contents on storage modulus as a function of strain (a) and Payne effect (b) of silica/CB-filled NR compounds.

Bound Rubber Content (BRC) was measured based on mass of rubber that is tightly adhered to the filler surface by both physical and chemical interactions and could not be dissolved by a good solvent anymore, i.e. toluene for NR. Chemically bound rubber content is widely accepted and used to indicate filler-elastomer interactions [31-33]. The results in Figure 5.5 show that the silica/CB-filled rubber compounds at every filler ratio have higher bound rubber contents than the mix with silica only, indicating their higher filler-elastomer interaction, derived from factors as high specific surface area of N134, better CB-rubber compatibility, higher extent of the silica-silanization due to a higher mixing temperature, more filler network and consequently more trapped or occluded rubber. Both the total bound rubber and chemically bound rubber contents of silica/CB-filled NR compounds show an optimum at CB content of 18 wt% relative to the total filler amount or at the ratio of silica/CB 45/10 phr. Thereafter, the values decrease and tend to stabilize with increasing CB content. The change of Mooney viscosity in Figure 5.2(b) corresponds well with this bound rubber content, mutually confirming each other. The sharp increases in viscosity and bound rubber content or filler-elastomer interaction when a small amount of high structure CB is added results in a restriction in filler mobility. But once the concentration of CB is high, its small particle size

and high specific surface area do actually facilitate filler network development by flocculation. The CB networking phenomenon is well recognized in previous reports [21,34-35].

Figure 5.5 Effect of CB N134 contents on total and chemically bound rubber contents of silica/CB-filled NR compounds.

5.3.3 Mechanical properties

The increasing CB proportion in silica/CB-filled NR compounds has only a minor influence on the 100% modulus (M100), but significantly raises the 300% modulus (M300) and reinforcement index (M300/M100), as shown in Figure 5.6(a). For CB reinforcement of elastomers, Fukahori [36] discussed that a large stress increases with filler content and increasing strain amplitude results from a strong stress concentration generated around CB particles and its transmission to the whole system. The model proposed showed double uncrosslinked polymer layers of different molecular mobility; an inner glassy hard (GH) layer and an outer sticky less hard (SH) layer, surrounding a carbon particle. Under large extensions where a stress-hardened superstructure is produced in the SH layer, a great increase in tensile stress is observed. This corresponds with the observation in the present work, that the increase of CB content leads to a large rise in modulus at large extension, i.e. at 300%. Moreover, as shown previously, the increase of CB content increases filler-filler and filler-rubber interactions that contribute to the stiffness of the materials.

Figure 5.6 Effect of CB N134 contents on 100% and 300% modulus, reinforcement index (a), tensile strength and elongation at break (b) of silica/CB-filled NR compounds.

Tensile strength and elongation at break of NR filled with silica in combination with various contents of CB show the same trend, as displayed in Figure 5.6(b), and resemble the change of bound rubber content in Figure 5.5. Both properties initially increase when CB is added, but later decrease slightly after the CB content exceeds 18 wt% relative to total filler amount. When compared to the pure silica-filled compound, there is a smaller change in the tensile strength when the CB content is increased, but the elongation at break tends to drop at high amount of CB, in line with the increase of modulus as shown in Figure 5.6(a).

The use of silica/CB hybrid filler further shows a clear improvement in tear strength and DIN abrasion resistance index compared to the pure silica-reinforced system as shown in Figure 5.7. By increasing the content of CB, tear strength of the silica/CB-filled NR rises sharply to reach the maximum at 18 wt% of CB relative to total filler amount, then decreases slightly and stabilizes at the level higher than the reference compound. The changes of tear and tensile strength with the CB content therefore show a similar trend and correspond to the bound rubber content, indicating that the increase of filler-elastomer interactions does enhance the strength of the rubber vulcanizates. This increase in strength will benefit for truck tires performance, as crack growth and cut-chip resistance are related to tear strength are important properties for their application.

As expected, the addition of Super Abrasion Furnace (SAF) black N134 into the silica-reinforced NR compound does enhance the abrasion resistance, indicated by the increased DIN abrasion resistance index as shown in Figure 5.7. This is due to the higher specific surface area of CB, which imparts improved abrasion resistance to rubber vulcanizates in general. The results correspond to the increase of modulus as seen in Figure 5.6(a), where it has been reported that rubber vulcanizates with higher modulus show better abrasion resistance [15].

Figure 5.7 Effect of CB N134 contents on tear strength, hardness and DIN abrasion resistance index of silica/CB-filled NR compounds.

5.3.4 SEM images of DIN abraded surfaces

The wear of rubber products remains difficult to predict [37] and abrasion resistance of specimens tested in a laboratory often do not agree with the wear of the articles during service. Tearing or fatigue under the action of high local stresses caused by friction have been blamed as the main causes of abrasion [37]. When rubber is abraded without change of direction, an “Abrasion pattern” or sets of parallel ridges appear on the surface of the samples at right angles to the direction of motion, often called Schallamach waves [38-39] and this abrasion pattern is assumed to influence the relative rates of tire wear under different service conditions. These periodic parallel ridges or abrasion patterns are initiated by microvibrations at the natural frequency of the rubber and propagate by stick-slip oscillations, both of which are generated during frictional sliding of rubber [40]. The abrasion patterns of silica/CB-filled vulcanizates

look different from that of pure silica-filled rubber as shown in Figure 5.8. At higher content of CB, the parallel ridges are more visible as the ridge spacings become smaller and ridge heights are larger. The increasing ratio of CB in the hybrid filler-reinforced NR increased the 300% modulus and tear strength, making the asperities more difficult to be torn off. On the other hand, due to the high natural strength of NR, it was reported that its DIN abrasion resistance index is relatively insensitive to the black loading [37]. The results in Figure 5.7 do show that by replacing silica with CB, the DIN abrasion resistance index increases by around 20%.

Figure 5.8 Effect of CB N134 contents on SEM images of DIN abraded surfaces of silica/CB-filled NR compounds (a= CB-0%, b= CB-18%, c= CB-55%, d= CB-91% and e= CB-100%).

5.3.5 Dynamic mechanical properties

In a laboratory scale test, dynamic mechanical analysis is commonly employed to predict tire performance with regard to wet grip and rolling resistance; tan delta at -20°C to $+20^{\circ}\text{C}$ is used to predict the wet traction of a tire while the tan delta at 60°C of vulcanizates indicates the loss energy of a rubber vulcanizate under dynamic deformation which relates to tire rolling resistance [41]. Figures 5.9(a) shows the tan delta at 60°C of silica/CB-filled compounds at various CB content from both RPA and DMA measurements. The tan delta values at 60°C remains at similar levels as that of pure silica-reinforced NR compounds when the CB content is in the range of 0-18 wt% relative to total filler content (based on the RPA results), or 0-55 wt% relative to total filler content (based on DMA results), thereafter a sharp increase is observed. The lowest tan delta at 60°C is observed for CB loading of 18 wt% relative to total filler content. With increasing the CB N134 content, the available surface area becomes larger and heat build-up as well as hysteresis of the rubber compound become greater. So, increasing of the CB proportion in the silica-filled NR compounds too much has a negative effect on tire rolling resistance. Moreover, as well known for the CB-reinforced rubber compounds, the adherence of rubber molecules on to the CB surface is mainly taking place in the form of physical adsorption, i.e. mainly physical interactions between CB and rubber. This is different from the case of silica/silane system wherein chemical bonds are created between silica and rubber. Under dynamic deformation conditions when rubber molecules with only physical interactions are detached and reattached to the filler surface, the compounds with more of these physical interactions create higher energy losses and thus higher tan delta at 60°C .

The increase of CB ratio in the silica/CB hybrid fillers increases the tan delta at 0°C continuously, but rises the tan delta at -20°C to the optimum at CB loading of 18 wt% relative to total filler content, thereafter the values decrease slightly. So, with regard to wet grip, the increasing content of CB gives a positive effect, whereas for ice traction at -20°C the ratio of silica/CB needs some optimization. As observed also for other properties earlier, the use of CB N134 at 18 wt% relative to total filler content shows optimum properties which indicate the best balance of both physical and chemical interactions as reflected in the optimum bound rubber contents (Figure 5.5), tensile strength and elongation at break (Figure 5.6(b)) and tear strength (Figure 5.7(a)).

Figure 5.9 Effect of CB N134 contents on tan delta at 60°C (a) and tan delta at -20°C and 0°C (b) of silica/CB-filled NR compounds.

5.4 Conclusions

The properties of silica/CB-filled NR compounds show a clear synergistic effect in dependence of the CB proportion in the hybrid fillers. An increasing ratio of CB in the compounds steadily increases the viscosities both during and after mixing, mixing temperature, cure rate index, 300% modulus and DIN abrasion resistance index. The Payne effect and tan delta at 0°C and 60°C are marginally changed at low content of CB, i.e. in the range of 0-36 wt% of CB relative to total filler content or 0-20 phr, but later clearly increase. Scorch and optimum cure times are shortened enabling an increase in productivity and energy saving. Bound rubber content, tensile strength, elongation at break, tear strength and tan delta at -20°C show an optimum at 18 wt% of CB relative to total filler content or at the ratio of silica/CB 45/10 phr. Summarizing from the perspective of tire performance, at optimum silica/CB ratio of 18 wt%, the abrasion resistance, wet grip and ice traction can be enhanced while maintaining the tire rolling resistance as indicated by the data from dynamic mechanical analysis.

These conclusions are summarized in the radar charts hereunder. Figure 5.10 shows the radar charts covering Mooney viscosity, cure properties, Payne effect, total bound rubber content of the compounds (Figure 5.10(a)), as well as mechanical properties of the vulcanizates (Figure 5.10(b)). These two charts are based on relative values versus the reference. The chart concerning tire performance as shown in Figure 5.11 is based on index-values: the higher the better.

Figure 5.10 Radar charts comparing Mooney viscosity, cure properties, Payne effect, total bound rubber content (a) and mechanical properties (b) of the silica-filled NR compounds without (CB-0%) and with the optimum amount of carbon black N134 as secondary filler at 18 wt% relative to the total amount of fillers (CB-18%).

Figure 5.11 Radar chart comparing key tire performances indicated by lab-indicators of the silica-filled NR compounds without (CB-0%) and with the optimum amount of carbon black N134 as secondary filler at 18 wt% relative to the total amount of fillers (CB-18%).

5.5 References

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CHAPTER 6

Enhancing Performance of Silica-Reinforced Natural Rubber Tire Tread Compounds by Applying Organoclay as Secondary Filler

Silica-reinforced Natural Rubber (NR) tire tread compounds are investigated using OrganoClay (OC) as secondary filler. By varying the loadings of OC in the silica-filled NR compounds from 0 to 36 wt% relative to total filler amount, the increased OC loadings decrease the Payne effect and compound viscosities, significantly shorten scorch and cure times and raise the tan delta at -20°C and 0°C as indications for ice traction and wet skid resistance of tire treads made thereof. The optimum loading of OC of 9 wt% relative to total filler content shows better Payne effect, cure rate index, tan delta at -20°C and 60°C indicative for rolling resistance, and DIN abrasion resistance index. The results indicate that the use of this hybrid filler may provide tires with better wet traction, lower rolling resistance and wear resistance compared to the pure silica-filled system.

6.1 Introduction

Natural rubber (NR) is widely used in all types of tires especially for heavy trucks and aircrafts in order to obtain low heat build-up. Many components of passenger car tires are also made from NR such as bead filler, sidewall and tread compounds, because it provides low heat build-up, good flex-fatigue and excellent mechanical properties. Particulate reinforcing fillers such as carbon black and silica are most commonly used in combination with NR for tire tread applications. Carbon black was the first reinforcing filler for rubber compounds to improve tensile strength, modulus, tear strength, abrasion resistance, skid resistance as well as other properties. Replacement of carbon black with silica, after the patent of Michelin [1] for passenger car tires, offers tire compounds with lower rolling resistance and higher wet grip [2], so less fuel consumption and better driving safety. However, the successful use of silica in rubber compounds requires sufficient bonding and/or interaction between the silica and the elastomer because of differences in polarity of silica and rubbers. Sulfur-containing silane coupling agents such as bis-(3-TriEthoxySilylPropyl)Tetrasulfide (TESPT) is commonly applied in such compounds vulcanized with a sulfur system. For better scorch safety, bis-(3-TriEthoxySilylPropyl)Disulfide (TESPD) can be used but when compared to TESPT, compounds with lower filler-rubber interactions, dispersion stability, tensile strength, and tear resistance were observed [3]. The mixing of silica with silane in rubber involves a chemical reaction, called silanization. The mixing temperature has a more dominant effect than mixing time on the silica-silane reaction [4]. The effect of mixing temperature for the silica-silane (TESPT) technology has been studied in different types of elastomers such as a Styrene-Butadiene Rubber (SBR) blend with Butadiene Rubber (BR) [5-6], Isoprene Rubber (IR) [7] and NR [7-8]. The silanization reaction between silica and silane coupling agent increases with increasing mixing dump temperature, as indicated by a reduction of filler-filler interactions monitored by the Payne effect, and increased filler-elastomer interactions as evidenced by higher chemically bound rubber content. The extent of silanization has a dramatic effect on the resulting compound properties [8-9]. Therefore, the effect of mixing dump temperature for hybrid fillers of silica and OC in NR compounds must be investigated. Even with small parts of silica replaced by OC a significantly improved balance of properties may be achieved.

New reinforcing fillers for rubber products have been introduced and one of the most widely studied is nanoclay. To enhance compatibility with tire elastomers, organo-modified clay or shortly organoclay which has been modified by cation exchange with ammonium salts or phosphonium salts to promote its hydrophobicity, is generally used [10]. The OC has a

dimension in the nanometer level and may be dispersed in single platelets or small silicate stacks with a high aspect ratio of 50-1000 [11]. Organoclay-elastomer composites with low nanofiller contents (usually 10 phr or less) show an improvement in mechanical properties, thermal stability, wear resistance and gas permeability. Recently, there is an increasing interest in hybrid fillers or combinations of silica and OC in order to achieve synergistic effects in rubber properties from each filler. A combination of silica and China clay in NR for a heavy-duty truck tire tread formulation was studied and the best balance of heat build-up and abrasion resistance was found at a silica/clay ratio of 60/20 [12]. Hybrid fillers of precipitated silica/MontMorillonite (MMT) in peroxide cured silicone rubber nanocomposites resulted in the improvement of tensile strength, Young's modulus, moduli at 100% and 300% strain (M100 and M300), elongation at break, hardness and crosslink density [13]. A SBR/silica/OC nanocomposite prepared by a latex mixing method with replacement of silica by 7 phr of OC was investigated in comparison with the use of pure silica at 60 phr loading. This work reported that the silica/OC gave an indication for better skid and rolling resistance with high 100% and 300% modulus [14]. The use of MMT and silica with TESPT as silane coupling agent in solution-SBR (SSBR)/BR tread compounds improved tensile strength, elongation at break and traction properties at low TESPT content while enhancing modulus, hardness, wear resistance, dry handling and rolling resistance at high TESPT content [15]. Hybrid filler systems consisting of precipitated silica and kaolin modified with a Sodium salt of Rubber Seed Oil (SRSO) in NR/BR blends demonstrated that a substitution of 5-10 phr of silica with SRSO modified kaolin resulted in lower Mooney viscosity, higher cure rate, increased chemical crosslink density index and bound rubber content [16], indicating a higher extent of rubber-rubber and rubber-filler interactions. This resulted in enhanced mechanical properties such as abrasion resistance, compression set, tensile- and tear-strength and elongation at break of the blend vulcanizates. The vulcanizate containing silica/SRSO hybrid filler also showed enhancement of dynamic mechanical properties, beneficial for tire tread applications. The reduction of filler networking in silica-based elastomeric nanocomposites with exfoliated organo-montmorillonite resulted in improved mechanical reinforcement and reduced energy dissipation and thus of fuel consumption and carbon footprint of tires made thereof [17].

In the present work, the effect of loading levels of OC on the hybrid filler system, still in combination with mixing temperature is fully explored. The cure characteristics, filler-filler interactions, filler-rubber interactions, tensile and tear properties, DIN abrasion resistance index,

dynamic mechanical properties and morphology in terms of clay dispersion of such silica/OC-filled NR compounds are studied.

6.2 Experimental

6.2.1 Materials

Natural rubber (Ribbed Smoked Sheet No.3, RSS3) was provided by Sri Trang Agro-Industry, Thailand. Silica ULTRASIL 7005 with a Cetyl-Trimethyl-Ammonium-Bromide (CTAB) and Brunauer-Emmett-Teller (BET) specific surface area of 171 and 190 m²/g, respectively, and silane coupling agent TESPD were obtained from Evonik, Germany. Organoclay Dellite 67G, which is a nanoclay derived from a natural montmorillonite, functionalized with 47 wt% of dimethyl dihydrogenated tallow ammonium chloride (2HT), with 115 meq/100 g of cation exchange capacity (CEC), was provided by Laviosa Chimica Mineraria S.p.A, Italy. The other ingredients: Treated Distillate Aromatic Extract oil (TDAE) (Vivatec 500) (Hansen & Rosenthal, Germany); diphenyl guanidine (DPG), N-cyclohexyl-2-benzothiazyl sulfenamide (CBS), 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) (all from Flexys, Belgium); zinc oxide (ZnO), stearic acid and sulfur were all commercial grades for the rubber industry.

6.2.2 Compound preparation

The compound formulations employed are given in Table 6.1. The compounds were prepared using a two-step mixing procedure: the first was to prepare a masterbatch of rubber and fillers, and the second was to prepare the final compounds including the curatives. For the first step, an internal mixer Brabender Plasticorder 350 ml was used, operated at a rotor speed of 60 rpm, fill factor of 70% and initial mixer temperature setting of 100°C in order to reach a dump temperature in the range of 135-150°C, as suggested in previous reports [8,18]. The OC as secondary filler was added together with the first half of silica, TESPD and DPG secondary accelerator in order to obtain a good dispersion. The other half of silica and TESPD were added later on in the first mixing step, together with TDAE extender oil. The second step was used for the addition and mixing of the other half of DPG, CBS primary accelerator, and sulfur at a rotor speed of 30 rpm, fill factor of 70%, and an initial temperature setting of the internal mixer of 70°C. The two-step mixing procedure is summarized in Scheme 6.1. A reference mix with silica only was prepared using an initial mixer temperature setting at 100°C according to a previous report [8]. For silica/OC compounds, the OC content was varied at 0, 2.5, 5, 7.5, 10, 15 and

20 phr or 0, 5, 9, 14, 18, 27 and 36 wt% relative to total filler amount, and the silica amount reduced accordingly.

To take into account the effect of solids content of fillers in the system as the OC contains 47 wt% of a modifier, an additional set of compounds was prepared by fixing the same amount of silica at 55 phr and variable amounts of OC, i.e. at 0, 5, 10, 15 and 20 phr, were added on top, keeping the amounts and types of the other ingredients the same as those of the reference formulation. Optimum temperature settings and mixing procedures are as described above.

Scheme 6.1 Two-step mixing procedures for compound preparations; NR/silica (a) and NR/silica+OC (b) compounds.

Table 6.1 Formulations of silica-filled NR compounds with organoclay as a secondary filler.

Ingredients	Amount (phr)						
	Reference	1	2	3	4	5	6
NR (RSS3)	100.0	100.0	100.0	100.0	100.0	100.0	100.0
ULTRASIL 7005	55.0	52.5	50.0	47.5	45.0	40.0	35.0
Dellite 67G (OC)	-	2.5	5.0	7.5	10.0	15.0	20.0
TESPD ^a	5.0	4.8	4.5	4.3	4.1	3.6	3.2
TDAE oil	8.0	8.0	8.0	8.0	8.0	8.0	8.0
ZnO	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Stearic acid	1.0	1.0	1.0	1.0	1.0	1.0	1.0
TMQ	1.0	1.0	1.0	1.0	1.0	1.0	1.0
DPG ^a	1.1	1.1	1.0	1.0	0.9	0.8	0.7
CBS	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5
OC amounts in wt%							
relative to total fillers	0	5.0	9.0	14.0	18.0	27.0	36.0
content ^b							
Solids content of fillers	55.0	53.8	52.6	51.5	50.3	47.9	45.5

^aAmounts of TESPD and DPG were added according to the following equations [19]:

$$\text{TESPD (phr)} = 0.00053 \times Q \times A \quad (1)$$

$$\text{DPG (phr)} = 0.00012 \times Q \times A \quad (2)$$

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

^bDesignation of the compounds: OC-0%, OC-5%, OC-9%, OC-14%, OC-18%, OC-27% and OC-36%.

6.2.3 Sample characterizations

6.2.3.1 Testing of compound and vulcanizate properties

Mooney viscosity, Payne effect, cure characteristics, tensile properties and dynamic mechanical properties of the silica- and silica/OC-filled NR compounds were investigated following the methods and using the equipments as described in Chapter 3. The methods and equipments for bound rubber content measurement, apparent crosslink density and tear strength

were described in Chapter 4. Hardness, DIN abrasion resistance index and its abraded surface were investigated following the methods and using the equipments as described in Chapter 5.

6.2.3.3 Fourier Transform Infrared Spectroscopy (FTIR)

The MMT and OC Dellite 67G were qualitatively analyzed by FTIR using a Perkin Elmer Spectrum 100 machine equipped with an Attenuated Total Reflectance (ATR) unit. The scanned wavenumber spectrum was within 650-4000 cm^{-1} .

6.2.3.2 X-Ray Diffraction (XRD)

X-ray diffraction analysis – The interlayer spacing (d-spacing) of the organoclay layers was determined by an X-ray diffractometer (Empyrean, PANalytical, Netherlands) with a $\text{CuK}\alpha$ radiation source ($\lambda=0.15406$ nm). The operating voltage and current of the X-ray emitting tube were 40 kV and 30 mA, respectively. The test was performed at room temperature with angular range from 1° to 10° (2θ) and a scan speed of $0.022^\circ/\text{min}$. By applying Bragg's law, the d-spacing of the clay platelets can be determined.

6.3 Results and discussion

By taking the initial mixer temperature setting of 100°C that results in the dump temperature of approximate 150°C as the optimum, the silica/OC-filled NR compounds with different loading levels of OC at 0, 2.5, 5, 7.5, 10, 15 and 20 phr, or 0, 5, 9, 14, 18, 27 and 36 wt% relative to total filler amount, and with the silica, TESPD and DPG amounts reduced accordingly as shown in Table 6.1. The compounds were prepared and the properties were evaluated in comparison with pure silica-filled NR compounds.

6.3.1 Mixing behavior, processability and cure properties

The mixing footprints, showing both mixing torques and temperatures curves, of the silica/OC-filled NR compounds with various contents of OC are presented in comparison with silica-filled NR are shown in Figure 6.1.

Figure 6.1 Masterbatch mixing profiles of silica/OC-filled NR compounds with various contents of organoclay (OC).

The dump torques and dump temperatures of the NR compounds filled with silica/OC hybrid filler with different loading levels of OC are given in Figure 6.2. The mixing torques after the addition of the second half of filler and the dump torques of silica/OC-filled compounds decrease sharply with the first loading of OC which can be due to a combination of different phenomena, to include the plasticizing effect derived from the organic modifying agent in the OC and the reduced silica network or lower filler-filler interaction in the presence of the secondary filler, so better filler dispersion, also adding to a lower viscosity. Interestingly, the presence of OC reduces the mixing torque compared to the silica only system which would indicate a better dispersion of the fillers. This can be due to reduction of the silica network by OC and/or influence of the modifying agent in OC that provides a plasticizing effect in the rubber compounds, as supported by the Payne effect results shown below. The long tail structure of dihydrogenated tallow in such modifying agent can plasticize the system causing an increasing free volume between the high molecular weight rubber chains to facilitate the flow. Moreover, the polar functional groups that are present in the modifying agent ($\text{C}=\text{O}$, $\text{C}-\text{O}$ and $-\text{N}=\text{}$) can interact with the left-over free silanol groups on the silica surface after the silanization reaction, providing a shielding effect that promotes hydrophobicity and interfacial compatibility between rubber and filler. However, the increase of OC loading has no significant effect anymore on the dump temperature, as seen in Figure 6.2.

Figure 6.2 Dump torque and dump temperature of silica-filled NR compounds with varying loadings of organoclay (OC).

6.3.2 Filler-filler interaction

Non-linear viscoelastic behaviors of the filled rubber compounds can be observed in a change of storage modulus (G') with strain as seen in Figure 6.3(a). By increasing the strain, the G' sharply decreases due to a breakdown of the filler network, i.e. a reduction of filler-filler interactions, and the difference between the modulus at low strain and high strain can be used to indicate the level of filler-filler interaction, called Payne effect [20]. This Payne effect may also be considered as an indirect indication for microdispersion of fillers within the rubber matrix. The influence of OC loadings on the filler-filler interactions and the filler network can be derived from the change of G' with strain as shown in Figure 6.3(a). From determining the difference of G' values at low and high strains, i.e. G' 0.56% and 100% respectively, the Payne effect ($\Delta G'$) is shown in Figure 6.3(b). The incorporation of OC remarkably reduces the G' at low strain of the silica-filled compounds, especially in the range of 0-9 wt% relative to total filler amount; thereafter only a small reduction is observed when the OC amount is increased. The reduction of G' and $\Delta G'$ by the modifying agent 2HT is in accordance with a previous observation [17] for blends of IR/SBR with constant 70 phr of silica and the amount of OC changed. It was discussed that the lipophilic ammonium cation of the modifying agent of OC acts as a plasticizer that results in a reduction of the G' of the matrix both at low and at large strains. Moreover, when the organically modified clay was below the threshold required

to establish a hybrid OC-silica filler network, reduction in filler networking was still observed [17]. In addition to the reduced modulus of the rubber matrix as observed in the high strain range after the breakdown of the filler network, the presence of this modifying agent in the silica-filled compounds also remarkably reduces filler-filler interactions at low strain which can be due to a better silanization and additional shielding effect. Moreover, the presence of OC as secondary filler may interrupt the silica-silica network too. A large decrease is observed when the OC loading is increased to 9 wt% relative to the total filler level or at the ratio of silica/OC of 50/5 phr, thereafter the Payne effect decreases only slightly.

Figure 6.3 Storage modulus as a function of strain (a) and Payne effect (b) of silica-filled NR compounds with varying loadings of organoclay (OC).

6.3.3 Mooney viscosities and cure properties

The minimum cure torques (M_L) and Mooney viscosities of NR filled with silica/OC decrease with increasing OC contents as shown in Figure 6.4(a) in line with the mixing torques as displayed in Figure 6.2. Both M_L and Mooney viscosity are indicative of rubber compound viscosity or its flowability. The lower viscosity means an improvement in processability. The suppression of the Payne effect or less filler networking by OC in silica/OC-filled rubber compounds in Figure 6.3(b) means that there is less filler network to obstruct flow and that the molecular chain mobility is enhanced. This can be attributed to the plasticizing effect caused by 2HT modifying agent for the OC, all contribute to the lower viscosities of the silica/OC-

filled system. On the other hand, the pure silica-filled reference compound is only affected by the silanization reaction. So, it shows a higher Mooney viscosity and minimum cure torque than the system with the OC-silica combination.

With regard to cure characteristics, the maximum cure torques (M_H) and cure torque differences ($M_H - M_L$) of the silica-filled NR compounds with different OC loadings are shown in Figure 6.4(b), and the scorch times (t_{s2}), optimum cure times (t_{c90}) and cure rate indices (CRI) in Figure 6.5. The changes of M_H and $M_H - M_L$ of the silica-filled NR compounds with increasing OC content resemble the change of compound viscosities. The levels of M_H and $M_H - M_L$ indicate the vulcanizate stiffness influenced by several contributions: chemical crosslinks by the vulcanization reaction, filler-rubber interactions and filler-filler interactions. The diminished filler-filler interactions as shown by the Payne effect in Figure 6.3(b) by the presence of OC play the most significant role in reducing the maximum cure torques.

Figure 6.4 Mooney viscosity, minimum cure torque (a), maximum cure torque and cure torque difference (b) of silica-filled NR compounds with varying loadings of organoclay (OC).

Figure 6.5 Scorch time, optimum cure time and cure rate index of silica-filled NR compounds with varying loadings of organoclay (OC).

The increasing loadings of OC significantly shorten both scorch and optimum cure times of the silica/OC-filled NR compounds due to an alkalinity of the organic modifying agent that accelerates the curing reactions resulting in the increase of cure rate index (CRI). The effect of OC on accelerating the curing reactions has previously been documented, but mainly for pure OC [17-18,21-29].

For the silica-filled NR compound, even though a silane coupling agent was utilized there are still some left-over silanol groups available, so accelerator adsorption and interference in the vulcanization reaction can still take place resulting in the longest scorch- and cure times. Galimberti *et al.* [17] indicated that the interaction between the cation and the sulfur based crosslinking system most likely via amine formation, was to promote higher interface crosslinking density.

6.3.4 Mechanical properties and apparent crosslink density

Tensile properties of the NR compounds reinforced with silica/OC combinations are shown in Figure 6.6. Tensile strength, elongation at break and 100% modulus (M100) change marginally with increased loading of OC, but the 300% modulus (M300) shows a sharp drop when the OC content is higher than 14 wt% relative to total fillers content: Figure 6.6(b). With high OC content the plasticizing effect due to its modifying agent becomes dominant as

well as the interfacial adhesion between rubber and OC may be reduced, and so the rubber vulcanizates show less resistance to deformation at moderate 300% elongation. The reinforcement index (M300/M100) of the silica/OC-filled NR compound consequently also tends to drop at higher loadings of OC.

Figure 6.6 Tensile strength and elongation at break (a), 100% modulus, 300% modulus and reinforcement index (b) of silica-filled NR compounds with varying loadings of organoclay (OC).

The silica/OC hybrid filler shows a clear impact on tear strength, apparent crosslink density, abrasion resistance and Shore A hardness, as shown in Figure 6.7(a)-(b). The apparent crosslink density values are decreased with increasing contents of OC, in correspondence with the values of maximum cure torque (M_H) and cure torque difference ($M_H - M_L$) in Figure 6.4(b). Tear strength and DIN abrasion resistance index show a similar trend when the OC ratio is increased in the silica/OC-hybrid filled blends, with almost unchanged hardness level. The abrasion resistance of rubber products relates to the service life and it indicates the ability to resist loss of material from the surface by mechanical action, such as erosion and scraping [30]. Both properties are initially increased when the OC content is raised to 9 wt% relative to total fillers content or at 50/5 phr of silica/OC, and then decrease. Both sharply decrease when the loading of OC exceeds 18 wt% relative to total fillers amount. As the presence of OC in silica-filled compounds suppresses the filler network and reduces the apparent crosslink density, the excess amount of OC leads to a reduction of tearing energy and wear resistance. Moreover, as the modifying agent in OC plasticizes the system and causes a reduction in shearing force

and compound viscosity during mixing, some re-agglomeration of OC can also have taken place at high loading of OC resulting in deterioration of the present properties.

Figure 6.7 Tear strength, apparent crosslink density (a), DIN abrasion resistance index and hardness (b) of silica-filled NR compounds with varying loadings of organoclay (OC).

Elucidating the role of organoclay by adding it on top of the compounds containing an identical silica content

Concerning the solids contents of fillers in this system, the higher the OC contents, the lower the solids contents of the fillers. Based on the composition of OC, it contains 47 wt% of a modifier, meaning that the changed silica/OC addition from 55.0/0 to 35/20 phr leads to different solid contents of fillers in the compounds, varying from 55.0 to 45.5 phr, as summarized in Table 6.1. This might raise a question whether the changes in properties, in particular apparent crosslink density, filler-rubber and filler-filler interactions and mechanical properties, are affected by the variation in this total solids content of fillers as the major factor. In order to clarify this matter, the results from an additional set of compounds have been taken into consideration. These compounds were prepared to have the same amount of silica, i.e. 55 phr, while adding the OC on top at variable amounts and keeping the amounts and types of the other ingredients the same to those for the reference formulation. The solids contents of fillers in these comparative compounds are 55.0, 57.3, 60.3, 62.9 and 65.6 phr for the

compounds with the OC at 0, 5, 10, 15 and 20 phr, respectively. The obtained results demonstrate an interesting influence of the OC on the technical properties of silica-filled NR compounds. Figure 6.8 depicts the effect of the OC amounts on total bound rubber content, apparent crosslink density, Payne effect and Mooney viscosity of these compounds containing 55 phr silica and variable amounts of OC.

Figure 6.8 Effect of organoclay contents on total bound rubber content, apparent crosslink density (a), Payne effect and Mooney viscosity (b) of the filled NR compounds all containing silica and TESPD silane coupling agent at 55 and 5 phr, and variable quantities of organoclay.

It is clear that the OC significantly reduces the bound rubber content or filler-rubber interaction as well as the apparent crosslink density of the compounds with increasing loading: see Figure 6.8(a). On the other hand, the Payne effect or filler-filler interaction is very much reduced with increasing the OC from 0-10 phr; but thereafter the Payne effect tends to increase again as shown in Figure 6.8(b). These results are indeed intriguing for interpreting the role of OC. Literally, it was expected that the addition of higher loadings of nanoclay would increase both filler-rubber and filler-filler interactions due to the higher filler contents. But, the results show differently. The decrease in filler-polymer interaction might be the result of the OC particles obstructing silica clusters during the mixing process, leading to a shielding effect that hinders the silanization reaction, and so gives a reduced extent of filler-rubber interaction. This in turn results in a lower apparent crosslink density of the final vulcanizates. A possible morphology of this system is postulated in Figure 6.9. The insertion and attachment of OC

particles inside the silica network of an actual silica-OC-filled compound was illustrated in a TEM image published in previous work of Galimberti *et al.* [17]. However, the interpretation regarding the shielding effect of the OC towards silanization during mixing has never been considered.

Figure 6.9 Postulated morphology of silica network with some organoclay particles inserted between and attached on the silica clusters in the silica-filled NR system with organoclay as secondary filler.

The results in this section illustrate the interference of OC in the silica-filled rubber system. Nevertheless, the intervention of OC particles gives a positive effect on a considerably reduced filler-filler interaction or Payne effect when loading it up to 10 phr (Figure 6.8), attributed to the effect of the modifier in OC, as discussed for Figure 6.3. After that, the Payne effect markedly increases (Figure 6.8), attributed to overloading of fillers giving an inclination towards the formation of a greater extent of filler network in the system. The OC still presents its polarity since the FTIR spectrum depicted in Figure 6.10 shows an absorption peak at the wavenumber of 3625 cm^{-1} which is assigned to polar hydroxyl groups (-OH) in the structure. Therefore, the affinity between silica and OC could be strong due to hydrogen bonding, leading to a high attraction between these two fillers. Mooney viscosity (Figure 6.8(b)) reduces with increasing OC content up to 10 phr and then levels off. This is due to the competitive effect between a lower filler-rubber interaction but a higher filler-filler interaction. The lowered filler-rubber interaction (Figure 6.8(a)) would continuously reduce the compound viscosity, however, the higher filler-filler interaction (Figure 6.8(b)) overrules leading to an

increased viscosity. Hence, these parameters balance the Mooney viscosity at higher loading levels of OC (>10 phr). The presence of the trace of –OH on OC also leads to a possibility of the reaction with the silane coupling agent. Based on the FTIR results shown in Figure 6.10, there are small absorption peaks at the wavenumbers 915 and 795 cm^{-1} which can be assigned to bond signals of Al-O and Mg-O present in the OC structure. So, it is clear that the Al-OH and Mg-OH groups containing in OC can react with the silane coupling agent as well. However, as these peaks are very small compared to the Si-O peak at 1000 cm^{-1} from silica, these reactions between the hydroxyl groups on OC are negligible, and the effective reactions of the silane coupling agent used in this study are primarily referred to as silanization between the silane coupling agent and the hydroxyl groups of the silica.

Figure 6.10 FTIR spectrum of unmodified nanoclay, i.e. monmorillonite (MMT) and organoclay used in this study.

Based on this extended investigation, the picture becomes more explicit in terms of the influence of OC as secondary filler on filler-rubber and filler-filler interactions of silica-filled NR compounds. The final properties of the compounds are mainly influenced by these two factors, which are significantly affected by the OC. The improvement of overall properties of the final vulcanizates when adding OC up to 9 wt% relative to total fillers content as presented earlier, in particular for tensile strength, as well as tear strength and abrasion resistance (Figure 6.7), is mainly attributed to improved micro-dispersion of the fillers caused by the hybridization effect of OC. Note that a better micro-dispersion could indirectly be estimated

from a lower Payne effect [31]. The dynamic mechanical properties of the vulcanizates are also in line with this interpretation, as to be discussed in the subsequent sections.

6.3.5 SEM images of DIN abraded surfaces

Based on the slight improvement in abrasion resistance at low loading of OC, i.e. at silica/OC of 50/5 or at 9 wt% of OC relative to total fillers content, and the clear deterioration of this property at high OC loadings, it is of interest to look at the abrasion pattern of the surfaces. The SEM images of the DIN abraded samples of silica/OC-filled NR compounds with OC 9, 18 and 36 wt% relative to total fillers contents are shown in comparison with that of the pure silica-filled one, as shown in Figure 6.11. The abrasion patterns on the DIN abraded surfaces agree well with the DIN abrasion resistance index. The compound with 9 wt% of OC relative to total fillers content that shows the best abrasion resistance demonstrates a smoother abraded surface with only small asperities. The ones with OC at higher contents, i.e. at 18 and 36 wt% relative to total fillers content with poorer abrasion resistance, show larger asperities and a rougher surface in accordance with their inferior tear strength. The abrasion patterns indicate that the asperities for the weaker materials with higher loadings of OC can be torn off easier. So that, in order to achieve positive mechanical reinforcement, OC should be used in low amount, below a certain threshold content [17]. It was reported earlier for 70 phr of silica-reinforced synthetic IR/SBR blends with the addition of Dellite 67G on top, that the threshold content of OC required to establish a hybrid OC-silica filler network was at about 7 phr, like found in the present study.

Figure 6.11 SEM photographs of DIN abraded surfaces of silica-filled NR compounds with various loadings of organoclay (OC), (a= OC-0%, b= OC-9%, c= OC-18% and d= OC-36%).

6.3.6 X-Ray Diffraction (XRD)

As discussed earlier that at high loading of OC re-agglomeration may occur, XRD patterns of the compounds with 9, 18 and 36 wt% of OC relative to total fillers content were therefore characterized. The results are shown in comparison with the XRD pattern of OC (Dellite 67G) itself in Figure 6.12.

By applying Bragg's law, interlayer spacing or d-spacing of the clay platelets can be determined. As shown in Figure 6.12(a), the rubber specimens with OC of 9 and 18 wt% relative to total fillers amount, show a very small trace of diffraction peaks with the 2θ values that can be converted to interlayer d-spacing as shown in Figure 6.12(b). An increased d-spacing is observed where the XRD pattern indicates that the OC is intercalated in the NR matrix or can as well be due to a too low concentration of the clay to be clearly visible [17]. However, at 36 wt% of OC relative to total fillers amount, the interlayer distance is slightly decreased again and the characteristic peaks of OC can be clearly observed, indicating re-agglomeration of the OC. Previous work on organomodified clay (Cloisite 20A)-filled NR reported that nearly an exfoliated structure was observed at an OC concentration of 5 phr [28]. Our data do not support this observation.

Figure 6.12 X-ray diffraction patterns (a) and interlayer spacing (b) of silica-filled NR compounds with various loadings of organoclay (OC).

6.3.7 Dynamic mechanical properties

To further evaluate potential use of silica/OC systems to reinforce NR tire tread compounds, tan delta or the loss tangent values of the rubber vulcanizates are given in Figure 6.13. The tan delta at 60°C, indicative of tire rolling resistance [32], obtained from both RPA and DMA analysis (Figure 6.13(a)) shows a minimum value in the range of 9-14 wt% of OC relative to total fillers amount, i.e. 5-7.5 phr of OC. Thereafter, the tan delta at 60°C tends to increase with increasing the OC content, especially after exceed 18 wt% relative to total fillers amount. The poorer elastic response at high loading of OC is in accordance with the poorer mechanical properties ascribed to the re-agglomeration of OC, the plasticizing effect by the modifying agent, and the silica-OC network beyond the threshold content. The reduced tan delta at 60°C of the compound with 5 phr of OC indicates that there is a potential to decrease rolling resistance of a tire when a suitable content of OC is used with silica.

Figure 6.13(b) shows the values of tan delta at -20°C and 0°C, indicative of ice and wet traction of the rubber vulcanizates respectively, as evaluated on the laboratory testing scale [32]. The tan delta at -20°C shows an optimum point at about 14 and 18 wt% relative to total fillers content, i.e. at 7.5-10 phr of OC, whereas the tan delta at 0°C is increased with increasing the OC loading and the values are higher than that of the pure silica reinforced NR compound. This result also favors tire wet grip in addition to the better rolling resistance as indicated by tan delta at 60°C.

Figure 6.13 Tan delta as a function of temperature (a), tan delta at 60°C (b) and tan delta at -20°C and 0°C (c) of silica-filled NR compounds with various loadings of organoclay (OC).

6.4 Conclusions

The properties of silica/OC-filled NR compounds when the loadings of OC were varied from 0-20 phr or from 0-36 wt% relative to total fillers content are compared to that of pure silica. The presence of OC only in small amounts, i.e. in the range of 2.5-7.5 phr or 5-14 wt% relative to total fillers content results in a remarkable decrease in compound viscosity,

Payne effect and scorch and cure times. The optimum silica/OC ratio is at 50/5 phr or at 9 wt% relative to total fillers content where the compound shows overall the best balance of properties. When compared to the pure silica-reinforced NR reference compound, the silica/OC combination provides compounds with lower Payne effect, higher cure rate index, similar tensile properties (modulus, tensile strength and elongation at break), and somewhat improved tear strength, DIN abrasion resistance index, and tan delta at 60°C. The silica/OC-filled NR compounds enable therefore overall processing benefits from easier flow and shorter cycle time, and by judicious incorporation of OC in combination with silica at the optimum ratio, i.e. at silica/OC ratio of 50/5 phr, the compounds show enhanced wear resistance, rolling resistance, ice traction and wet grip, which are favored for tire applications.

These conclusions are summarized in the radar charts hereunder. Figure 6.14 shows the radar charts covering cure properties and Payne effect of the compounds (Figure 6.14(a)), as well as mechanical properties of the vulcanizates (Figure 6.14(b)). These two charts are based on relative values versus the reference. The chart concerning tire performance as shown in Figure 6.15 is based on index-values: the higher the better.

Figure 6.14 Radar charts comparing cure properties, Payne effect (a) and mechanical properties (b) of the silica-filled NR compounds without organoclay (OC-0%) and with the optimum amount of organoclay as secondary filler at 9 wt% relative to the total amount of fillers (OC-9%).

Figure 6.15 Radar chart comparing the key tire performances indicated by lab-indicators of the silica-filled NR compounds without organoclay (OC-0%) and with the optimum amount of organoclay as secondary filler at 9 wt% relative to the total amount of fillers (OC-9%).

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CHAPTER 7

Effect of Clay-Modifier on the Properties of Silica- and Silica/Nanoclay-Reinforced Natural Rubber Compounds

OrganoClay (OC) is one of the potential secondary fillers to be applied in silica-reinforced rubber compounds for tire applications. As commercial OC contains a large proportion of surface modifying agent, i.e. dimethyl dihydrogenated tallow ammonium chloride (2HT) type, that has an influence on the rubber compound properties, this work is to investigate the effect of such modifying agent on the properties of silica-reinforced Natural Rubber (NR) truck tire tread compounds comparing between the use of silica/2HT, silica/OC, and silica/MontMorillonite (MMT)/2HT. The loading levels of 2HT were varied at 0-9.5 phr with incremental steps. By increasing the amount of 2HT, compound viscosity, Payne effect and scorch times are significantly decreased. As determined by the properties of both unvulcanized compounds and vulcanizates in terms of Payne effect, tensile properties, DIN abrasion resistance index, apparent crosslink density, tan delta at -20°C and tan delta at 60°C, the overall best balance of properties was observed at 4.7 phr of the modifying agent for a silica-filled and silica/MMT-filled NR compound, while at 5.0 phr of OC that contained 2.4 phr of the modifying agent for a silica/OC-filled system. However, the silica/2HT compounds show different trends of property changes with 2HT content when compared to the silica/OC and silica/MMT/2HT systems, especially with respect to cure properties, reinforcement index and tear strength, due to the different filler characteristics. With the optimum content of 2HT as the filler surface modifying agent, a lower Payne effect, higher cure rate index, higher tan delta at -20°C and lower tan delta at 60°C can be achieved, all showing the beneficial potential of utilization of the modifying agent to improve processability, rolling resistance, wet traction and abrasion resistance of silica-based compounds for tire treads.

7.1 Introduction

Tires with better energy saving, safety and durability are required to meet more stringent customer's requirement as well as new legislations/regulations. Reinforcement materials such as Carbon Black (CB) and silica are added to rubber compounds to improve some basic requirement in properties such as modulus, hardness, tensile strength and tear resistance. Moreover, key tire tread performances which include wet traction, rolling resistance and wear resistance need to be optimized. Carbon Black (CB) was the first generation of fillers for tire rubber compounds that has the ability to improve the tensile and tear strength, abrasion resistance, skid resistance as well as other properties of rubber. Tires generally contain 30-35% of CB of several grades that are used for different parts [1]. After 1992 when Michelin first introduced silica for passenger car tire tread compounds [2] showing that it could reduce rolling resistance and enhance wet grip, silica-reinforced tire treads became the subject of investigations worldwide in order to produce tires with better energy savings and driving safety [3]. However, mixing of silica into tire rubbers faces several difficulties such as poor dispersion and distribution in the rubber matrix, incompatibility with non-polar rubbers and poor filler-rubber interaction due to the highly polar and hydrophilic surface of silica that causes high filler-filler interaction and re-agglomeration. To overcome those problems, silane coupling agents that contain sulfur in the structure such as bis-(3-TriEthoxySilylPropyl)Tetrasulfide (TESPT) are generally used in silica-reinforced rubber compounds to promote silica-rubber interaction, better silica dispersion and also to suppress accelerator adsorption on the silica surface so that it has less interference with the vulcanization reaction. As TESPT has some drawbacks like short scorch time and premature crosslinking in a rubber compound [4], so a silane coupling agent with lower sulfur rank like bis-(3-TriEthoxySilylPropyl)Disulfide (TESPD) can be applied. Comparing between TESP and TESPT, it has been demonstrated that TESP provides better scorch safety but lower filler-rubber interactions, dispersion stability, tensile strength and tear resistance than TESPT [4]. By mixing rubber with silica-TESP or -TESPD silane coupling agents, the silanization reaction takes place during mixing and the extent of reaction is mainly governed by the mixing temperature [5-9]. The silanization reaction between silica and the silane coupling agent increases with increasing mixing discharge temperature, as indicated by a reduction of filler-filler interactions or Payne effect, and an increase of filler-elastomer interactions as evidenced by higher chemically bound rubber content. The extent of the silanization has a dramatic effect on the resulting compound properties [9-10]. The effect of mixing dump temperature for hybrid fillers of silica/OC and

silica/CB (N134) in Natural Rubber (NR) compounds at 45/10 phr was recently reported [11], in which the tensile properties increased with increasing dump temperature until about 150°C due to a better silanization reaction between silica and TESPD, and thereafter the tensile properties dropped as a result of degradation of NR at higher temperature. Additionally, compatibilization between silica and NR by means of Epoxidized Natural Rubber (ENR) as compatibilizer has been investigated. The results showed a reduction in Payne effect and enhancement of filler-rubber interaction, silica dispersion and tensile strength by adding either ENR [12] or Epoxidized Low Molecular Weight Natural Rubber (ELMWNR) [13] as compatibilizer when compared with the compound without ENR. However, based on the optimized ENR or ELMWNR loadings, the overall properties were still somewhat lower than those of the reference silica-TESPT silane compound.

Nowadays, a new generation of reinforcing fillers as nanofillers which have at least one characteristic length scale in the nanometer level, attracts a lot of interests for material development including rubber compounds for high performance products. This is due to their potential to improve compound properties at lower content used (usually less than 10 phr) as compared to conventional reinforcing fillers like CB and silica (usually higher than 30 phr) [14-15]. The large specific surface area of nanofillers provides larger contact spots between polymer and filler, and if the interfacial interaction between nanofiller and polymer is strong enough, an efficient stress transfer from the matrix to filler will be obtained. Nanoclay has been widely studied as nanofiller in rubber compounds because it has the potential to offer a very high degree of reinforcement, high thermal stability, improved impermeability to gases, vapor and liquids, good optical clarity, and enhanced flame retardancy with reduced smoke emission [16]. The commonly used nanoclay layered silicates are 2:1 phyllosilicates including hecrite, saponite, montmorillonite, and synthetic mica. MontMorilloniTe (MMT) has been widely investigated due to its low cost, abundance in nature, high surface area, high aspect ratio, and good surface reactivity [1]. However, original MMT appears in the form of stacks of clay platelets with hydrophilic silicate surfaces. So, it is incompatible with non-polar rubbers like NR, Styrene Butadiene Rubber (SBR), Butadiene Rubber (BR) that are conventional rubbers for tire applications. To enhance the dispersion and promote intercalation/exfoliation of clay in the rubber matrix, cation exchange with ammonium salts or phosphonium salts is the most commonly used technique to alter the hydrophilic to hydrophobic surface. The obtained material is called organically modified clay or shortly OrganoClay (OC) [17]. The OC may be dispersed in single platelets or small silicate stacks with a high aspect ratio of 50-1000 [18].

The use of OC as a single filler in elastomers shows an improvement in mechanical properties, thermal stability, wear resistance and gas impermeability.

As the use of nanofillers alone cannot meet the requirements for most of high performance rubber products, especially for tire applications, that require a certain modulus and hardness level, a combination of nanofiller with conventional fillers either CB or silica is therefore an alternative. The ideal is to obtain a synergistic reinforcing effect from each filler type. Hybrid fillers of silica with different types of fillers have been investigated such as silica/CB [19-24], silica/China clay [25], silica/MMT [26-27], silica/organomodified kaolin [28] and silica/OC [11,29-30]. The utilization of silica/China clay hybrid fillers for a heavy-duty truck tire tread formulation based on NR [25] revealed that the best balance of heat build-up and abrasion resistance was observed at the ratio of silica/clay at 60/20. The use of precipitated silica/MMT in peroxide cured silicone rubber showed the improvement of tensile strength, elongation at break, Young's modulus, modulus at 100% and 300% strain, hardness and crosslink density [26]. The use of silica/MMT with TESPT as silane coupling agent in SSBR/BR tread compounds improved tensile strength, elongation at break and traction properties at low TESPT content while enhanced modulus, hardness, wear resistance, dry handling and rolling resistance at high TESPT content [27]. Substitution of 5-10 phr of silica with the sodium salt of rubber seed oil modified kaolin in NR/BR blends [28] resulted in lower Mooney viscosity, higher cure rate, increased chemical crosslink density index and bound rubber content, indicating a higher extent of rubber-rubber and filler-rubber interactions. Moreover, the mechanical properties such as abrasion resistance, compression set, tensile- and tear strength of the blend vulcanizates were enhanced, as well as the dynamic mechanical properties that are beneficial for tire tread applications. A comparison between the use of silica 60 phr and silica/OC nanocomposite prepared by a latex mixing method with a replacement of silica by 7 phr of OC in SBR showed that the silica/OC system gave better skid and rolling resistance with higher 100% and 300% moduli [29]. The reduction of filler networking in silica-based elastomeric nanocomposites with exfoliated OC resulted in improved mechanical reinforcement and reduced energy dissipation and thus fuel consumption as well as carbon footprint [30]. Our own recent work on a hybrid filler system of silica/OC-filled NR at 45/10 phr [11] revealed several positive effects when compared to reference pure silica-NR compounds, as the hybrid filler gave lower Payne effect (i.e. lower silica networking), higher cure rate index (i.e. better productivity in terms of reduced product cycle time), higher tan delta at -20°C (i.e. better ice traction), and lower tan delta at 60°C (i.e. reduced rolling resistance).

The OC contains an organic modifying agent or cationic surfactant that is used to increase the d-spacing between clay layers and to change the clay surface characteristic to be more hydrophobic. The presence of this active surfactant in the rubber compounds also plays a role on the properties. The most important end groups of cationic surfactants are primary-, secondary- and tertiary-amino groups, and quaternary ammonium groups. Some of the works that studied the effect of surfactant or modifying agent on silica-filled rubber compounds are such as the study of loadings of a diamine salt of fatty acid, called a multifunctional additive, on a silica-filled NR compound [31] that demonstrated improvement of mechanical properties due to better silica dispersion and crosslink density; a modification of silica by cyclohexylamine [32] that resulted in the improvement of filler dispersion and mechanical properties, lower tan delta value at 60°C, and higher crosslink density of silica-filled NR; and the use of alkanolamide for silica-reinforced NR [33] that resulted in faster vulcanization, and better cure torque differences, tensile strength, 100% and 300% moduli, hardness and crosslink density at the optimum loading of alkanolamide (5.0 phr).

The effect of the concentration of OCTadecylamine (OCT) as organic modifying agent on the preparation of OC was investigated [34]. Based on the modification of MMT with different concentrations of OCT, an optimum OCT content was observed at 1.5 times the cation exchange capacity of MMT as determined by a larger d-spacing of the clay and a higher degree of OC dispersion in the NR matrix that led to improved mechanical properties of the NR/OC nanocomposites. By varying the loadings of N,N-dimethyl-dodecylamine for MMT modification [35] for SBR-OC nanocomposites prepared by the latex mixing method that was later used to mix with silica to obtain hybrid filler compounds of silica/OC at 20/5 phr, with increasing the N,N-dimethyl-dodecylamine content in SBR the scorch time and cure time decreased while the cure torque differences, tensile strength and wear resistance increased due to the increase of crosslink density and improved dispersion of the silicate layers in the SBR matrix.

To fully explore and better understand the influence of the modifying agent in the OC that affects the rubber compound properties of a silica/OC dual system, this present work employs 2HT which is a quaternary ammonium type of surfactant. The effect of modifying agent loadings on three different compound types: silica-filled NR, silica/OC-filled NR with the 2HT already included in the OC, and silica/MMT-filled NR compounds, which contain TESPD as coupling agent, are investigated in comparison with a silica only compound without modifying agent as reference. The mixes are subjected to characterization in terms of cure

characteristics, filler-filler interactions, filler-rubber interactions, tensile and tear properties, DIN abrasion resistance, dynamic mechanical properties and morphology.

7.2 Experimental

7.2.1 Materials

The NR (Ribbed Smoked Sheet, RSS3) was locally produced in Thailand. Silica ULTRASIL 7005 and silane coupling agent TESPD were obtained from Evonik, Germany. Organoclay Dellite 67G, functionalized with 47 wt% of dimethyl dihydrogenated tallow ammonium chloride (2HT), 115 meq/100 g of cation exchange capacity and interlayer distance of 34.3 Å was provided by Laviosa Chimica Mineraria S.p.A, Livorno LI, Italy. Montmorillonite clay was provided by Thai Nippon Chemical Industry, Thailand. 2HT was purchased from Sigma Aldrich. The other ingredients: Treated Distillate Aromatic Extract oil (TDAE oil), DiPhenyl-Guanidine (DPG), N-Cyclohexyl-2-Benzothiazyl Sulfenamide (CBS), 2,2,4-TriMethyl-1,2-dihydroQuinoline (TMQ), Zinc Oxide (ZnO), stearic acid and sulfur were of commercial grade quality for the rubber industry.

7.2.2 Compound preparation

The NR based truck tire tread compounds were prepared using the formulations as shown in Table 7.1-7.3 and a two-step mixing procedure as displayed in Scheme 7.1. The first step was executed by using an internal mixer, Brabender® 50EHT, (Brabender® GmbH & Co.KG, Germany) with a mixing chamber volume of 70 ml, at a rotor speed of 60 rpm, fill factor of 70% and initial mixer temperature setting of 120°C in order to reach a dump temperature in the range of 135-150°C, as suggested in previous reports [9,11]. For silica-filled NR and silica/MMT-filled NR, all of the modifying agents were added together with the first halves of silica, TESPD and DPG. For silica/OC-filled NR, the OC was added with the first half of silica. The other halves of silica and TESPD were later added together with TDAE oil in the second interval of the first mixing step. The second step was for the preparation of the reactive or final compounds by mixing the obtained masterbatches with the other halves of DPG, CBS primary accelerator, and sulfur by using the same instrument operated at a rotor speed of 30 rpm, fill factor of 70%, and an initial mixer temperature setting of 70°C. The OC loadings were varied at 0-20 phr at incremental steps, which possessed modifying agent contents from 0-9.5 phr, respectively. By taking the amounts of surface modifying agent in the OC as references, 2HT was added to the silica-filled NR and silica/pristine MMT-filled compounds.

Table 7.1 Formulations of silica-filled NR compounds with varying amount of modifying agent.

Ingredients	Amount (phr)						
	Reference	1	2	3	4	5	6
NR (RSS3)	100.0	100.0	100.0	100.0	100.0	100.0	100.0
ULTRASIL 7005	55.0	55.0	55.0	55.0	55.0	55.0	55.0
2HT	-	1.2	2.4	3.5	4.7	7.1	9.5
TESPD ^a	5.0	5.0	5.0	5.0	5.0	5.0	5.0
TDAE oil	8.0	8.0	8.0	8.0	8.0	8.0	8.0
ZnO	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Stearic acid	1.0	1.0	1.0	1.0	1.0	1.0	1.0
TMQ	1.0	1.0	1.0	1.0	1.0	1.0	1.0
DPG ^a	1.1	1.1	1.1	1.1	1.1	1.1	1.1
CBS	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5

^aAmounts of TESPD and DPG were added according to the following equations [36]:

$$\text{TESPD (phr)} = 0.00053 \times Q \times A \quad (1)$$

$$\text{DPG (phr)} = 0.00012 \times Q \times A \quad (2)$$

where Q is the amount of silica (phr) and A is the Cetyl-Trimethyl-Ammonium-Bromide (CTAB) specific surface area of the silica (171 m²/g).

Table 7.2 Formulations of silica-filled NR compounds with organoclay as a secondary filler.

Ingredients	Amount (phr)						
	Reference	1	2	3	4	5	6
NR (RSS3)	100.0	100.0	100.0	100.0	100.0	100.0	100.0
ULTRASIL 7005	55.0	52.5	50.0	47.5	45.0	40.0	35.0
Dellite 67G (OC)	-	2.5	5.0	7.5	10.0	15.0	20.0
TESPD ^a	5.0	4.8	4.5	4.3	4.1	3.6	3.2
TDAE oil	8.0	8.0	8.0	8.0	8.0	8.0	8.0
ZnO	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Stearic acid	1.0	1.0	1.0	1.0	1.0	1.0	1.0
TMQ	1.0	1.0	1.0	1.0	1.0	1.0	1.0
DPG ^a	1.1	1.1	1.0	1.0	0.9	0.8	0.7
CBS	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Amounts of 2HT included in the OC	-	1.2	2.4	3.5	4.7	7.1	9.5

^aAmounts of TESPD and DPG were added according to the following equations [36]:

$$\text{TESPD (phr)} = 0.00053 \times Q \times A \quad (1)$$

$$\text{DPG (phr)} = 0.00012 \times Q \times A \quad (2)$$

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

Table 7.3 Formulations of silica/MMT-filled NR compounds with varying amount of modifying agent.

Ingredients	Amount (phr)						
	Reference	1	2	3	4	5	6
NR (RSS3)	100.0	100.0	100.0	100.0	100.0	100.0	100.0
ULTRASIL 7005	55.0	52.5	50.0	47.5	45.0	40.0	35.0
MMT	-	2.5	5.0	7.5	10.0	15.0	20.0
2HT	-	1.2	2.4	3.5	4.7	7.1	9.5
TESPD ^a	5.0	4.8	4.5	4.3	4.1	3.6	3.2
TDAE oil	8.0	8.0	8.0	8.0	8.0	8.0	8.0
ZnO	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Stearic acid	1.0	1.0	1.0	1.0	1.0	1.0	1.0
TMQ	1.0	1.0	1.0	1.0	1.0	1.0	1.0
DPG ^a	1.1	1.1	1.0	1.0	0.9	0.8	0.7
CBS	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5

^aAmounts of TESPD and DPG were added according to the following equations [36]:

$$\text{TESPD (phr)} = 0.00053 \times Q \times A \quad (1)$$

$$\text{DPG (phr)} = 0.00012 \times Q \times A \quad (2)$$

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

7.2.3 Sample characterizations

7.2.3.1 Characterization of filler-filler interaction

Payne effect – The storage shear moduli (G') of the unvulcanized rubber compounds with curatives were evaluated using a Dynamic Rubber Process Analyzer (D-RPA 3000, MonTech Rubber Testing Solutions, Germany) at a temperature of 100°C, frequency of 0.5 Hz and varying strains in the range of 0.56-100%. The Payne effect was calculated from the difference in storage shear moduli at low strain (0.56%) and high strain (100%).

Scheme 7.1 Two-step mixing procedures for compound preparations: (a) NR/silica without clay MMT or OC, nor 2HT; (b) NR/silica+2HT, NR/silica+OC and NR/silica+MMT+2HT compounds.

7.2.3.2 Complex viscosity and cure characteristics

Complex viscosity – The complex viscosities were analyzed using a D-RPA 3000, in a frequency sweep test in the range of 0.01–100 Hz at 0.558% strain and 100°C.

Cure characteristics – Cure characteristics of the compounds were measured by using the D-RPA 3000, at a temperature of 150°C, frequency 0.833 Hz and 2.79% strain for 30 minutes. The CRI was calculated to equal $[100/(\text{optimum cure time } (t_{c90}) - \text{scorch time } (t_{s2}))]$.

7.2.3.3 Characterization of Bound Rubber Content (BRC)

Bound rubber content (BRC) – An amount of 0.25 g of uncured compound (without curatives) was put into a metal cage and immersed in 40 ml of toluene for 7 days at room temperature. Then the sample was removed from the toluene, dried at 105°C in an oven for 24 h and weighed. The bound rubber content was calculated using the following equation.

$$BRC(\%) = \frac{(m - m_s)}{m_r} \times 100 \quad (3)$$

where m is the weight of sample after extraction, m_s and m_r are the weights of filler and rubber in the original sample respectively.

7.2.3.4 Apparent crosslink density

Apparent crosslink density, vulcanizate samples with a dimension of 3 x 5 x 2 mm³ were immersed in toluene at room temperature for 7 days. Thereafter, the swollen samples were taken out and blotted lightly with paper to remove excess toluene from the surface. The weights of the rubbers before and after swelling were measured and the swelling ratio (Q) was calculated according to the following equation:

$$\text{Swelling ratio } (Q) = (M_t - M_0)/M_0 \quad (4)$$

where M_0 and M_t are the weights of the samples before and after swelling, respectively. The apparent crosslink density was calculated from the reciprocal of swelling ratio (i.e. 1/Q) [37], because the real crosslink density by for example the Flory-Rehner approach [38] is not feasible to acquire with the varying filler loadings.

7.2.3.5 Tensile and tear properties

Tensile and tear properties – The compounds were vulcanized for their optimum cure times (t_{c90}) by using a compression molding press (CT Compression Machine, Charoen Tut Co, Ltd, Samut Sakhon, Thailand) at 150°C and 100 bars into 2 mm thick sheets. For tensile properties, Type 2 dumb-bell test specimens were die-cut from the press-cured sheets and tests were carried out with a tensile tester (Hounsfield Test Equipment Co., Ltd., Surrey, England) at a crosshead speed of 500 mm/min according to ASTM D412. For tear strength, the vulcanized rubbers were tested at room temperature using Delft-type specimens with a Zwick tensile tester Model Z1.0/TH1S (Zwick Roell Group, Ulm, Germany) and the same crosshead speed as applied for tensile tests according to ISO 34-2.

7.2.3.6 DIN abrasion resistance index and its abraded surface

DIN abrasion resistance index and its abraded surface – The DIN Abrasion Resistance Index (ARI) was tested using a DIN abrader (GOTECH Testing Machines Inc, Taichung, Taiwan) according to method A of DIN 53516. The test specimens had a diameter of 16 ± 2 mm with a minimum thickness of 6 mm. The pure silica-filled NR without 2HT was used as reference rubber. The ARI was calculated according to the following equation:

$$ARI = \left(\frac{\Delta m_r \cdot d_t}{\Delta m_t \cdot d_r} \right) \cdot 100 \quad (5)$$

where Δm_r is mass loss of the reference rubber (g), d_r is density of the reference rubber (g/cm^3), Δm_t is mass loss of the test rubber (g), and d_t is density of the test rubber (g/cm^3).

The DIN abraded surface was characterized by scanning electron microscopy (SEM, Quanta 400, FEI Company, the Netherlands). The surface was coated with gold prior to being analyzed.

7.2.3.7 Dynamic mechanical properties

Dynamic mechanical properties – The loss tangent or tan delta at 60°C of the vulcanizates was determined using the D-RPA 3000 at strain 3.49% with varying frequencies in the range of 0.05-33.00 Hz. The samples were cured in the RPA chamber at 150°C to reach their optimum cure times before being tested. In addition, dynamic mechanical properties of silica-filled NR vulcanizates under a temperature sweep from -80°C to 80°C were characterized by using a Metravib Viscoanalyzer VA 2000. The samples of a dimension of $6 \times 4 \times 2 \text{ mm}^3$ were tested in tension mode at a frequency of 10 Hz and 0.1% strain. Tan delta values at -20°C, 0°C are used as indicative for ice traction and wet grip respectively, and tan delta at 60°C is to indicate rolling resistance of a tire tread.

7.3 Results and discussion

7.3.1 Masterbatch mixing behavior

The mixing dump torques and temperatures are shown in Figure 7.1. The mixing dump torque of a rubber compound is generally related to its viscosity. The decreasing mixing dump torque therefore means reduced compound viscosities which can be caused by several factors including lower filler-filler interactions, better filler dispersion in the rubber matrix, and plasticization by some of the ingredients present in the compound. Figure 7.1(a) shows the dump torques that gradually decrease with increasing loadings of modifying agent for all three compound series. It should be noted that TESPD silane coupling agent was used in combination with silica for all compounds to ensure the silica-rubber interactions. The presence of surface modifying agent further reduces filler-filler networking and provides a plasticizing effect in the rubber compounds to result in less resistance to flow and so reduced mixing torques. The increase of loadings of modifying agent reduces the dump temperature slightly and there is no difference between the silica-filled NR compounds without and with MMT as seen in Figure 7.1(b). The reduced dump temperature at least does not account for the lower dump torques, as the opposite should have been observed.

Figure 7.1 Dump torque (a) and dump temperature (b) of silica-filled NR, silica/OC-filled NR and silica/MMT-filled NR compounds with varying loadings of modifying agent 2HT.

7.3.2 Filler-filler interaction

All three series of compounds with varying loadings of modifying agent: i.e. pure silica, silica/OC-, and silica/MMT-filled NR compounds, show surprising nearly the same non-linear behavior of storage modulus that decreases with increasing %strain due to breakdown of the filler network, i.e. reduction of filler-filler interactions, as shown in Figures 7.2(a)-(c). The difference between values of the storage modulus at low strain (0.56%) and high strain (100%) indicates the Payne effect that reflects the level of filler-filler interaction [39] as shown in Figure 7.2(d). The increase of the modifying agents greatly reduces the Payne effect of all types of compounds to similar levels indicating a further reduction of filler networking by the presence of 2HT, in addition to the effect of the silanization reaction between the alkoxy groups of TESPD and the silanol groups of the silica. As only a portion of the silanol groups could react with the silane due to the limited accessibility after the first silane molecules are grafted on to the silica surface, it has been reported that the availability of alcohols or amines to shield and increase the hydrophobation of the silica surface is helpful [40-41]. By the incorporation of dimethyl dihydrogenated tallow ammonium chloride (2HT) into the compounds, better hydrophobation and filler dispersion in the rubber matrix is obtained. Moreover, this 2HT may also enhance the silanization because of its basicity. The Payne effect of all the compounds decreases sharply with increasing modifying agent loadings up to 4.7 phr

and thereafter tends to level off. This reduction in filler networking by the modifying agent is in accordance with work reported by Galimberti and coworkers [30]. The presence of the quaternary ammonium salt also plasticizes the system and results in the reduction of the modulus of the filled-rubber, as observed in the range of high strain after the breakdown of the filler network.

Figure 7.2 Storage modulus as a function of strain of silica-filled NR (a), silica/OC-filled NR (b), silica/MMT-filled NR (c) compounds and Payne effect (d) of silica-filled NR, silica/OC-filled NR and silica/MMT-filled NR compounds with varying loadings of modifying agent 2HT.

7.3.3 Complex viscosities and cure properties

In correspondence with the mixing torque (Figure 7.1) and Payne effect (Figure 7.2(d)), the increasing loadings of the modifying agent reduce the complex viscosities of all compound types, as shown in Figure 7.3, due to the reduced filler-filler networking, shielding effect and plasticization. By taking the values of the complex viscosities at 10 Hz at various loadings of modifying agent, the viscosities of the different filled compounds are comparatively displayed in Figure 7.3(d).

The shear thinning exponent values (n) were determined by using the power law following the Wagener and Reisinger equation as shown below [42]:

$$\eta = A\omega^n \quad (6)$$

where η is the viscosity, A is the sample specific exponential factor, ω is the frequency, and n is the shear thinning exponent. A plot of $\log \eta$ vs. $\log \omega$ gives a slope equaling the shear thinning exponent value n . A higher n -value means better reinforcement [43] and interaction with the polymer matrix [42]. From the n -values as given in Figure 7.4(a), the increase of modifying agent loadings in silica-filled NR compounds either with or without clay lowers the n -values slightly, i.e. reduces the reinforcement and/or filler-rubber interaction. The decrease of filler-rubber interaction is also reflected in the reduction of total bound rubber content [44] as shown in Figure 7.4(b). The sharp drop in total bound rubber content with increasing modifying agent is in accordance with the fall in Payne effect in Figure 7.2(d). These results together indicate that the incorporation of 2HT as surface modifying agent contributes to physical interactions rather than chemical interactions. When comparing the total bound rubber contents of the three systems, the silica-filled NR shows a higher bound rubber content than silica/MMT and silica/OC-filled NR, respectively. This indicates that the silica-filled NR with silane coupling agent has a higher filler-rubber interaction than the mixes with dual fillers of silica/MMT or OC.

Figure 7.3 The effect of loadings of modifying agent (2HT) on complex viscosity of silica-filled NR (a), silica/OC-filled NR (b), silica/MMT-filled NR (c) compounds and complex viscosity at 10 Hz (d) of silica-filled NR, silica/OC-filled NR and silica/MMT-filled NR compounds with varying loadings of modifying agent 2HT.

Figure 7.4 Shear thinning exponent (n -value) (a), and total bound rubber content (b) of silica-filled NR, silica/OC-filled NR and silica/MMT-filled NR compounds with varying loadings of modifying agent 2HT.

Based on the cure characteristics shown in Figures 7.5(a)-(c) for all compound types, the incorporation of modifying agent clearly suppresses filler flocculation before the onset of vulcanization when compared to the pure silica without 2HT in which the flocculation is noticeably observed despite the use of TESPD in combination with silica. This filler flocculation manifests itself by the initial hub in the curing curve, before real vulcanization takes over. The addition of modifying agent in whichever form loadings has a strong influence on both cure torques and times. The minimum cure torque (M_L) indicates compound viscosity which is generally related to molecular chain entanglements of the polymer and filler-related parameters like type, amount, filler-rubber interaction and filler-filler interaction or the filler network. When the filler content is increased and the formation of the filler network is enhanced, the M_L increases [45]. With increasing the modifying agent content in the silica-filled compounds, the M_L gradually reduces as observed in Figure 7.5(d), in agreement with the dump torques (Figure 7.1(a)) and complex viscosity (Figure 7.3(d)). As seen in Figure 7.2(d), the Payne effect is greatly reduced by the addition of 2HT, so the filler-filler interaction is disrupted. In addition, the total bound rubber content is also decreased with increasing the 2HT content. So, there is less obstruction to flow. Moreover, the modifying agent has a long tail structure of dihydrogenated tallow that can plasticize the system, causing increasing free

volume between the high molecular weight elastomer chains to facilitate flow. Meanwhile, the polar functional groups that are present in the modifying agent (C=O , C-O and -N=) can interact with the left-over free silanol groups on the silica surface after the silanization reaction, providing a shielding effect that promotes hydrophobicity and interfacial compatibility between rubber and filler. For these various reasons, the rubber compound viscosities of every filler system: i.e. silica, silica/OC and silica/MMT, are remarkably decreased with increasing the modifying agent loading causing improved processability. It has been reported before that by substituting silica with OC, the compound viscosity was similarly affected [30,46].

After vulcanization, the maximum cure torques (M_H) and cure torque differences (M_H-M_L) of the silica-, silica/OC- and silica/MMT-filled NR compounds with different modifying agent loadings show the same trends, as shown in Figures 7.6(a)-(b). Since the rheometer torque increases by formation of crosslinks, the cure torque difference or delta torque is related to the crosslink density. However, the levels of M_H and M_H-M_L which indicate the vulcanizate stiffness are also influenced by several additional factors, combining contributions from chemical crosslinks by the vulcanization reaction, filler-rubber interactions and filler-filler interactions. As displayed in Figure 7.6, the M_H and M_H-M_L of all the compound types decrease when the modifying agent content is increased, but to different levels. The silica/OC-filled and silica/MMT-filled NR compounds show similar behaviors and the reduction in M_H and M_H-M_L is much larger compared with the pure silica-filled NR. As the filler-filler interactions or Payne effect (Figure 7.2(d)) and filler-rubber interactions as indicated by total bound rubber contents (Figure 7.4(b)) are not much different, the clear difference in M_H and M_H-M_L of silica only-filled NR when compared to the mixes with OC and MMT is most likely derived from the filler network reformed due to flocculation, as distinctively displayed on the cure curves (Figure 7.5). The reduction of the cure torque difference when the modifying agent loading is raised, in addition to the reduced filler-filler and filler-rubber interaction with excess amount of the modifying agent, means that the crosslink density may be reduced as a result of diluting effects and interference with the polar curatives.

Figure 7.5 The effect of loadings of modifying agent (2HT) on the cure profiles of silica-filled NR (a), silica/OC-filled NR (b), and silica/MMT-filled NR (c) compounds, with varying loadings of modifying agent 2HT, and minimum cure torques (d) of all compounds.

Figure 7.6 Maximum cure torque (a) and cure torque difference (b) of silica-filled NR, silica/OC-filled NR and silica/MMT-filled NR compounds with varying loadings of modifying agent 2HT.

Figure 7.7 Scorch time (a) and optimum cure time (b) of silica-filled NR, silica/OC-filled NR and silica/MMT-filled NR compounds with varying loadings of modifying agent 2HT.

The scorch times (t_{s2}) and optimum cure times (t_{c90}) are displayed in Figures 7.7(a)-(b). As the modifying agent is an amino-based compound composed of an ammonium salt, it has an accelerating effect on the vulcanization reaction, that can be beneficial by reducing the

required processing cycle time. The increasing loadings of modifying agent progressively shorten t_{s2} of all the compound types studied, but a different behavior is observed for the t_{c90} . For the silica/OC- and silica/MMT-filled NR compounds, the t_{c90} are gradually reduced with increasing the modifying agent content, but for silica-filled NR the t_{c90} decreases to reach a minimum at the 2HT content of 3.5 phr and thereafter increases again. As observed in Figure 7.5(a), the cure curves of silica-filled NR with the addition of 2HT start to show marching modulus torques when the modifying agent loading reaches 4.7 phr and marching is more pronounced at 7.1 and 9.5 phr of 2HT. In this pure silica system wherein the optimum content of silane coupling agent is used, the addition of the polar compound like the modifying agent in excess amounts may cause interference with the vulcanization reaction, possibly due to interactions between the modifying agents and accelerators. For the compounds containing silica and OC or MMT, the delaminated clay introduces more polar functional groups on the edges that the modifying agent needs to shield. So, in these systems, there will be less free modifying agent to interrupt the vulcanization reaction. Comparing among the three systems, the use of silica/OC results in the shortest t_{s2} and t_{c90} as the surface of pretreated OC should be most efficiently protected by the modifying agent. The effect of modifying agent in OC on accelerating the curing reactions has been previously documented [35,47-54] by various authors.

Overall, the benefit of adding 2HT in either form is that it substantially reduces the scorch time and optimum cure time, which otherwise are comparatively long in comparison with silica reinforced compounds. This greatly improves the vulcanization processability of pure silica reinforced compounds [55].

7.3.4 Mechanical properties and apparent crosslink density

The effect of modifying agent loadings on tensile properties of silica-filled NR, silica/OC-filled NR and silica/MMT-filled NR compounds are shown in Figures 7.8(a)-(b) and Figure 7.9(a). The 100% modulus of all the compound types are quite similar with a tendency to reduce slightly with increasing modifying agent content. However, the moduli values at 300% elongation are different. The silica/MMT-filled NR shows the lowest 300% modulus which decreases with increase of the modifying agent loading. While the 300% modulus of silica-filled NR and silica/OC-filled NR compounds show optimum values. The addition of small amounts of modifying agent increases the 300% modulus first but soon reaches a maximum and thereafter reduces. Optimum values are observed for 3.5 and 2.4 phr of 2HT for

silica-filled- and silica/OC-filled NR compounds, respectively. For the silica/OC system, the optimum of 300% modulus is observed at a loading of OC of 5 phr which corresponds to 2.4 phr of modifying agent. The lowest modulus overall of the silica/MMT-filled system indicates poorest compatibility with the rubber matrix. The lower reinforcement effect of silica/MMT hybrid filler in rubber compounds compared to conventional silica was previously observed [26-27] and interpreted as a result of hydrogen bonding between the silica and the polar surface of MMT that lowers the compatibility between MMT and the non-polar rubber [17]. At higher content of modifying agent, a plasticizing effect becomes dominant and so the rubber vulcanizates show less resistance to deformation at moderate 300% elongation.

Figure 7.8 Modulus at 100% and 300% strains (a) and elongation at break (b) of silica-filled NR, silica/OC-filled NR and silica/MMT-filled NR compounds with varying loadings of modifying agent 2HT.

Figure 7.9 Tensile strength (a) and tear strength (b) of silica-filled NR, silica/OC-filled NR and silica/MMT-filled NR compounds with varying loadings of modifying agent 2HT.

The highest 300% modulus of silica-filled NR compounds results in the lowest elongation at break of the materials as seen in Figure 7.8(b). However, the compounds with different filler combinations show various trends of elongation at break when the modifying agent loading is increased. The silica/OC-filled NR compound shows an optimum value of elongation at break at 2.4 phr of 2HT or at 5 phr of OC, as observed also for the 300% modulus. In general, the elongation at break of a vulcanizate is inversely proportional to the crosslink density, that is, the vulcanizate with higher crosslink density has a shorter elongation at break [44]. For the filled systems, in addition to crosslink density, more complications arise from filler-rubber interactions, filler networking and interfacial adhesion between filler and the rubber phase. The properties therefore can vary depending on the dominant factor in that compound.

Figure 7.10 Apparent crosslink density (a) and DIN abrasion resistance index (b) of silica-filled NR, silica/OC-filled NR and silica/MMT-filled NR compounds with varying loadings of modifying agent 2HT.

Tensile strength of silica-filled NR, silica/OC-filled NR and silica/MMT-filled NR compounds increases slightly or remains at a similar level when the amount of modifying agent added is low. But this property starts to drop clearly after the modifying agent loading exceeds 4.7 phr as a result of a plasticizing effect and lower total bound rubber content, in correspondence with a reduction of the apparent crosslink density as shown in Figure 7.10(a). Tear strength shows a different response, to increase with the modifying agent loading in the compounds of silica-filled NR. It shows enhanced tear strength with increasing modifying agent loading up to 4.7 phr and thereafter decreases, whilst the silica/OC- and silica/MMT-filled vulcanizates show a continuous drop in tear strength. The loadings of modifying agent also have an influence on DIN abrasion resistance index as shown in Figure 7.10(b). Silica-filled NR has the highest abrasion resistance and the incorporation of 2HT improves this property when compared with the one without. The silica/OC-filled NR shows an optimal DIN abrasion resistance index at 2.4 phr of modifying agent or at 5 phr for OC. But for silica/MMT-filled compounds, the DIN abrasion resistance index drops gradually with increasing amount of modifying agent.

7.3.5 SEM images of DIN abraded surfaces

The SEM images of the DIN abraded samples of silica-filled NR, silica/OC-filled NR and silica/MMT-filled NR compounds containing different loadings of modifying agent are analyzed in comparison with that of pure silica-filled NR without modifying agent, as shown in Figure 7.11. The abrasion patterns of the DIN abraded surfaces agree well with the DIN abrasion resistance indices. The silica-filled compounds that have a higher DIN abrasion resistance index show smoother abraded surfaces when compared to the silica/OC- and silica/MMT-filled compounds. The silica-filled NR with 9.5 phr of modifying agent in which the abrasion resistance starts to decrease shows more tear lines and larger asperities. For the silica/OC-filled NR compound that shows optimum abrasion resistance at the modifying agent of 2.4 phr, the abraded surface is clearly smoother than those with 4.7 and 9.5 phr of modifying agent. The lowest abrasion resistance of silica/MMT-filled NR compounds results in abraded surfaces with larger asperities and rougher surfaces. The asperities of the weaker material with higher loading of modifying agent can be torn off easier and become more visible on the abrasion patterns. The results are corresponding with their mechanical properties as tensile strength, 300% modulus, tear strength and apparent crosslink density.

Overall, the silica only-filled NR compound shows better mechanical properties than the silica/clay dual filler systems. The use of silica/TESPD as silane coupling agent with a small amount (2.4-4.7 phr) of 2HT further improves the mechanical properties, i.e. 300% modulus, tear strength and abrasion resistance, as this modifying agent could provide an additional shielding effect on the silica surface. For silica/clay-filled compounds, the silica/OC gives better mechanical properties than the silica/MMT. The pre-modified OC gives a higher apparent crosslink density that is derived from better filler-rubber interaction compared to the use of pristine MMT with modifying agent added *in situ* during mixing. The optimum properties of silica/OC-filled NR are observed at 5 phr of OC that contains 2.4 of modifying agent.

Figure 7.11 SEM photographs of DIN abraded surfaces of silica-filled NR, silica/OC-filled NR and silica/MMT-filled NR compounds with varying loadings of modifying agent 2HT.

7.3.6 X-Ray Diffraction (XRD)

Figure 7.12(a) shows the X-ray diffraction (XRD) patterns of Na-MMT and 2HT modified Na-MMT (OC). By applying Bragg's law, the interlayer spacing, called d-spacing, of the clay platelets can be determined. The maximum peaks of OC are shifted towards smaller 2θ angles than for the unmodified Na-MMT, indicating a larger d-spacing. The XRD pattern of Na-MMT shows a single peak of 2θ at 5.7° which corresponds to a d-spacing of $15.4 \text{ \AA}$. The OC shows three peaks of 2θ , of which the two larger ones are at 2.3° and 4.5° that correspond

to d-spacings at 38.2 Å and 19.7 Å, respectively. The larger d-spacing corresponding to the highest peak for OC is caused by the insertion of modifying agent molecules into the galleries of the pristine clay platelets.

The XRD patterns of silica/OC-filled NR and silica/MMT-filled NR compounds with different amounts of modifying agent are shown in Figures 7.12(b)-(c). Figure 7.12(b) shows the rubber specimens that contain modifying agent at 2.4, 4.7 and 9.5 phr or 5, 10 and 20 phr of the OC. An increased d-spacing is observed for 2.4 and 4.7 phr of modifying agent in the OC and the XRD patterns indicate that the OC is well intercalated in the NR matrix because the peak at 2θ around 2 is only vaguely visible. However, at 9.5 phr of modifying agent or 20 phr of OC, the characteristic peaks of OC are clearly visible again with a d-spacing of 39.5 Å which is almost the same value as that of the pure OC (Figure 7.12(a)), indicating improper dispersion of the OC at such high concentration. It has been reported previously for organomodified clay (Cloisite 20A)-filled NR that an exfoliated structure was obtained at an OC concentration of 5 phr [53]. It remains a point of discussion whether the vague visibility of the OC-peaks at low loadings is a sign of exfoliation, or just a too low concentration to be able to be properly visible. The silica/MMT-filled NR compounds with varied loadings of modifying agent show different XRD patterns compared to that of silica/OC. The results in Figure 7.12(c) show that the materials having MMT of 5 and 10 phr, or with 2.4 and 4.7 phr of modifying agent, respectively, show no clear characteristic peaks of clay, which is often claimed to be an indication of exfoliation, but in the present case must be due to a too low concentration of the clay to be clearly visible [30]. However, at higher loading of MMT and modifying agent, i.e. at 20 phr of MMT and 9.5 phr of modifying agent, the silica/MMT-filled NR displays a clear peak again at the interlayer distance at 45.3 Å, indicating improper dispersion again of MMT in the NR matrix at high concentration as observed also in the case of silica/OC.

Figure 7.12 X-ray diffraction patterns and interlayer spacing of unmodified MMT and organically modified clay (a), silica/OC-filled NR (b), and silica/MMT-filled NR (c) compounds with varying loadings of modifying agent 2HT.

7.3.7 Dynamic mechanical properties

Figure 7.13 compares the values of tan delta at -20°C and 0°C of the silica-filled NR, silica/OC-filled NR and silica/MMT-filled NR vulcanizates with varying loadings of modifying agent, taken from dynamic mechanical analysis in the temperature range from -80 to 80°C, at a frequency of 10 Hz and 0.1% strain. Figures 7.13(a)-(b) are indicative of ice and wet traction of

tire tread rubber vulcanizates respectively, as evaluated on laboratory testing scale [56]. The tan delta at -20°C shows some improvement with the addition of modifying agent but has no clear trend. The silica-filled NR and silica/MMT-filled NR compounds show optimum tan delta values at -20°C at modifying agent content of 4.7 phr. However, there is no improvement of tan delta at 0°C . The silica/OC-filled NR shows an optimum tan delta at -20°C at 2.4 phr of modifying agent, or at 5 phr of OC loading, and then clearly drops at higher loadings of OC due to the re-agglomeration of clay platelets as shown by the XRD results in Figure 7.12(b), while the tan delta at 0°C shows comparable results as that of the pure silica-filled NR compound.

Figure 7.13 Tan delta at -20°C (a) and tan delta at 0°C (b) of silica-filled NR, silica/OC-filled NR and silica/MMT-filled NR compounds with varying loadings of modifying agent 2HT.

Figure 7.14 Tan delta at 60°C from DMA (a) and tan delta at 60°C from RPA (b) of silica-filled NR, silica/OC-filled NR and silica/MMT-filled NR compounds with varying loadings of modifying agent 2HT.

The tan delta at 60°C is indicative of tire rolling resistance on a laboratory scale [56] in which a lower tan delta value at a temperature of 60°C indicates a reduced tire rolling resistance. These results obtained from both RPA and DMA analysis are shown in Figure 7.14. The tan delta at 60°C of silica-filled NR is generally reduced with increasing modifying agent, while the silica/MMT-filled NR compound shows an optimum point at 4.7 phr of modifying agent content and the silica/OC-filled NR compound shows an optimum point at 2.4 phr of modifying agent or at 5.0 phr of OC loadings. With optimum loadings of modifying agent, lower tan delta at 60°C can be obtained indicating the feasibility to reduce tire rolling resistance.

7.4 Conclusions

Overall, the addition of modifying agent to silica-reinforced rubber, either in the form of pre-modified MMT, or in combination with MMT or even added in pristine form to silica compounds, provides many benefits. Dependent on the properties of choice, different amounts of modifying agent need to be employed. The incorporation of modifying agent in a range of 0 to 9.5 phr in silica-filled NR, silica/OC-filled NR and silica/MMT-filled NR compounds results in a decreases of compound viscosity, Payne effects and scorch times. The optimum amount of modifying agent for silica-filled and silica/MMT-filled NR compounds are observed

at 4.7 phr as seen in the best balance of properties, i.e. lower Payne effects, higher tensile properties (tensile strength, 300% modulus, reinforcement index, tear strength), higher DIN abrasion resistance index, higher apparent crosslink density, higher tan delta at -20°C and lower tan delta at 60°C. For silica/OC-filled, an optimum loading of modifying agent is observed at 2.4 phr or at 5.0 phr of OC where lower Payne effect, higher cure rate index, higher tensile properties (tensile strength, 300% modulus, reinforcement index, tear strength), higher DIN abrasion resistance index, higher apparent crosslink density, higher tan delta at -20°C and lower tan delta at 60°C are obtained. The shorter scorch time, lower compound viscosities respectively particularly indicate better productivity by reduced cycle times for vulcanization and better processability. The lower tan delta at 60°C is an indication of improved rolling resistance which can be achieved with tire treads based on such compounds. Also the higher tan delta at -20°C and DIN abrasion resistance index are indications for enhanced ice traction and wear resistance, which are favored for tire applications. So, irrespective in which form the modifying agent is added: included in OC or added separately, it has great potential to further improve NR/silica reinforced tire technology.

These combined results are summarized in the radar charts hereunder. Figure 7.15 shows the radar charts covering cure properties and Payne effects of the compounds (Figure 7.15(a)), as well as mechanical properties of the vulcanizates (Figure 7.15(b)). These two charts are based on relative values versus the reference. The chart concerning tire performance as shown in Figure 7.16 is based on index-values: the higher the better.

Figure 7.15 Radar charts comparing cure properties, Payne effect (a) and mechanical properties (b) of the NR compound filled with 55 phr silica without organoclay as secondary filler: reference (S), the 55 phr silica-filled NR compound with clay-modifier at an optimum amount of 4.7 phr (S55 (2HT 4.7)), the NR compound filled with 50 phr silica and 5 phr organoclay as secondary filler (S-OC/50-5), and the NR compound filled with 50 phr silica and 5 phr unmodified nanoclay plus clay-modifier at 4.7 phr (S-MMT/45-10 (2HT 4.7)).

Figure 7.16 Radar chart comparing key tire performances indicated by lab-indicators of the NR compound filled with 55 phr silica without organoclay as secondary filler: reference (S), the 55 phr silica-filled NR compound with clay-modifier at an optimum amount of 4.7 phr (S55 (2HT 4.7)), the NR compound filled with 50 phr silica and 5 phr organoclay as secondary filler (S-OC/50-5), and the NR compound filled with 45 phr silica and 10 phr unmodified nanoclay plus clay-modifier at 4.7 phr (S-MMT/45-10 (2HT 4.7)).

7.5 References

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CHAPTER 8

Influence of Secondary Polymers in Shifting Tire Tread-Related Properties of Silica-Reinforced Natural Rubber Compounds

To improve the properties of silica truck tire tread compounds especially abrasion resistance, the effect of loadings of Butadiene Rubber (BR) or Solution-Styrene Butadiene Rubber (SSBR) as secondary polymers in silica-filled natural rubber (NR) compounds is investigated compared to pure silica-reinforced NR compounds. By increasing the loading levels of BR or SSBR from 0, 10, 20, to 30 phr in combination with NR at 100, 90, 80, and 70 phr, respectively, the loadings of BR and SSBR lead to longer scorch times and optimum cure times, and decreased mechanical properties. With increasing high-cis-BR contents, a better tan delta at 60°C as indicative for reduced rolling resistance of tire treads made thereof, apparent crosslink density and the DIN abrasion resistance index are obtained related to a decreased glass transition temperature of the resulting compounds. With increasing high vinyl-SSBR contents, the results show reduced filler-filler interaction by the Payne effect, and also improved DIN abrasion resistance index, and tan delta at -20 and 0°C indicative of wet and ice traction of tire treads made thereof. The results also shows an optimum loading of NR in combination with BR and SSBR at ratio 80/20 phr as indicated by bound rubber contents and 300% modulus. With optimal compound composition 56% improvement in DIN abrasion resistance can be achieved.

8.1 Introduction

Lower rolling resistance, higher wet traction, and higher abrasion resistance are key tire performance criteria. Replacement of Carbon Black (CB) with silica as reinforcing fillers in tire tread compounds, after the introduction of Michelin [1], offers tires with higher wet traction and lower rolling resistance resulting in enhanced safety and energy savings [2]. Additionally, tensile strength, heat build-up, cut-, chip-, chunking-resistance and tear strength are improved [3]. Natural rubber (NR) is most commonly used for truck tire tread compounds as a result of its excellent mechanical properties and low heat build-up. NR provides high tensile and tear strength due to the strain-induced crystallization of the high molecular chains, resulting in superior chipping/chunking resistance. However, NR is limited in oxygen-, ozone- and light-resistance due to its unsaturation in the main chain, but it can be improved by addition of antioxidants and antiozonants. Styrene Butadiene Rubber (SBR) is the largest volume synthetic rubber that offers better wear resistance and wet traction, often used for passenger car tire tread compounds. There are basically two classes of SBR: Emulsion-SBR (ESBR) and Solution-SBR (SSBR), where the first is conventionally used in CB-filled and the second in silica-filled tire compounds. Butadiene Rubber (BR) is the second largest volume synthetic rubber obtained from the polymerization of 1,3-butadiene, which can be polymerized in three different configurations: cis-1,4, trans-1,4 and vinyl-1,2. High-cis 1,4-content BR improves the wear resistance of tire tread compounds, and also gives excellent resilience resulting in decreased heat build-up. The properties of BR are normally controlled by the cis-1,4 and vinyl-1,2 contents. When the cis-1,4 content decreases and vinyl-1,2 content increases, the abrasion resistance, resilience and low temperature properties become inferior. BR is used for tire applications in blends with other rubbers, especially NR and SBR.

A recent study on silica-reinforced NR tire compounds shows that, under optimal conditions and formulations, silica can effectively reinforce NR [4-5]. However, the question remains regarding the performance of such tires in terms of abrasion or wear resistance. High abrasion resistance is one of the key tire performance criteria in terms of economics and the environment, related to the service life of rubber products, not only tire treads but also e.g. belts, hoses, and shoe soles. The abrasion mechanism of rubber vulcanizates is very complex involving several factors, where the fillers and polymers strongly influence this property. When compared to CB, the interaction between silica and hydrocarbon rubber is weak, but with effective use of a silane coupling agent, the abrasion resistance of silica-filled compounds can be considerably promoted which enables them to be used in tire tread compounds [6].

Many studies had tried to improve the abrasion resistance by combining the advantages of different fillers with silica or hybrid fillers such as silica/CB [7-9] and silica/nanoclay [10-13]. For example, the simplest combination is silica/CB as both types of fillers are already commonly used in tire compounds.

Rubber blends or hybrid polymers are produced by mixing at least two polymers together to create a new material with different physical properties. It is a useful method for developing new materials with superior properties having not only the main properties of each blends component but also modified or specific ones. In the tire industry, rubber blends are commonly used due to three main reasons: cost reduction, enhanced processing, and to modify the final product performance. One example is a NR/SBR blend in tire tread compounds in which SBR provides good wet grip and NR gives good strength [14].

It has been recognized that the silica-silane technology works well with special easy-dispersion silica (or so-called highly dispersible silica) in combination with synthetic SSBR and BR in tire compounds [15]. ESBR and NR contain non-rubber components; the former one from surfactants and the latter from non-rubber constituents in the original latex, mainly proteins, fatty acids and phospholipids. Silica-reinforced tire compounds based on these elastomers exhibit inferior abrasion resistance due to their poorer filler-rubber interaction when compared to the SSBR case [6]. In addition, the vinyl-microstructure and more linear molecular structure of SSBR play a role in the success of silica/silane reinforcement [16]. Blends of SBR and NR are immiscible, as shown by the presence of two relaxation peaks corresponding to the respective glass transition temperatures (T_g 's) of SBR and NR [17]. When the NR concentration is increased, tensile strength and elongation at break improve, while the storage modulus of the system decreases. The styrene- and vinyl-content in SBR are known to affect its T_g and viscoelastic behavior. The influences of the vinyl-structure in the butadiene part and the styrene groups in SBR were studied using two types of SBR (Krynol 1721 and Buna VSL 5025-1) in comparison with general purpose SBR with 23.5 wt% styrene (Krynol 1712) in blends with NR (SMR 5) [18]. The 50:50 blends of NR with Krynol 1721 (styrene 40%) and Buna VSL 5025-1 (vinyl 50%) showed markedly lower rebound resilience while other mechanical properties are considered acceptable. With increasing the ratio of the SBR, the rebound resilience was reduced where the effect of Buna VSL 5025-1 was more pronounced than of Krynol 1721, in line with their T_g 's. The relation of the rheological properties of rubber compounds based on NR/SBR with their thermal behaviors has been investigated [19]. Degradation of SBR took place at a higher temperature than NR, and as the SBR content in the

blend increased, degradation temperature was shifted to a higher temperature, indicating higher thermal stability of the samples.

Ternary blends of NR/BR/SBR (25:25:50) reinforced with varying contents of CB N330 were investigated for their mechanical properties and thermal aging behavior [20]. With increasing CB content tensile strength and elongation at break decreased and hardness values increased with aging time. The change in mechanical properties depended on the aging temperature, time and the CB content. Larger changes in mechanical properties were observed at longer aging time and higher CB contents. The phase morphology of cryogenically cracked surfaces of the NR/BR/SBR/CB (25/25/50/80) showed a uniform fracture morphology that indicated good interactions between the polymer matrix and CB. A series of NR blends containing various amounts of ultra-high cis-polybutadiene rubber (UBR) (98% cis units) had been investigated in an attempt to develop a high performance tire [21]. The strain-induced crystallization in the blends was only associated with the NR, where the crystallization was retarded by the UBR chains. The presence of UBR chains speeds up overall chain orientation of the blend upon stretching, but they do not play a role as nucleation sites for the NR chains to crystallize. The results showed that the crystallite size became larger with UBR content, which was attributed to a smaller number of nuclei formation by the presence of UBR chains. Stress-strain behavior revealed a higher overall stress level for the rubbers with higher UBR content, where network chain density derived from stress-strain curves also increased as UBR content increased.

The present chapter 8 is to study the effect of loadings and types of secondary polymers: BR and SSBR having different levels of microstructure such as cis-content, vinyl-content, glass transition temperature (T_g) well as styrene content in SSBR, in combination with NR on the properties of silica-reinforced truck tire tread compounds. The cure characteristics, filler-filler interactions, filler-rubber interactions, tensile and tear properties, DIN abrasion resistance, dynamic mechanical properties and morphology are investigated. With optimal compound composition 56% improvement in DIN abrasion resistance can be achieved.

8.2 Experimental

8.2.1 Materials

The NR (Ribbed Smoked Sheet, RSS3) was locally produced in Thailand. The high-cis content BR (CB22) was obtained from Arlanxeo, Germany and the high-vinyl SSBR (SL563) from JSR Corporation, Japan. The raw material properties of each elastomer are shown in Table 8.1.

Silica ULTRASIL 7005 and silane coupling agent bis-(3-TriEthoxySilylPropyl)Disulfide (TESPD) were supported by Evonik, Germany. The other ingredients; Treated Distillate Aromatic Extract oil (TDAE oil), DiPhenyl Guanidine (DPG), N-Cyclohexyl-2-Benzothiazyl Sulfenamide (CBS), 2,2,4-TriMethyl-1,2-dihydroQuinoline (TMQ), Zinc Oxide (ZnO), stearic acid and sulfur are of commercial grade for rubber industry.

Table 8.1 Raw material properties of elastomers used in this study.

Types of rubber	Content (%)		Tg (°C)	ML(1+4), 125°C*
	Vinyl	Styrene		
NR unmasticated	-	-	-70	98
NR masticated	-	-	-70	55
BR (CB22)	<1	-	-104	60
SSBR (SL563)	55	20	-35	59

*The ML(1+4), 125°C was tested in this study.

8.2.2 Compound preparation

The truck tire compound formulations employed are given in Table 8.2. One requirement for proper mutual dispersion of a rubber blend or hybrid polymer is equality of the viscosity of raw elastomers. Raw NR (RSS3) has a higher viscosity than BR and SSBR. Therefore, at first NR was masticated by two-roll milling in order to achieve the same level of Mooney viscosities as shown in Table 8.1. The truck tire tread compounds were prepared using a two-step mixing procedure: the first was to prepare a masterbatch of rubber and fillers, and the second was to prepare the final compounds including the curatives. For the first step, an internal mixer, Brabender® 50EHT, (Brabender® GmbH & Co.KG, Germany) with a mixing chamber volume of 70 ml was used. The mixing conditions were set at a rotor speed of 60 rpm, fill factor of 70% and initial mixer temperature setting of 120°C in order to reach a dump temperature in the range of 135-150°C, as required as already reported [4,13]. BR or SSBR as secondary polymers were added together with masticated NR. Then the first half of silica was added, TESPd silane coupling agent and DPG secondary accelerator. The other halves of silica and TESPd were added later on in the first mixing step, together with TDAE extender oil. The second step was for the addition and mixing of the other half of DPG, CBS primary accelerator, and sulfur at a rotor speed of 30 rpm, fill factor of 70%, and an initial mixer temperature setting of 70°C. The two-step mixing procedure is summarized in Scheme 8.1.

The BR or SSBR contents were varied at 0, 10, 20 and 30 phr, with corresponding reductions in the amount of NR.

Table 8.2 Formulations for study of the effect of loadings of BR or SSBR as secondary polymers.

Ingredients	Amount (phr)			
	Reference	90/10	80/20	70/30
Natural rubber (RSS3)	100.0	90.0	80.0	70.0
BR or SSBR ^a	-	10.0	20.0	30.0
ULTRASIL 7005	55.0	55.0	55.0	55.0
TESPD ^b	5.0	5.0	5.0	5.0
TDAE oil	8.0	8.0	8.0	8.0
ZnO	3.0	3.0	3.0	3.0
Stearic acid	1.0	1.0	1.0	1.0
TMQ	1.0	1.0	1.0	1.0
DPG ^b	1.1	1.1	1.1	1.1
CBS	1.5	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5	1.5

^aBR and SSBR were CB22 and SL563, respectively.

^bTESPD and DPG were calculated according to the following equations [15].

$$\text{TESPD (phr)} = 0.00053 \times Q \times A \quad (1)$$

$$\text{DPG (phr)} = 0.00012 \times Q \times A \quad (2)$$

where Q is the amount of silica (phr) and A is the Cetyl-Trimethyl-Ammonium-Bromide (CTAB) surface area of the silica (171 m²/g).

8.2.3 Sample characterizations

8.2.3.1 Testing of compound and vulcanizate properties

Payne effect, cure characteristics, apparent crosslink density, tensile properties, tear properties, dynamic mechanical properties, DIN abrasion resistance index and its abraded surface of the silica-filled NR and silica-filled NR/BR or SSBR compounds were investigated following the methods and using the equipments as described in Chapter 7.

8.2.3.2 Characterization of Bound Rubber Content (BRC)

Bound rubber content (BRC) – An amount of 0.25 g of uncured compound (without curatives) was put into a metal cage and immersed in 40 ml of toluene for 7 days at room temperature in a normal or an ammonia atmosphere. The ammonia atmosphere was used in order to cleave the physical linkages between silica and rubber but leave the chemical links intact. Then the sample was removed from the toluene, dried at 105°C in an oven for 24 h and weighed. The bound rubber content was calculated using the following equation.

$$BRC(\%) = \frac{(m - m_s)}{m_r} \times 100 \quad (3)$$

where m is the weight of sample after extraction, m_s and m_r are the weights of filler and elastomer in the original sample, respectively.

Scheme 8.1 Two-step mixing procedures for compound preparations; NR/silica (a) and NR/BR/silica or NR/SSBR/silica (b) compounds.

8.3 Results and discussion

8.3.1 Masterbatch mixing behavior

The masterbatch mixing profiles of silica-filled NR with different loadings of BR and SSBR as secondary polymers are presented in Figure 8.1. The mixing dump torque of a rubber compound is generally related to the viscosity of that mixture. Unfortunately, this could not be

independently confirmed by measuring compound Mooney viscosities, by lack of sufficient material coming from the small 70 ml mixer. In Figure 8.2 the dump torque at the end of the mixing cycle, as well as the dump temperatures are given. The increasing dump torque with the amount of secondary polymer added, more so for BR than for SSBR, is due to a higher viscosity. One possibility is that this corresponds with a lower temperature at dump, but this is opposite to what was observed in Figure 8.2: the dump temperature is increasing. So this increase must be due to a really increased viscosity due to a different interaction between the NR and the BR, respectively SSBR. This can be due to an effect of the different microstructure of the BR and the SSBR. The silica-filled NR/BR provides higher dump torques than silica-filled NR/SSBR, because on the one hand the high cis-content of the BR interacts or mixes better with NR, providing higher viscosities of the resulting compounds. Or otherwise, the high 55% vinyl-content of SSBR is more reactive towards the silane coupling agent and therefore acts as a sort of plasticizer, lowering the viscosity. This corresponds to the previous work for CB-filled SBR/BR blends [23], CB-filled NR/BR [24] and silica-filled SBR/BR [23].

Figure 8.1 Mixing profiles of silica-filled NR/BR (a) and silica-filled NR/SSBR (b) compounds with varying types and loadings of secondary polymers.

Figure 8.2 Dump torque and dump temperature of silica-filled NR compounds with varying types and loadings of secondary polymers.

8.3.2 Filler-filler interaction

Non-linear viscoelastic behaviors of the silica-filled NR/BR and NR/SSBR compounds can be observed in the storage modulus which decrease with increasing strain percentage, as displayed in Figure 8.3. The difference between the modulus at low strain (0.56%) and high strain (100%) can be used to indicate the level of filler-filler interaction, called Payne effect [25]. The Payne effects are quite different between the NR/BR and NR/SSBR compounds. In the former case all curves are close and differ little from the one for pure NR-silica. For the latter, NR/SSBR the storage modulus at low strain decreases substantially, although at high strain there is again little difference between the various curves or even in comparison with the NR/BR-curves.

Summarizing the Payne effects in term of Δ storage modulus between 0.56% and 100% strain, as presented in Figure 8.4, it is clear that with respect to filler-filler interaction the replacement of a little NR by BR has little effect, rather a slight increase. On the contrary, there is a strong effect of the SSBR, again most probably because of the enhanced interaction of the vinyl-groups of this polymer with silane coupling agent, resulting in some sort of plasticization effect and consequent decrease in the low shear modulus and decrease in Payne effect.

Figure 8.3 Storage modulus as a function of strain of silica-filled NR/BR (a) and silica-filled NR/SSBR (b) compounds with varying types and loadings of secondary polymers.

Figure 8.4 Payne effect of silica-filled NR compounds with varying types and loadings of secondary polymers.

8.3.3 Bound rubber content

BRC is the measurement for filler-rubber interactions [26]. The total BRC and chemically BRC of silica-filled NR compounds with varied loadings of BR and SSBR are

shown in Figure 8.5. The total BRC and chemically BRC of NR/BR and NR/SSBR blends are almost at the same level, but the blend ratio 80/20 phr shows a slightly higher total BRC than at other ratios for both NR/BR and NR/SSBR. The chemically BRC of NR/SSBR blend also shows the same trend as the total BRC, where the blend ratio of 80/20 phr shows a slightly higher value than the other blend ratios. Overall, these results differ little from the pure silica-filled NR system and little conclusion can be drawn from this.

Figure 8.5 Total bound rubber content and chemically bound rubber content of silica-filled NR compounds with varying types and loadings of secondary polymers.

8.3.4 Cure properties

The summarized cure or vulcanized properties of the various compounds are given in Figures 8.6-8.7. The minimum cure torques (M_L) of the various compounds are presented in Figure 8.6(a). The M_L can commonly be related to the viscosities of rubber compounds: lower viscosity of a rubber compound means improvement in processability and ease to flow. The M_L of the silica-filled NR/BR tends to increase with increasing BR content, again due to the high cis content, while SSBR loadings tends to decrease the M_L . This is again most probably the effect of the high vinyl content of the SSBR and the consequent interaction with the silane coupling agent. This is in agreement with the Payne effect results as displayed in Figure 8.4.

The maximum cure torques (M_H) and cure torque differences ($M_H - M_L$) of the silica-filled NR compounds with different loadings of BR and SSBR are shown in Figure 8.6(b). Since the rheometer torque increases by formation of crosslinks, delta torque is related to the crosslink density.

The M_H and $M_H - M_L$ of silica-filled NR/BR and silica-filled NR/SSBR compounds decrease with the increasing BR and SSBR contents. The M_H levels and $M_H - M_L$ indicate the vulcanizate stiffness that is influenced by several factors, combining contributions from chemical crosslinks by the vulcanization reaction, by filler-rubber interactions and by filler-filler interactions [27]. The effect of loadings of BR and SSBR on the apparent crosslink density is displayed in Figure 8.7(b). The apparent crosslink density of NR/BR blends is higher than for the NR/SSBR blends due to the same higher cis-contents and higher amount of allylic hydrogen of BR [28].

The scorch times (t_{s2}) and optimum cure times (t_{c90}) are displayed in Figure 8.7(a). With increasing BR and SSBR contents, the t_{s2} and t_{c90} of the rubber blends tend to increase due to less unsaturation in BR and SSBR compared to NR. The vulcanization rate is dependent on the allylic hydrogen-contents, where NR has the highest content compare to BR and SSBR [28]. While NR/SSBR blends show higher t_{s2} and t_{c90} this is again due to the lower unsaturation than NR/BR blends. The shorter t_{s2} and t_{c90} with higher cis contents has already been reported before [23,28].

Figure 8.6 Minimum cure torque (a), maximum cure torque and cure torque difference (b) of silica-filled NR compounds with varying types and loadings of secondary polymers.

Figure 8.7 Scorch time, optimum cure time (a) and apparent crosslink density (b) of silica-filled NR compounds with varying types and loadings of secondary polymers.

8.3.5 Mechanical properties

Figure 8.8 Tensile strength, elongation at break (a), 300% modulus and reinforcement index (b) of silica-filled NR compounds with varying types and loadings of secondary polymers.

The effect of types and loadings of BR and SSBR as secondary polymers on the tensile properties of silica-filled NR, silica-filled NR/BR and silica-filled NR/SSBR compounds are

shown in Figure 8.8. The tensile strength of pure silica-filled NR are higher than for all silica-filled NR/BR and silica-filled NR/SSBR blends where the elongation at break of the silica-filled NR reference compounds are lower than for all silica-filled NR/BR and at low loading of SSBR contents. The fact that the tensile strength and elongation at break decrease with increasing BR and SSBR contents is the result of the materials's properties themselves: NR has much higher strength than BR and SSBR due to its typical strain-induced crystallization [24,29]. Comparison of the two hybrid polymer systems shows that the silica-filled NR/BR has a slightly higher tensile strength and elongation at break than the silica-filled NR/SSBR compounds. This may be due to the high cis contents of BR which provides more allylic hydrogen and consequently higher crosslink densities than the high vinyl SSBR. High cis BR may also show some strain-induced crystallization which enhances the stress-strain properties as well [30].

Figure 8.8(b) shows the effect of types and loadings of BR and SSBR on the 300% modulus and reinforcement index of the compounds under investigation. The 300% modulus of NR/BR blends tends to decrease with increasing amount of BR while the loading of SSBR in combination with NR at 20 phr shows a slight optimum relative to the other loadings. The reinforcement indexes of silica-filled NR/BR and NR/SSBR compounds decrease with increasing loadings of BR and SSBR.

The effects of types and loadings of BR and SSBR on mechanical properties are also confirmed by the tear strengths in Figure 8.9. The tear strength of both silica-filled NR/BR and silica-filled NR/SSBR compounds decrease with increasing BR and SSBR loadings. However, the results cannot properly be correlated with the tensile properties as shown in Figure 8.8. Moreover, 30 phr of SSBR in the NR/SSBR combination shows the lowest tear strength value. In anticipation of the next paragraph this strong influence of the SSBR on the tear strength may be related to the much higher effect on Tg of the NR/SSBR blends and de-mixing phenomena (see later) than for NR/BR blends, as related to the starting Tg's of the pure rubbers in Table 8.1.

Figure 8.9 Tear strength of silica-filled NR compounds with varying types and loadings of secondary polymers.

8.3.6 DIN abrasion resistance

The effect of loadings of BR and SSBR as secondary polymers on DIN abrasion resistance index is shown in Figure 8.10. The DIN abrasion resistance index of silica-filled NR/BR and NR/SSBR increases with increasing BR and SSBR loadings due to the properties of BR and SSBR themselves that enhance abrasion resistance [29]. A higher DIN abrasion resistance index was observed for the NR/BR blends due to the fact that this BR has high cis-content. The DIN abrasion resistance index results are in agreement with the apparent crosslink density as displayed in Figure 8.7(b).

As the abrasion resistance was the main purpose for this study, the results indicate a very significant increase for NR/BR rather than for NR/SSBR. Actually, an increase of 56% was achieved with 30 phr of BR replacing NR. However, the real cause of this enormous improvement for the NR/BR combination is still a question. Is it because of the high cis content of BR, a lack of interaction with the silica because the NR and BR lack vinyl groups, an effect of the T_g , an effect of homogeneity of the compounds after mixing, an effect of crosslink density, an effect of strain induced of crystallization? A look at the DIN abraded surfaces with SEM may elucidate some of these questions and otherwise reference is made to the next chapter of this thesis.

Figure 8.10 DIN abrasion resistance index of silica-filled NR compounds with varying types and loadings of secondary polymers.

8.3.7 SEM images of DIN abraded surfaces

There is a difficulty to predict the practical wear resistance of rubber products [31], as the abrasion resistance results from laboratory tests often do not agree with the results of actual tire products. Tearing or fatigue under the action of high local stresses caused by friction have been blamed as the main causes of abrasion [31]. When rubber is abraded without change of direction, an “Abrasion pattern” or sets of parallel ridges appear on the surface of the samples at right angles to the direction of motion, often called Schallamach waves [32-33] and this abrasion pattern is assumed to influence the relative rates of tire wear under different service conditions. These periodic parallel ridges or abrasion patterns are initiated by microvibrations at the natural frequency of the rubber and propagate by stick-slip oscillations, both of which are generated during frictional sliding of rubber [34]. The SEM images of the DIN abraded samples of silica-filled NR/BR and silica-filled NR/SSBR compounds with different loadings of BR and SSBR are analyzed in comparison with that of the pure silica-filled NR compound, as shown in Figure 8.11. The abrasion patterns on the DIN abraded surfaces agree well with the DIN abrasion resistance indexes. The smoothest abraded surfaces were observed for the silica-filled NR/BR compounds with the exception of 30 phr BR, while rougher surfaces were observed for NR/SSBR at 10 and 20 phr of SSBR.

Figure 8.11 SEM photograph of DIN abraded surfaces of silica-filled compounds with varying types and loadings of secondary polymers, (100X).

8.3.8 Dynamic mechanical properties

Figure 8.12 Tan delta at -20°C, tan delta at 0°C (a) and tan delta at 60°C (b) of silica-filled NR compounds with varying types and loadings of secondary polymers.

Figure 8.13 Tan delta as a function of temperature of silica-filled NR/BR (a) and silica-filled NR/SSBR (b) compounds with varying types and loadings of secondary polymers.

Figure 8.14 Loss modulus as a function of temperature of silica-filled NR/BR (a) and silica-filled NR/SSBR (b) compounds with varying types and loadings of secondary polymers.

Figure 8.15 Glass transition temperature at tan delta peak and loss modulus peak of silica-filled NR compounds with varying types and loadings of secondary polymers.

Figures 8.12 shows the comparison of dynamic mechanical properties of the silica-filled NR, silica-filled NR/BR and silica-filled NR/SSBR vulcanizates with varying loadings of BR and SSBR in the temperature range from -80°C to 80°C , at a frequency of 10 Hz and 0.1% strain.

The results show the values of tan delta at -20°C and 0°C, indicative of ice traction and wet traction of the rubber vulcanizates respectively as evaluated on laboratory testing scale [35]. The tan delta at -20°C and 0°C of silica-filled NR/BR compounds tend to decrease with increasing BR contents, while the results for silica-filled NR/SSBR compounds tend to increase with increasing SSBR contents, due to the higher vinyl and styrene contents in this SSBR. Therefore, the combination of NR with SSBR as secondary polymer for silica compounds offers the potential to improve ice traction and wet traction [35].

An ideal material that is able to reach the high-performance tire requirements should have a low tan delta value at a temperature of 60°C in order to reduce rolling resistance [35]. The tan delta at 60°C of silica-filled NR/SSBR compounds in Figure 8.12(b) tends to increase with increasing SSBR loadings, but the tan delta at 60°C of silica-filled NR/BR compounds decreases with increasing loadings of BR due to the high cis-content of BR. A lower tan delta at 60°C of high cis-content BR in combination with SSBR silica compounds [23] and CB-filled NR/BR [24] has been reported before. A higher tan delta at 60°C for a compound with SBR with high vinyl content has also been reported [30]. So, the NR/BR blend has the potential to improve rolling resistance, meaning better energy saving of the tire.

The Tg from the tan delta peak and loss modulus peak is shown in Figure 8.15. These are two ways to register Tg, which commonly result in a small shift in values. The Tg values can be used as an indication of abrasion resistance, the lower Tg the better abrasion resistance [36]. The Tg values of NR/BR blends tend to decrease with increasing BR contents because of the low Tg of the pure BR and good miscibility with NR as demonstrated by single peaks of tan delta versus temperature for all secondary polymer BR contents up till 30 phr, see Figure 8.13(a). The best DIN abrasion resistance of the NR/BR blends is in agreement with that. The tan delta data for NR/SSBR blends show clear signs of de-mixing at SSBR contents of 20 phr and higher, see Figure 8.13(b), and so are discarded. From the transition in the loss modulus a reasonable Tg estimation can still be made as displayed in Figure 8.14. Because the starting Tg of the pure SSBR was only -35°C and the poor miscibility with NR, only a small increase of the Tg of the blends was found. This corresponds with the DIN abrasion data where the SSBR had only a small effect.

8.4 Conclusions

The properties of silica-filled NR compounds with different amounts of high-cis BR or high vinyl SSBR as secondary polymers show effects on the cure properties as shown by higher

scorch and optimum cure times. Increasing loadings of high-cis BR in the silica-filled NR compounds show better apparent crosslink density, tan delta at 60°C and DIN abrasion resistance index with corresponds to reduction of Tg by full miscibility up till quantities of 30 phr BR. Increasing high-vinyl SSBR contents show improvement in Payne effect, tan delta at -20 and 0°C but only a little in DIN abrasion resistance index. The main reason is a sign of immiscibility of SSBR at quantities of 20 phr and more with NR. It has become clear that miscibility of the secondary polymer with NR is a major factor, which needs further study in the next chapter.

These conclusions are summarized in the radar charts hereunder. Figure 8.16 shows the radar charts covering cure properties and Payne effect of the compounds (Figure 8.16(a)), as well as mechanical properties of the vulcanizates (Figure 8.16(b)). These two charts are based on relative values versus the reference. The chart concerning tire performances as shown in Figure 8.17 is based on index-values: the higher the better.

Figure 8.16 Radar charts comparing cure properties, Payne effect (a), and mechanical properties (b) of the silica-filled NR compounds without and with an optimized proportion of BR or SSBR as secondary filler (NR-BR/80-20 and NR-SSBR/80-20, respectively).

Figure 8.17 Radar chart comparing the key tire performances indicated by lab-indicators of the silica-filled NR compounds without and with an optimized proportion of BR or SSBR as secondary filler (NR-BR/80-20 and NR-SSBR/80-20, respectively).

8.5 References

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CHAPTER 9

Improvement in Silica-Reinforced Natural Rubber Tire Tread Compounds by Joint Hybridization with Small Amounts of Secondary Fillers and Polymers

To improve the properties of silica truck tire tread compounds, especially abrasion resistance, the effect of vinyl-contents in Butadiene Rubber (BR) or Solution-Styrene Butadiene Rubber (SSBR) as secondary polymers in silica-filled Natural Rubber (NR) compounds at a ratio of 80/20 phr, is investigated in the first part. By increasing the vinyl-content in BR in combination with NR, a better Payne effect, 300% modulus, reinforcement index, tan delta at -20°C and 0°C are obtained, whereas tensile strength, elongation at break and DIN abrasion resistance index decrease with increasing vinyl-content. Increasing vinyl-contents in SSBR show improvements in Payne effect, 300% modulus, tan delta at -20°C and 0°C and a little in DIN abrasion resistance index. The combination of secondary filler and polymer in silica-filled NR are covered in the second part of the present study. Silica/Carbon Black (CB)-filled NR/BR and NR/SSBR, respectively, silica/OrganoClay (OC)-filled NR/BR and NR/SSBR show positive effects on the scorch time, optimum cure time, with slightly changed Payne effect, tensile properties, tan delta at -20°C and 0°C, and DIN abrasion resistance as compared to the compound with CB N134. The use of OC shows enhancement in Payne effect and tan delta at 60°C, indicative of a reduced filler-filler network, and consequently lower rolling resistance of the tire tread compound compared to the compound without OC.

9.1 Introduction

Natural rubber (NR) is cis-1,4-polyisoprene which is the largest elastomer used for truck tire tread compounds because of its excellent mechanical properties and low heat build-up. NR provides high tensile and tear strengths due to the strain-induced crystallization of the high molecular chains, resulting in superior chipping/chunking resistance. However, NR is limited in oxygen- and ozone- resistance due to its unsaturation in the main chain, but this can be improved by addition of antioxidants and antiozonants [1]. Styrene Butadiene Rubber (SBR) is a general purpose and largest volume synthetic rubber used in many applications, that offers better crack-initiation resistance, good flex resistance, abrasion resistance, wet grip, and weather resistance than NR [2,3]. There are basically two classes of SBR: Emulsion-SBR (ESBR) and Solution-SBR (SSBR), where the first is conventionally used in Carbon Black (CB)-filled and the second in silica-filled tire compounds. Butadiene Rubber (BR) is the second largest volume synthetic rubber obtained from the polymerization of 1,3-butadiene, which can result in three different configurations: cis, trans and vinyl. The cis-1,4 and vinyl-1,2 contents are important factors for the properties of BR. High-cis 1,4-content BR improves the abrasion resistance of tire tread compounds, and also gives excellent resilience resulting in decreased heat build-up. With high vinyl-1,2 content with decreased cis-1,4 content, the abrasion resistance, resilience and low temperature properties become inferior. Normally, BR is blended with other rubbers, especially NR and SBR, often used in tire applications [1].

The mixing of at least two rubbers to create a new material with superior properties, is named rubber blends or hybrid polymers. The compound properties come from the main properties of each rubber in the blends. In the tire industry, rubber blends are commonly used for three main reasons: enhanced processing, cost reduction, and to modify the final product performance. One example is a NR/SBR blend in tire tread compounds in which SBR provides good wet grip and NR gives good strength [4]. Blends of SBR and NR are immiscible, as shown by the presence of two relaxation peaks corresponding to the respective glass transition temperatures (T_g 's) of SBR and NR [3]. When the NR concentration is increased, tensile strength and elongation at break improve, while the storage modulus of the system decreases. The styrene- and vinyl-contents in SBR are known to affect its T_g and viscoelastic behavior. The influences of the vinyl-structure in the butadiene part and the styrene groups in SBR were studied using two types of SBR (Krynol 1721 (styrene 40 wt%) and Buna VSL 5025-1 (vinyl 50 wt%)) in comparison with general purpose SBR with 23.5 wt% styrene (Krynol 1712) in blending with NR (SMR 5) [5]. 50:50 blends of NR with Krynol 1721 and Buna VSL 5025-1

showed markedly lower rebound resilience while other mechanical properties were considered acceptable. With increasing the ratio of the SBR, the rebound resilience was reduced where the effect of Buna VSL 5025-1 was more pronounced than of Krynol 1721, in line with their T_g 's. The relation of the rheological properties of rubber compounds based on NR/SBR with their thermal behaviors has also been investigated [6]. Degradation of SBR took place at a higher temperature than NR, and as the SBR content in the blend increased it shifted to a higher temperature, indicating higher thermal stability of the samples.

A series of NR blends containing various amounts of Ultra-high cis-polyButadiene Rubber (UBR) (98% cis-units) were investigated in an attempt to develop a high performance tire [7]. The strain-induced crystallization in the blends was only associated with the NR, where the crystallization was retarded by the UBR chains. The presence of UBR chains speeds up overall chain orientation of the blend upon stretching, but they do not play a role as nucleation sites for the NR chains to crystallize. The results showed that the crystallite size became larger with UBR content, which was attributed to a smaller number of nuclei formation by the presence of UBR chains. Stress-strain behavior revealed a higher overall stress level for the rubbers with higher UBR content, where network chain density derived from stress-strain curves also increased as UBR content increased.

Reduction of rolling resistance, high wet grip, and high abrasion resistance are the key tire performances to develop in modern tire technology. The replacement of CB with silica as reinforcing fillers in tire tread compounds, after the introduction of the patent of Michelin [8], offers tires with higher wet traction and lower rolling resistance, resulting in enhanced safety and fuel savings [9]. Additionally, tensile strength, heat build-up, cut-, chip-, chunking-resistance and tear strength are improved [10]. However, mixing of silica into rubber faces several difficulties such as incompatibility with non-polar rubbers such as NR, BR and SBR which are commonly used in the tire industry [11], poor dispersion and distribution in the rubber matrix, and poor filler-rubber interaction. This is because silica has high polarity silanol groups, a hydrophilic surface and so tends to re-agglomeration or high filler-filler interaction. To overcome those problems, silane coupling agents need to be used in tire tread compounds, to result in higher filler-rubber interaction between the silica and rubber matrix, better silica dispersion and also to prevent accelerator adsorption on the silica surface, that means less of a negative effect on vulcanization properties.

It has been well recognized that the silica-silane technology works well with special easy-dispersion silica (or so-called highly dispersible silica) in combination with synthetic

SSBR and BR in tire compounds [12]. Silica-reinforced tire compounds based on ESBR and NR exhibit inferior abrasion resistance due to their poorer filler-rubber interaction when compared to the SSBR case [13]. In addition, the vinyl-microstructure and more linear molecular structure of SSBR play a role in the success of silica/silane reinforcement [13]. Recent studies on silica-reinforced NR tire compounds show that, under optimal conditions and formulations, silica can effectively reinforce NR [14-15]. However, the question remains regarding the performance of such tires in terms of abrasion or wear resistance. High abrasion resistance is one of the key tire performance criteria in terms of economics and the environment, related to the service life of rubber products, not only tire treads but also e.g. belts, hoses and shoe soles. The abrasion mechanism of rubber vulcanizates is very complex involving several factors, where the fillers and polymers strongly influence this property. When compared to CB, the interaction between silica and hydrocarbon rubber is weak, but with effective use of a silane coupling agent, the abrasion resistance of silica-filled compounds can be considerably promoted which enables them to be used in tire tread compounds [16]. Many studies had tried to improve the abrasion resistance by combining the advantages of different fillers with silica or hybrid fillers such as silica/CB [17-19] and silica/nanoclay [20-23]. For example, the simplest combination is silica/CB as both types of fillers are already commonly used in tire compounds. The use of a silica and CB combination in NR-based truck tread compounds was investigated before and the results indicated that when CB N220 was completely replaced by bis-(3-TriEthoxySilylPropyl)Tetrasulfide (TESPT)-modified silica, the rolling resistance was improved by about 30% while there was little change in the tread wear index (abrasion resistance) and wet traction [17]. A study on mechanical properties of NR reinforced with various ratios of CB N330/silica hybrid fillers with silane coupling agent showed that vulcanizates containing 20 and 30 phr of silica in a total of mixed filler of 50 phr exhibited the best overall mechanical properties. The abrasion resistance as measured by abrasion loss tended to decrease when the silica content was more than 10 phr due to silica dispersion or strong filler-filler interaction at higher loadings of silica [18]. The addition of a small amount of silica (VN3) into SSBR/CB (N330) compounds, such as by the use of a CB/silica ratio of 45/5 phr, decreased the filler cluster branching and increased the reinforcement efficiency [19]. This decreased filler networking and more homogeneous filler dispersion subsequently resulted in better abrasion resistance, lower rolling resistance and better wet skid resistance, i.e. better dynamic mechanical properties. However, when the silica proportion was raised, filler cluster branching increased quickly and deteriorated the properties.

A combination of silica and China clay in NR for a heavy-duty truck tire tread formulation was studied and the best balance of heat build-up and abrasion resistance was found at a silica/clay ratio of 60/20 [20]. The use of MontMorillonite clay (MMT) and silica with TESPT as silane coupling agent in SSBR/BR tread compounds improved tensile strength, elongation at break and traction properties at low TESPT content while enhancing modulus, hardness, wear resistance, dry handling and rolling resistance at high TESPT content [21]. Hybrid filler systems consisting of precipitated silica and kaolin modified with a Sodium salt of Rubber Seed Oil (SRSO) in NR/BR blends demonstrated that substitution of 5-10 phr of silica with SRSO modified kaolin resulted in lower Mooney viscosity, higher cure rate, increased chemical crosslink density index and bound rubber content [22], indicating a higher extent of rubber-rubber and rubber-filler interactions. This resulted in enhanced mechanical properties such as abrasion resistance, compression set, tensile- and tear-strengths and elongation at break of the blend vulcanizates. The vulcanizate containing silica/SRSO hybrid filler also showed enhancement of dynamic mechanical properties, beneficial for tire tread applications. Recently, the effect of mixing dump temperature on the hybrid filler of silica/CB-filled NR and silica/OrganoClay (OC)-filled NR compounds at 45/10 phr were also studied in our previous work [23]. The use of OC showed higher tan delta at -20°C and a lower tan delta at 60°C, indicating better ice traction and reduced rolling resistance. The results also showed a positive effect on lower Payne effect and higher cure rate index, better from the perspective of lower silica-silica networks and better productivity in terms of reduced product cycle time. The use of CB N134 in combination with silica showed that the tensile properties increased with increasing dump temperature until about 150°C due to better silanization between silica and bis-(3-TriEthoxySilylPropyl)Disulfide (TESPD) as silane coupling agent. Above 150°C a drop of tensile properties was observed due to NR degradation. Results also showed a higher cure rate index and 300% modulus for silica/CB-filled NR compounds compared to a pure silica-filled system.

A further refinement of the beneficial effects of blending small amounts of BR or SBR into NR, also in combination with blends of fillers, is presented in this chapter. For the first part, the effects of different types of BR and SSBR as secondary polymers in NR: with different levels of microstructure such as cis-content, vinyl-content, glass transition temperature (T_g) in BR, as well as styrene content in SSBR, on the properties of silica-reinforced truck tire tread compounds are studied. For the second part, the combination of silica with CB N134 and OC as secondary filler on silica-filled NR together with BR and SSBR as secondary polymer are

also studied. The cure characteristics, filler-filler interactions, filler-rubber interactions, tensile properties, DIN abrasion resistance, dynamic mechanical properties and morphology are investigated.

9.2 Experimental

9.2.1 Materials

NR (Ribbed Smoked Sheet, RSS3) was locally produced in Thailand. The BR with different vinyl contents at <1% (CB22), 11% (CB60) were obtained from Arlanxeo, Germany and 77% (HV80) was obtained from Versalis S.p.A., Italy. The SSBR with different vinyl contents at 30% (SLR3402) was obtained from Trinseo Deutschland GmbH, Germany, 55% (SL563) from JSR Corporation, Japan, and 62% (SLR4602) was also obtained from Trinseo Deutschland GmbH, Germany. The raw material properties of each elastomer are shown in Table 9.1. Silica ULTRASIL 7005 with a Cetyl-Trimethyl-Ammonium-Bromide (CTAB) and Brunauer-Emmet-Teller (BET) specific surface area of 171 and 190 m²/g, respectively, and silane coupling agent bis-(3-TriEthoxySilylPropyl)Disulfide (TESPD) were kindly provided by Evonik, Germany. Carbon black (N134) with a CTAB and BET specific surface areas of 134 and 145 m²/g, respectively, was provided by Phillips Carbon Black Limited, India. Organoclay Dellite 67G, functionalized with 47 wt% of dimethyl dihydrogenated tallow ammonium chloride (2HT), 115 meq/100 g of Cation Exchange Capacity (CEC) and interlayer distance of 34.3 Å, was provided by Laviosa Chimica Mineraria S.p.A, Italy. The other ingredients: Treated Distillate Aromatic Extract oil (TDAE oil), DiPhenyl-Guanidine (DPG), N-Cyclohexyl-2-Benzothiazyl Sulfenamide (CBS), 2,2,4-TriMethyl-1,2-dihydroQuinoline (TMQ), Zinc Oxide (ZnO), stearic acid and sulfur are commercial grades for the rubber industry.

Table 9.1 The raw material properties of the rubber used in this study.

Types of rubber	Content (%)		Tg (°C)	ML(1+4), 125°C ^a
	Vinyl	Styrene		
NR unmasticated	-	-	-70	98
NR masticated	-	-	-70	55
	-	-	-70	40 ^b
BR (CB22)	<1	-	-104	60
BR (CB60)	11	-	-93	58
BR (HV80)	77	-	-31	55
SSBR (SLR3402)	30	15	-61	63
SSBR (SL563)	55	20	-35	59
SSBR (SLR4602)	62	21	-25	37

^aThe ML(1+4), 125°C tested in this study.

^bNR masticated for NR/SSBR (SLR4602) blends.

9.2.2 Compound preparation

One requirement for proper mutual dispersion of a rubber blend or hybrid polymer is equality of the viscosity of the raw elastomers. Raw NR (RSS3) has a higher viscosity than BR and SSBR. Therefore, at first NR was masticated on a two-roll mill in order to achieve approximately the same level of Mooney viscosities as shown in Table 9.1. The compound formulations employed for the first part of this study are given in Table 9.2, with the ratios of NR blended with BR or SSBR of 80/20 phr. The vinyl-content in the BR was varied at <1, 11 and 77%, while the vinyl-contents in SSBR were varied at 30, 55 and 62%. Truck tire tread compounds were prepared using a two-step mixing procedure: the first was to prepare a masterbatch of rubber and fillers, and the second was to prepare the final compounds including the curatives. For the first step, an internal mixer, Brabender® 50EHT, (Brabender® GmbH & Co.KG, Germany) with a mixing chamber volume of 70 ml was used. The mixing conditions were set at a rotor speed of 60 rpm, fill factor of 70% and initial mixer temperature setting of 120°C in order to reach a dump temperature in the range of 135-150°C, required as reported before [14,23]. BR or SSBR as secondary polymers were added together with the masticated NR. Then the first half of silica was added, half the TESPD silane coupling agent and DPG secondary accelerator. The other halves of silica and TESPD were added later on in the first mixing step, together with the TDAE extender oil. ZnO, stearic acid and TMQ were added at

the end of the first mixing step. The second step was for the addition and mixing of the other half of DPG, CBS primary accelerator and sulfur at a rotor speed of 30 rpm, fill factor of 70%, and an initial mixer temperature setting of 70°C. The two-step mixing procedure is summarized in Scheme 9.1(a) for the silica-filled NR compound, and Scheme 9.1(b) for silica-filled NR/BR or NR/SSBR compounds. The compound formulations employed for the second part of this study are given in Table 9.3. The mixing procedure was almost the same as the first part. The optimum loadings of CB N134 or OC as secondary fillers as taken from the previous work at 10 and 5 phr, respectively, were added together with the first half of the silica as shown in Scheme 9.1(c).

Table 9.2 Formulations to study the effect of vinyl-contents in BR or SSBR as secondary polymers.

Ingredients	Amount (phr)		
	Reference	NR/BR	NR/SSBR
Natural rubber (RSS3)	100.0	80.0	80.0
BR ^a	-	20.0	-
SSBR ^b	-	-	20.0
ULTRASIL 7005	55.0	55.0	55.0
TESPD ^c	5.0	5.0	5.0
TDAE oil	8.0	8.0	8.0
ZnO	3.0	3.0	3.0
Stearic acid	1.0	1.0	1.0
TMQ	1.0	1.0	1.0
DPG ^c	1.1	1.1	1.1
CBS	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5

^aBR was CB22, CB60 and HV80, containing vinyl-contents of <1%, 11% and 77%, respectively.

^bSSBR was SLR3402, SL563 and SLR4602, containing vinyl-contents of 30%, 55% and 62%, respectively.

^cThe amounts of TESPD and DPG were based on the following equations [12]:

$$\text{TESPD (phr)} = 0.00053 \times Q \times A \quad (1)$$

$$\text{DPG (phr)} = 0.00012 \times Q \times A \quad (2)$$

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

Table 9.3 Formulations to study the effect of combination of secondary fillers and polymers.

Ingredients	Amount (phr)			
	Reference	Silica	Silica/CB	Silica/OC
Natural rubber (RSS3)	100.0	80.0	80.0	80.0
Secondary polymers ^a	-	20.0	20.0	20.0
ULTRASIL 7005	55.0	55.0	45.0	50.0
Secondary fillers ^b	-	-	10.0	5.0
TESPD ^c	5.0	5.0	4.1	4.6
TDAE oil	8.0	8.0	8.0	8.0
ZnO	3.0	3.0	3.0	3.0
Stearic acid	1.0	1.0	1.0	1.0
TMQ	1.0	1.0	1.0	1.0
DPG ^c	1.1	1.1	0.9	1.0
CBS	1.5	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5	1.5

^aSecondary polymers were BR (HV80) and SSBR (SL563), containing vinyl-contents of 77% and 55%, respectively.

^bSecondary fillers were carbon black (N134) and organoclay (Dellite 67G).

^cThe amounts of TESP and DPG were based on the following equations [12]:

$$\text{TESPD (phr)} = 0.00053 \times Q \times A \quad (1)$$

$$\text{DPG (phr)} = 0.00012 \times Q \times A \quad (2)$$

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

9.2.3 Sample characterizations

9.2.3.1 Testing of compound and vulcanizate properties

Payne effect, cure characteristics, tensile properties, dynamic mechanical properties, DIN abrasion resistance index and its abraded surface of the silica-filled NR and silica-filled NR/BR or SSBR compounds were investigated following the methods and using the equipments as described in Chapter 7. The bound rubber content was tested following the method as explained in Chapter 8.

Scheme 9.1 Two-step mixing procedures for compound preparations; masterbatch compounds of NR+silica (a), NR/BR or SSBR+silica (b), NR/BR or SSBR+silica+secondary filler (c), and final compounds (d).

9.3 Results and discussion

9.3.1 Effect of vinyl-contents of the secondary polymers on silica-filled rubber compounds.

9.3.1.1 Filler-filler interaction

The difference between the modulus at low strain (0.56%) and high strain (100%) can be used to indicate the level of filler-filler interaction, called Payne effect [24]. The Payne effects of silica-filled hybrid NR compounds with different vinyl-contents in BR and SSBR are shown in Figure 9.1. Comparison between the pure silica-filled NR and the silica-filled NR/BR and NR/SSBR hybrid polymers shows that the Payne effect of the pure NR compound is higher than for both hybrid polymer systems. It is clear that the effect of vinyl-content of BR and SSBR in combination with NR at the ratio of 80/20 phr is to decrease the Payne effect with increasing vinyl-content. This is clearly due to improvement of the interaction of TESPD silane coupling with the vinyl-groups in the BR or SSBR elastomers used in this study. NR lacks such vinyl-groups which provide an enhanced reactivity towards the sulfur-moieties in the TESPD. To compare the Payne effect results between BR and SSBR, the 1% and 11% vinyl-contents of BR show higher Payne effects than the hybrid compounds containing high vinyl-contents. The 77% vinyl-content BR shows a comparable Payne effect to

the 55% and 62% vinyl-contents SSBR. More reduction of silica-silica interaction was observed with the 1,2 vinyl-units in BR due to more interaction with the silica than the cis-1,4- and trans-1,4 butadiene-units in BR which is of major influence on the filler-filler interaction and also the modulus of the rubber compounds [25-27].

Figure 9.1 Payne effects ($\Delta G'$) of silica-filled NR/BR (a) and silica-filled NR/SSBR (b) compounds with varying vinyl-contents in BR and SSBR as secondary polymers.

9.3.1.2 Bound rubber content

The filler-rubber interactions were investigated by Bound Rubber Content (BRC) [28]. The total BRC and chemically BRC of silica-filled NR compounds with varied vinyl-contents in BR and SSBR, are shown in Figure 9.2. The total BRC and chemically BRC of the NR/BR blends decrease with increasing vinyl-content, but the lowest vinyl-content of 1%, or high cis-content shows the highest values. All other blends, with BR as well as SSBR show more or less similar BRC's, irrespective of the vinyl-contents. These results are overall surprising in comparison with the filler-filler interactions seen in the previous paragraph. With reduced filler-filler interaction one would have expected an increased rubber-filler interaction. The results in this paragraph are quite the opposite. Further study would be necessary to elucidate this apparent contradiction.

Figure 9.2 Total bound rubber content and chemically bound rubber content of silica-filled NR/BR (a) and silica-filled NR/SSBR (b) compounds with varying vinyl-contents in BR and SSBR as secondary polymers.

9.3.1.3 Cure properties

The summarized cure or vulcanized properties of the various compounds are given in Figures 9.3-9.5. The minimum cure torques (M_L) of the various compounds are presented in Figure 9.3. The M_L can commonly be related to the viscosity of rubber compounds: lower viscosity of a rubber compound means improvement in processability and ease to flow and this is also related to the filler network like registered by the Payne effect; a higher M_L refers to the formation of a stronger filler network, enhanced when the filler content is increased [29]. The M_L of silica-filled NR/BR blends tends to decrease with increasing vinyl-content BR contents. This is again most probably the effect of the increasing vinyl-content of the BR and the consequent interaction with the silane coupling agent. The effects of the vinyl-contents on the M_L of silica-filled NR/SSBR blends show lower M_L results than for the pure silica-filled NR compounds and for different vinyl-contents the M_L are almost at the same level. The first is obviously the result of the higher degree of mastication of the NR for this series, resulting in lower Mooney viscosity to start with. The second seems more in agreement with the increase in BRC's in Figure 9.2 than with the reduced filler-filler interaction in Figure 9.1. Higher compound viscosities with higher cis-content, so lower vinyl-content of BR have also been reported for CB-filled NR/BR [30], silica-filled SBR/BR and CB-filled SBR/BR blends [31].

Figure 9.3 Minimum cure torques of silica-filled NR/BR (a) and silica-filled NR/SSBR (b) compounds with varying vinyl-contents in BR and SSBR as secondary polymers.

The maximum cure torque (M_H) levels and cure torque differences ($M_H - M_L$) indicate the vulcanizate stiffness that is the result of several factors, combining contributions from chemical crosslinks by the vulcanization reaction, from filler-rubber interactions and from filler-filler interactions [32]. The M_H and $M_H - M_L$ of the silica-filled NR/BR and NR/SSBR compounds with different vinyl-contents are shown in Figure 9.4. They are lower than for the pure silica-filled NR compound. Moreover, with increasing vinyl-content the M_H and $M_H - M_L$ tend to decrease for NR/BR, while staying the same for NR/SSBR. The M_H and $M_H - M_L$ again resemble most the results on rubber-filler interaction in Figure 9.2, tentatively indicating that this has a stronger influence on the cure properties than the remaining filler-filler bonds, irrespective of whether this is now the effect of the vinyl-content of the secondary elastomers or of other factors.

The scorch times (t_{s2}) and optimum cure times (t_{c90}) are displayed in Figure 9.5. With the use of BR and SSBR in the silica-filled NR compounds, greatly increased t_{s2} and t_{c90} of the rubber blends are observed due to less allylic hydrogen in BR and SSBR compared to NR. For the silica-filled NR/BR with increasing vinyl-content, the t_{s2} and t_{c90} increase. While no significant effect of vinyl-content on t_{s2} and t_{c90} is seen for the silica-filled NR/SSBR blends. The vulcanization rate is dependent on the allylic hydrogen-contents, where NR has the highest content compared to BR and SSBR [33].

Overall, the different BR have more effects on the cure properties of their blends with NR than SSBR. Whether the vinyl-contents of the butadiene-moieties are the main influencing factors or others remains somewhat unclear and deserves deeper study.

Figure 9.4 Maximum cure torques and cure torque differences of silica-filled NR/BR (a) and silica-filled NR/SSBR (b) compounds with varying vinyl-contents in BR and SSBR as secondary polymers.

Figure 9.5 Scorch times and optimum cure times of silica-filled NR/BR (a) and silica-filled NR/SSBR (b) compounds with varying vinyl-contents in BR and SSBR as secondary polymers.

9.3.1.4 Mechanical properties

The effects of the vinyl-content of BR and SSBR as secondary polymers on the tensile properties of silica-filled NR, silica-filled NR/BR and silica-filled NR/SSBR compounds are shown in Figures 9.6-9.7. The tensile strength and elongation at break of pure silica-filled NR are higher than for all silica-filled NR/BR and silica-filled NR/SSBR blends. This is due to the materials's properties themselves: NR has much higher strength than BR and SSBR due to its typical strain-induced crystallization [1,31]. The silica-filled NR/BR has a slightly lower tensile strength and elongation at break for higher vinyl-contents. This may be due to the lowest vinyl- and high cis-content of BR (V1) which may also show some strain-induced crystallization, enhancing the stress-strain properties as well [34]. The tensile strengths and elongations at break of the silica-filled NR/SSBR compounds are almost on the same level.

Figure 9.7 shows the effect of vinyl-content of BR and SSBR on the 300% modulus and reinforcement indices of the compounds under investigation. The 300% modulus and reinforcement index of NR/BR blends tend to increase somewhat with increasing vinyl-content BR. The 300% modulus of NR/SSBR blends also increase somewhat with increasing vinyl-content but the reinforcement indices are almost on the similar level of the pure silica-filled NR compound. These effects are so little that they can hardly be considered as relevant.

Figure 9.6 Tensile strength and elongation at break of silica-filled NR/BR (a) and silica-filled NR/SSBR (b) compounds with varying vinyl-contents in BR and SSBR as secondary polymers.

Figure 9.7 300% modulus and reinforcement index of silica-filled NR/BR (a) and silica-filled NR/SSBR (b) compounds with varying vinyl-contents in BR and SSBR as secondary polymers.

9.3.1.5 Dynamic mechanical properties

The dynamic mechanical properties of the silica-filled NR/BR and silica-filled NR/SSBR vulcanizates with varying vinyl-contents of BR and SSBR as secondary polymers, compared to the silica-filled NR compound in the temperature range from -80 to 80°C , at a frequency of 10 Hz and 0.1% strain, are shown in Figures 9.8-9.10. Figures 9.8 shows the results of tan delta at -20°C and 0°C as indicative of ice traction and wet traction of the rubber vulcanizates respectively, as evaluated on laboratory testing scale [35]. The tan delta at -20°C and 0°C of silica-filled NR/BR and NR/SSBR compounds increase with increasing vinyl-contents, particularly for NR/SSBR. The ice and wet traction are related to the T_g , where higher T_g means a better ice and wet traction [35]. The resultant T_g 's with increasing vinyl-content in the NR/BR and NR/SSBR compounds are shown in Figure 9.10. These are clearly in agreement with the observed increases of tan delta at -20°C and 0°C . The combination of NR with BR or SSBR as secondary polymer for silica compound offer the potential to improve ice traction and wet traction.

Another key tire performance criteria for tires is a low rolling resistance, as can be derived from the tan delta value at a temperature of 60°C on laboratory scale. A lower tan delta at 60°C indicates a better/lower rolling resistance [35]. Figure 9.9 shows the tan delta at 60°C of the silica-filled NR/BR and NR/SSBR compounds with different vinyl-contents in BR and

SSBR. The pure silica-filled NR shows the lowest tan delta at 60°C compared to the silica-filled NR/BR and NR/SSBR blends. The lower tan delta at 60°C of high cis-content BR in combination with SSBR silica compounds [31] and CB-filled NR/BR [30] has been reported. Similarly, a higher tan delta at 60°C with increasing vinyl-content of SBR compound has been reported [31].

The glass transition temperatures from the tan delta peak and loss modulus peak are shown at Figure 9.10. The T_g values may be used as indication of abrasion resistance: the lower the T_g, the better the abrasion resistance [35]. The T_g values of NR/BR blends tend to increase with increasing vinyl-contents in BR. This is in line with the increase of the T_g of BR with the vinyl-concentration as already seen in Table 9.1 [34-36]. Similarly, the T_g values of NR/SSBR blends also tend to increase with increasing vinyl-content in the SSBR. The high T_g with high vinyl-content in SSBR is also known [37].

Figure 9.8 Tan delta at -20°C and tan delta at 0°C of silica-filled NR/BR (a) and silica-filled NR/SSBR (b) compounds with varying vinyl-contents in BR and SSBR as secondary polymers.

Figure 9.9 Tan delta at 60°C of silica-filled NR/BR (a) and silica-filled NR/SSBR (b) compounds with varying vinyl-contents in BR and SSBR as secondary polymers.

Figure 9.10 Glass transition temperatures from the tan delta peak and loss modulus peak of silica-filled NR/BR (a) and silica-filled NR/SSBR (b) compounds with varying vinyl-contents in BR and SSBR as secondary polymers.

9.3.1.6 DIN abrasion resistance

Figure 9.11 DIN abrasion resistance index of silica-filled NR/BR (a) and silica-filled NR/SSBR (b) compounds with varying vinyl-contents in BR and SSBR as secondary polymers.

The effect of vinyl-content in BR and SSBR as secondary polymers on the DIN abrasion resistance index is shown in Figure 9.11. The DIN abrasion resistance indices of the silica-filled NR/BR and NR/SSBR are higher than for pure silica-filled NR due to the properties of BR and SSBR themselves that are known to enhance abrasion resistance [1]. The effect of the vinyl-content of BR and SSBR on the DIN abrasion resistance index apparently is significant. With increasing vinyl-content the DIN abrasion resistance index tends to decrease for both NR/BR and NR/SSBR blends. These results correspond well with the decreased abrasion resistance for higher T_g [35]. A high abrasion resistance has already been observed for NR blended with high cis-BR at 50/50 phr [38], and ultra high cis BR [39].

9.3.1.7 SEM images of DIN abraded surfaces

There is a difficulty to predict the wear resistance of rubber products [40]. The abrasion resistance results from laboratory experiments often do not agree with the results of actual tire tests. Tearing or fatigue under the action of high local stresses caused by friction have been blamed as the main causes of abrasion [40]. When rubber is abraded without change of direction, an “Abrasion pattern” or sets of parallel ridges appear on the surface of the samples

at right angles to the direction of motion, often called Schallamach waves [41-42] and this abrasion pattern is assumed to influence the relative rates of tire wear under different service conditions. These periodic parallel ridges or abrasion patterns are initiated by microvibrations at the natural frequency of the rubber and propagate by stick-slip oscillations, both of which are generated during frictional sliding of rubber [43]. The SEM images of the DIN abraded samples of silica-filled NR/BR and silica-filled NR/SSBR compounds with different vinyl-contents of BR and SSBR were analyzed in comparison with that of the pure silica-filled NR compound, as shown in Figure 9.12. The abrasion patterns on the DIN abraded surfaces agree well with the DIN abrasion resistance indices. The smoothest abraded surfaces are generally observed for the silica-filled NR/BR and NR/SSBR compounds with the highest abrasion resistance indices. The worse the abrasion resistance, the more there are signs of Schallamach waves.

Figure 9.12 SEM photograph of DIN abraded surfaces of silica-filled NR/BR and NR/SSBR compounds with varying vinyl-contents in BR and SSBR as secondary polymers.

9.3.2 Effect of the combination of secondary fillers and polymers on silica-filled NR compounds

9.3.2.1 Filler-filler interaction

The Payne effects of silica-filled NR with BR or SSBR as secondary polymers, and CB N134 or OC as secondary fillers were also investigated as shown in Figure 9.13. The Payne effect of the pure silica-filled NR is much higher than for the other compounds. Silica/CB-filled NR/BR and NR/SSBR show higher Payne effects than straight silica-filled NR/BR and NR/SSBR compounds, whereas the small particle size and high specific surface area of CB N134 with less filler particle-particle distances favors filler network formation and thus increases the Payne effect. On the other hand, the silica/OC-filled NR/BR and NR/SSBR compounds show much lower Payne effects than straight silica-filled NR/BR and NR/SSBR compounds due to the effect of the clay-modifier in OC, acting as a plasticizer and resulting in a reduction of filler networking. The use of OC reducing the Payne effect has been reported before [44].

Figure 9.13 Effect of the combination of secondary fillers and polymers on the Payne effect of silica/CB-filled (a) and silica/OC-filled (b) compounds.

9.3.2.2 Cure properties

The summarized cure or vulcanized properties of the various compounds are given in Figures 9.14-9.16. The minimum cure torques (M_L) of the various compounds are presented in Figure 9.14. The M_L of the silica/CB-filled NR/BR blend is almost at the same level as for the

straight silica-filled NR compound, while the silica/CB-filled NR/SSBR blend shows a lower M_L than for silica/CB-filled NR/BR, silica-filled NR/BR and the pure NR systems. The use of OC on silica-filled NR/BR and NR/SSBR shows much lower M_L results than the silica-filled NR/BR, NR/SSBR and pure NR systems, which is again due to the plasticizing effect of clay-modifier in OC resulting in lower filler-filler interaction. The M_L results are in agreement with the Payne effect as indicated in Figure 9.13.

The maximum cure torques (M_H) and cure torque differences ($M_H - M_L$) of the various compounds are presented in Figure 9.15. The M_H and $M_H - M_L$ of the pure silica-filled NR compound are higher than for all other types of compound. The silica/CB-filled NR/BR blend is almost at the same level as for the straight silica-filled NR/BR compound, while the silica/CB-filled NR/SSBR blend is also almost at the same level as the silica-filled NR/SSBR blends. The silica/OC-filled NR/BR and NR/SSBR compounds show lower M_H and $M_H - M_L$ than straight silica-filled NR/BR and NR/SSBR compounds due to the effect of the clay-modifier in OC, acting as a plasticizer and resulting in a reduction of filler networking. These results are in agreement with the Payne effect results as displayed in Figure 9.13.

Figure 9.14 Effect of the combination of secondary fillers and polymers on minimum cure torque of silica/CB-filled (a) and silica/OC-filled (b) compounds.

Figure 9.15 Effect of the combination of secondary fillers and polymers on maximum cure torque and cure torque difference of silica/CB-filled (a) and silica/OC-filled (b) compounds.

Figure 9.16 Effect of the combination of secondary fillers and polymers on scorch times and optimum cure times of silica/CB-filled (a) and silica/OC-filled (b) compounds.

The effect of combination of secondary fillers and polymers on scorch times (t_{s2}) and optimum cure times (t_{c90}) are displayed in Figures 9.16. The use of CB in silica-filled NR/BR and NR/SSBR reduces the t_{s2} and t_{c90} due to the high thermal conductivity of CB, as compared to the pure silica compounds [23,45-46]. The use of OC in silica-filled NR/BR and NR/SSBR

reduces the t_{s2} and t_{c90} even more as compared to the pure silica-filled systems. The reduction of the t_{s2} and t_{c90} of OC compounds is again due to the effect of the ammonium-based modifying agent that accelerates the curing reaction [23,47-52]. So the presence of CB N134 and OC can be beneficial from a processing aspect, as it can increase the productivity and thus reduce the energy required for vulcanization.

9.3.2.3 Mechanical properties

The effect of CB N134 and OC on the tensile properties of silica-filled NR/BR and SSBR as secondary polymers, compared to the pure silica-filled NR compound are shown in Figures 9.17-9.18. There is no significant effect of the combination of secondary polymer and secondary filler compared to the pure silica compound systems on the tensile strength and elongation at break. The effect of the secondary polymers on the lower tensile strength of the silica/CB-filled NR/BR and NR/SSBR blends due to the lower strain-induced crystallization of BR and SSBR rubbers is similar to what was observed for the systems without secondary fillers in part 1 of this chapter [1,33].

Figure 9.18 shows the effect of combination of secondary polymers BR or SSBR, and secondary fillers CB N134 or OC on the 300% modulus and reinforcement index of the compounds. The silica/CB-filled NR/BR blend shows a slight improvement of the 300% modulus due to the high specific surface area and high structure of CB N134, whereas the other hybrid compounds are almost at the same level of 300% modulus and reinforcement index compared to the pure silica compounds. The silica/OC-filled NR/BR and NR/SSBR blends show a drop of 300% modulus and reinforcement index as displayed in Figure 9.18(b), again due to the plasticizing effect of the modifying agent of the OC.

Figure 9.17 Effect of the combination of secondary fillers and polymers on tensile strength and elongation at break of silica/CB-filled (a) and silica/OC-filled (b) compounds.

Figure 9.18 Effect of the combination of secondary fillers and polymers on 300% modulus and reinforcement index of silica/CB-filled (a) and silica/OC-filled (b) compounds.

9.3.2.4 Dynamic mechanical properties

The effects of the combination of secondary polymer and filler on the dynamic mechanical properties of silica-filled NR with BR or SSBR as secondary polymers and CB N134 or OC as secondary fillers are depicted in Figures 9.19-9.20, compared to the pure silica-

filled NR compounds. When compared to the silica-filled NR system, the tan delta at -20°C and 0°C are improved for all hybrid polymer with secondary filler systems like already seen for the hybrid polymer systems: Figure 9.8. The use of CB N134 on the silica-filled NR/BR and silica-filled NR/SSBR shows almost similar levels of tan delta at -20°C and 0°C , whereas the use of OC shows a drop in tan delta at -20°C and 0°C . The combination of NR with BR or SSBR as secondary polymer with CB N134 as secondary filler for silica compounds offers therefore the potential to improve ice and wet traction.

The tan delta at 60°C of silica-filled NR/BR or NR/SSBR with CB N134 or OC as secondary filler compounds are shown in Figure 9.20. The results show that the use of BR and SSBR tends to increase the tan delta at 60°C , where the use of CB N134 tends to increase the tan delta at 60°C further. However, the silica/OC-filled NR/BR and NR/SSBR show improvements of the tan delta at 60°C . So, the use of OC has the potential to improve the rolling resistance of a tire to bring it back to the level for a pure silica, pure NR compound. This corresponds to our previous work as presented in Chapter 6 [23].

Figure 9.19 Effect of the combination of secondary fillers and polymers on tan delta at -20°C and tan delta at 0°C of silica/CB-filled (a) and silica/OC-filled (b) compounds.

Figure 9.20 Effect of the combination of secondary fillers and polymers on tan delta at 60°C of silica/CB-filled (a) and silica/OC-filled (b) compounds.

9.3.2.5 DIN abrasion resistance

Figure 9.21 Effect of the combination of secondary fillers and polymers on DIN abrasion resistance index of silica/CB-filled (a) and silica/OC-filled (b) compounds.

The effects of the combination of secondary polymers and fillers on the DIN abrasion resistance index of silica-filled NR with BR or SSBR as secondary polymer and CB N134 or OC as secondary filler are presented in Figure 9.21, compared to the pure silica-filled NR

compound. The DIN abrasion resistance index of silica-filled NR/BR and NR/SSBR shows much higher values than straight silica-filled NR, as already seen in part 1 of this chapter. However, slight decreases of DIN abrasion resistance index are observed for silica/CB-, and more so for the silica/OC-filled NR/BR and NR/SSBR compounds.

9.3.2.6 SEM images of DIN abraded surfaces

The SEM images of the DIN abraded samples of silica-filled NR/BR and silica-filled NR/SSBR compounds in combination with CB N134 and OC are analyzed in comparison with that of the pure silica-filled NR compound, as shown in Figure 9.22. The abrasion patterns on the DIN abraded surfaces agree well with the DIN abrasion resistance indices. Smoother abraded surfaces are observed for the silica-, silica/CB- and silica/OC-filled NR/BR compounds, whereas rougher surfaces are seen for the silica-, silica/CB-, and silica/OC-filled NR/SSBR compounds. A slightly higher tendency for Schallamach waves may be seen for the OC-filled than for the CB-filled compounds, which corresponds to the lowest DIN abrasion resistances of the first ones.

Figure 9.22 Effect of the combination of secondary fillers and polymers on DIN abraded surfaces of silica/CB-filled (a) and silica/OC-filled (b) compounds.

9.4 Conclusions

The properties of silica-filled NR compounds with different vinyl-contents in BR and SSBR as secondary polymers show effects on the cure properties as shown by higher scorch and optimum cure times. Increasing amounts of vinyl-configurations in BR in the silica-filled NR compounds show better Payne effects, 300% modulus, reinforcement index, tan delta at -20°C and tan delta at 0°C, whereas decreasing tensile strength, elongation at break and DIN abrasion resistance index. Increasing vinyl-contents in SSBR show improvements in Payne effect, 300% modulus, tan delta at -20 and 0°C but only a little in DIN abrasion resistance index, at the cost of increased thus worse tan delta at 60°C, indicative of rolling resistance. In the present study, the combination of secondary fillers and secondary polymers in silica-filled NR were also investigated. Silica/CB-filled NR/BR and NR/SSBR, respectively, silica/OC-filled NR/BR and NR/SSBR show positive effects on the scorch time, optimum cure time, with slightly changed Payne effect, tensile properties, tan delta at -20°C, tan delta at 0°C, and DIN abrasion resistance as compared to the compound with CB N134. The combination silica/CB-filled NR/SSBR shows a large deterioration in tan delta at 60°C, so indication of a major increase in rolling resistance. The use of OC shows enhancement in Payne effect and tan delta at 60°C, indicative for reduced filler-filler networking, and rolling resistance of a tire tread compound compared to the compound without OC. So, overall the combination of BR and OC shows the best performance. With this, the basic objectives of this project has been achieved: see Chapter 1.

These conclusions are summarized in the radar charts hereunder. Figures 9.23, 9.25 and 9.27 show the radar charts covering cure properties and Payne effects of the compounds (Figures 9.23(a), 9.25(a) and 9.27(a)), as well as mechanical properties of the vulcanizates (Figures 9.23(b), 9.25(b) and 9.27(b)). These charts are based on relative values versus the reference. The charts concerning tire performance as shown in Figures 9.24, 9.26 and 9.28 are based on index-values: the higher the better.

Optimizing secondary polymers for silica-filled NR compounds

Figure 9.23 Radar charts comparing cure properties, Payne effect (a), and mechanical properties (b) of the silica-filled NR compounds containing an optimized secondary polymer, either BR or SSBR with a vinyl-content of 77 and 55 wt% (NR/BR V77 and NR/SSBR V55), respectively. The silica-filled NR compound without secondary polymer is considered as reference (NR).

Figure 9.24 Radar chart comparing the key tire performances indicated by lab-indicators of the silica-filled NR compounds containing an optimized secondary polymer, either BR or SSBR with a vinyl-content of 77 and 55 wt% (NR/BR V77 and NR/SSBR V55), respectively. The silica-filled NR compound without secondary polymer is considered as reference (NR).

Optimized formulations of silica-filled NR compounds with secondary polymers and carbon black as secondary filler

Figure 9.25 Radar charts comparing cure properties, Payne effect (a), and mechanical properties (b) of the silica-filled NR compounds with an optimized BR or SSBR as secondary polymer without carbon black N134 as secondary filler (NR/BR (S) and NR/SSBR (S)) and with carbon black N134 (NR/BR (S+CB) and NR/SSBR (S+CB)). The silica-filled NR compound without secondary polymer and secondary filler is considered as reference (NR).

Figure 9.26 Radar chart comparing the key tire performances indicated by lab-indicators of the silica-filled NR compounds with an optimized BR or SSBR as secondary polymer without carbon black N134 as secondary filler (NR/BR (S) and NR/SSBR (S)) and with carbon black N134 (NR/BR (S+CB) and NR/SSBR (S+CB)). The silica-filled NR compound without secondary polymer and secondary filler is considered as reference (NR).

Optimized formulations of silica-filled NR compounds with secondary polymers and organoclay as secondary filler

Figure 9.27 Radar charts comparing cure properties, Payne effect (a), and mechanical properties (b) of the silica-filled NR compounds with an optimized BR or SSBR as secondary polymer without organoclay as secondary filler (NR/BR (S) and NR/SSBR (S)) and with organoclay (NR/BR (S+OC) and NR/SSBR (S+OC)). The silica-filled NR compound without secondary polymer and secondary filler is considered as reference (NR).

Figure 9.28 Radar chart comparing the key tire performances indicated by lab-indicators of the silica-filled NR compounds with an optimized BR or SSBR as secondary polymer without organoclay as secondary filler (NR/BR (S) and NR/SSBR (S)) and with organoclay (NR/BR (S+OC) and NR/SSBR (S+OC)). The silica-filled NR compound without secondary polymer and secondary filler is considered as reference (NR).

9.5 References

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Summary

Green tires made from silica reinforcing filler instead of Carbon Black (CB) show better wet grip and rolling resistance as indicative for safety and fuel savings. However, silica contains silanol groups on the surface that are acidic and interact with basic accelerators, thus retard the curing reaction. Another limitation of the silanol groups on the silica surface are poor filler-rubber interactions or strong filler-filler interactions, consequently poor dispersion and distribution of the silica in the rubber matrix, and incompatibility with non-polar elastomers like Natural Rubber (NR), Styrene Butadiene Rubber (SBR) and Butadiene Rubber (BR) which are conventional rubbers in the tire industry. To overcome these limitations, it is necessary to use silane coupling agents to improve the interaction with rubber and the filler dispersion by the so-called silanization reaction. Generally used silane coupling agents are bis-(3-TriEthoxySilylPropyl)Tetrasulfide (TESPT) and bis-(3-TriEthoxySilylPropyl)Disulfide (TESPD), bi-functional compounds that act as chemical bonding agents between silica and the rubber matrix during vulcanization. When compared to CB tires, silica tires still provide poorer abrasion resistance as indicative for tire durability. To enhance the abrasion resistance of silica tires, a combination of silica with different fillers or hybrid fillers as well as hybrid polymers in combination with silica-reinforced NR are the main topic of this PhD thesis. An introduction into the development of silica technology for tires is given in **Chapter 1**. A literature review of hybrid fillers of silica with CB and OrganoClay (OC) as secondary fillers and hybrid polymers of silica-reinforced NR in combination with BR or SBR as secondary polymers are given in **Chapter 2**.

The experimental part is started with the optimization of the mixing conditions, mainly to check the effect of mixing temperature for silica-reinforced NR with small amounts of secondary fillers, as presented in **Chapter 3**. The variation of the initial temperature setting of the internal mixer for a combination of silica with CB N134 is studied as well as a combination of silica with OC at a ratio of 45/10 phr. With increasing initial mixer temperature setting of the internal mixer, the increased dump temperature for silica/secondary fillers-filled NR compounds leads to a better silanization reaction between the silica and the coupling agent TESPD. However, a drop in compound properties at too high mixing temperature is observed due to NR degradation. The silica/CB-filled NR shows higher cure rate and tensile moduli, while maintaining similar ultimate tensile properties and tan delta at 60°C compared to a pure silica-filled system. Silica/OC-filled NR shows a lower Payne effect, higher cure rate, lower

moduli combined with similar ultimate tensile properties to silica or silica/CB, higher tan delta at -20°C and 0°C, indications for better ice and wet grip performance of tire-treads made thereof, respectively a lower tan delta at 60°C compared to the silica-filled system, indicative for reduced rolling resistance of tires. The use of hybrid fillers, small amounts of secondary fillers as CB and in particular OC next to silica in NR, therefore offers the potential of further improvement in wear resistance, wet traction and rolling resistance of tire treads.

As the hybrid fillers of silica/CB N134 and silica/OC show the potential to improve compound properties, especially the key tire performances compared to pure silica systems, a good filler dispersion in the rubber matrix is an important factor to obtain good reinforcement and compound properties. As processing conditions in term of mixing temperature and procedure have an effect on dispersion and thus properties, taking the optimized mixing temperature for silica-reinforced NR compounds is crucial. **Chapter 4** compares three different mixing sequences for loading of secondary fillers to the silica compounds and optimizes the loadings of TESPD to silica/secondary filler hybrid systems at a ratio of 45/10 phr. The loading of CB N134 or OC together with a first half of silica results in optimum compound properties as indicated by low Payne effect, higher total Bound Rubber Content (BRC), higher tear strength, lower tan delta at 60°C, and higher tan delta at -20°C compared to pure silica. By varying the TESPD loading, both hybrid filler systems show a decrease of Payne effect and compound viscosities, an increase of cure torque difference, apparent crosslink density, modulus and tensile strength with increasing TESPD loading, while tear strength and dynamic mechanical properties show an optimum. Based on these overall properties, the optimum TESPD content is fixed at 2.3 phr for silica/OC and 4.1 phr for silica/CB hybrid filler systems, which means a reduced amount of silane coupling agent and consequently lower costs of the rubber products.

Silica-silane technology has been implemented to replace conventional CB in tire tread compounds, mainly for passenger car tires to achieve rubber treads with lower rolling resistance, higher wet traction and similar abrasion or wear resistance. Such technology can also be applied for NR-based truck tire tread compounds. However, as the wear resistance influences mileage and this is a concern for silica-reinforced tire tread compounds, **Chapter 5** focusses on the effect of CB at low amounts as secondary filler on the properties of highly dispersible silica-filled NR compounds. The partial replacement of silica by high specific surface area and high structure CB N134 shows a clear synergistic effect on overall performance. Different loadings of CB N134 are used in substitution of silica in the compound

formulation to keep the total filler content at the same level of 55 phr. An increasing ratio of CB in the hybrid fillers steadily increases the compound viscosities, cure rate index, 300% modulus and DIN abrasion index. At low content of CB, i.e. in the range of 0-36 wt% of CB relative to total filler amount, the Payne effect and tan delta at both 0°C and 60°C as indications for wet traction and rolling resistance, are marginally changed, but thereafter gradually increase. Scorch and cure times are shortened in the presence of CB, facilitating an increase in productivity. Bound rubber content and mechanical properties as tensile strength, elongation at break, tear strength and tan delta at -20°C indicative for ice traction show an optimum at 18 wt% of CB relative to the total filler content or at a ratio of silica/CB 45/10 phr. With regard to tire performance as indicated by the laboratory test results, the abrasion resistance, wet grip and ice traction can therefore be enhanced while maintaining the tire rolling resistance at the optimum level for this silica/CB ratio.

The use of OC in combination with silica or hybrid filler shows the potential to enhance the performance of silica tires as indicated by a lower Payne effect, higher tan delta at -20°C and 0°C, indicative for better ice and wet grip performance, respectively a lower tan delta at 60°C compared to the pure silica-filled system, indicative for reduced rolling resistance. **Chapter 6** is to investigate the effect of loading of OC as secondary filler at 0-36 wt% relative to total filler content, or at 0-20 phr, in combination with silica and TESPD as silane coupling agent. With increasing the loading levels of OC in silica-filled NR compounds, it reduces the Payne effect and compound viscosities that are indicative for lower filler-filler interaction and better processability. The results show shortened scorch and cure times that have the potential to improve productivity while cycle times are reduced, and increased tan delta at -20°C and 0°C are observed. The optimum OC content at 9 wt% relative total fillers amount or at the ratio of silica/OC of 50/5 phr gives a good balance in compound properties as indicated by Payne effect, cure rate index, tan delta at -20°C, tan delta at 60°C and DIN abrasion resistance index. The results indicate that the use of hybrid filler may provide the tires with better wet traction, lower rolling resistance and improved wear resistance compared to the pure silica-filled system.

Organoclay in this present thesis contains 47 wt% of surface modifying agent, i.e. dimethyl dihydrogenated tallow ammonium chloride (2HT) type. **Chapter 7** is to investigate the effect of this surface modifying agent on the properties of silica-reinforced NR truck tire tread compounds, comparing between the use of silica/2HT, silica/OC, and silica/Mont-MorilloniTe (MMT)/2HT. The loading levels of 2HT were varied from 0-9.5 phr, this amount calculated from the 2HT content in OC. By increasing the amount of 2HT, compound viscosity,

Payne effect and scorch times are significantly decreased. As determined by the properties of both unvulcanized compounds and vulcanizates in terms of Payne effect, tensile properties, DIN abrasion resistance index, apparent crosslink density, tan delta at -20°C and tan delta at 60°C, the overall best balance of properties was observed at 4.7 phr of the modifying agent for a silica-filled and silica/MMT-filled NR compound, while at 5.0 phr of OC that contained 2.4 phr of the modifying agent for a silica/OC-filled system. With the optimum content of 2HT as the filler surface modifying agent, a lower Payne effect, higher cure rate index, higher tan delta at -20°C and lower tan delta at 60°C could be achieved, showing the potential of the utilization of the pure modifying agent to improve processability, rolling resistance, wet traction and abrasion resistance of silica-based compounds for tire treads.

To improve the properties of silica truck tire tread compounds, especially abrasion resistance, the effect of loadings of high-cis-content BR or high-vinyl-content Solution-SBR (SSBR) as secondary polymers in silica-filled NR compounds was investigated compared to pure silica-reinforced NR compounds in **Chapter 8**. The loadings of BR or SSBR from 0 to 30 phr in combination with NR at 100 to 70 phr lead to longer scorch times and optimum cure times, and decreased mechanical properties. With increasing high-cis BR contents, a better tan delta at 60°C as indicative for reduced rolling resistance of tire treads made thereof, apparent crosslink density and the DIN abrasion resistance index are obtained related to a decreased glass transition temperature of the resulting compounds. With increasing high-vinyl SSBR contents, the results show reduced and so lower filler-filler interaction by the Payne effect, and also improved DIN abrasion resistance index, and tan delta at -20 and 0°C indicative of wet and ice traction of tire treads made thereof. The results also shows an optimum loading of NR in combination with BR or SSBR at a ratio of 80/20 phr as indicated by bound rubber contents and 300% modulus. With the optimal ratio of NR/BR silica filled compound, 56% improvement in DIN abrasion resistance can be achieved.

To further study the properties of silica truck tire tread compounds, the effect of vinyl-contents in BR or SSBR as secondary polymers in silica-filled NR compounds at an optimum ratio of 80/20 phr as well as the combination of optimum amount of secondary fillers and polymers in silica-filled NR compounds are investigated in **Chapter 9**. With increasing vinyl-content in BR in combination with NR, a better Payne effect, 300% modulus, reinforcement index, tan delta at -20°C and 0°C are obtained, whereas tensile strength, elongation at break and DIN abrasion resistance index decrease with increasing vinyl-content. Increasing vinyl-contents in SSBR show improvements in Payne effect, 300% modulus, tan delta at -20°C and

0°C and a little in DIN abrasion resistance index. Silica/CB N134-filled NR/BR and NR/SSBR, respectively, silica/OC Dellite 67G-filled NR/BR and NR/SSBR show positive effects on the scorch time, optimum cure time, with slightly changed Payne effect, tensile properties, tan delta at -20°C and 0°C, and DIN abrasion resistance as compared to the compound with CB. The use of OC shows enhancement in Payne effect and tan delta at 60°C, indicative of a reduced filler-filler network, and consequently lower rolling resistance of the tire tread compound compared to the compound without OC.

Even though the pure silica-filled rubber compounds show better key tire performances such as lower rolling resistance and better wet traction, the abrasion resistance is still lower than for CB-filled rubber compounds. To further enhance the key tire properties of silica-filled rubber compounds by using secondary fillers like CB N134 or OC with different filler characteristics, their use in combination with silica or hybrid filler system is investigated. Overall this thesis mainly focusses on the key tire performances, as given by tan delta at -20°C and 0°C for ice and wet traction, respectively, and tan delta at 60°C for rolling resistance and DIN abrasion resistance index on a laboratory scale. An optimum ratio of silica/CB N134 hybrid fillers at 45/10 phr leads to better ice and wet traction, abrasion resistance, while maintaining the tire rolling resistance. At the optimum ratio of silica/OC at 50/5 phr, better ice traction, lower rolling resistance and also slightly improved wet traction and wear resistance are obtained compared to the pure silica-filled NR system. Further investigation concerns the influence of secondary polymers like BR or SSBR which have different glass transition temperature and/or different microstructures, together with NR or a hybrid polymer system on properties of the compounds. The optimum ratio of NR/high-vinyl BR at 80/20 phr shows a large improvement in ice and wet traction, as well as abrasion resistance, while maintaining rolling resistance. On the other hand, the optimum ratio of NR/high-vinyl SSBR at 80/20 gives better ice and wet traction, as well as abrasion resistance, but poorer rolling resistance of tires. The last part of this present thesis is the combination of optimum loading of secondary fillers and polymers in silica-filled NR compounds. Silica/CB-filled NR/BR and NR/SSBR show positive effects on ice and wet traction, respectively abrasion resistance, but poorer rolling resistance. On the other hand silica/OC-filled NR/BR and NR/SSBR also give positive results on ice and wet traction, respectively abrasion resistance, but maintain the good rolling resistance. Overall, therefore the combination of OC and BR with silica-reinforced NR shows the best key tire performances, especially abrasion resistance which was the main goal of this thesis.

Samenvatting

“Groene Banden” geproduceerd met silica als versterkende vulstof in plaats van roet (Carbon Black, CB) hebben een betere natte grip en rolweerstand, bedoeld voor grotere veiligheid en brandstof-besparingen. Silica heeft echter silanol-groepen op het oppervlak, die zuur reageren en een wisselwerking aangaan met basische vulkanisatie-versnellers en daardoor de vulkanisatie-reactie vertragen. Een andere beperkende factor van de silanol-groepen op het silica oppervlak zijn sterke vulstof-vulstof interacties, en dientengevolge slechte dispersie en verdeling van de silica in de rubber-matrix, en onverdraagzaamheid met niet-polaire elastomeren als Natuur-Rubber (NR), Styreen Butadiëen Rubber (SBR) en Butadiëen Rubber (BR), welke rubbers gebruikt worden in de banden industrie. Om deze beperkingen te verhelpen moeten silaan koppelings-agentia (silane coupling agents) worden toegepast om de interactie met rubber en de vulstof-dispersie te verbeteren via de zogenaamde silaniserings-reactie. Gebruikelijke silaan coupling agents zijn bis-(3-TriEthoxySilylPropyl)Tetrasulfide (TESPT) en bis-(3-TriEthoxySilylPropyl)Disulfide (TESPD), bifunctionele verbindingen die werken als chemische koppeling tussen silica en de rubber matrix bij vulkanisatie. In vergelijking met CB banden hebben silica banden wel een slechtere weerstand tegen slijtage, bepalend voor de duurzaamheid van de banden. Om deze slijtage- weerstand van silica banden te verbeteren zijn de combinatie van silica met verschillende vulstoffen, ofwel hybride vulstoffen, en hybride polymeren in combinatie met silica-versterkte NR het voornaamste onderwerp van dit PhD proefschrift. Een inleiding in de ontwikkeling van de silica-technologie voor banden wordt gegeven in **Hoofdstuk 1**. Een literatuur-overzicht betreffende hybride vulstoffen van silica met CB en OrganoClay (OC) als secundaire vulstoffen en hybride polymeren voor silica-versterkte NR in combinatie met BR of SBR als secundaire polymeren wordt gegeven in **Hoofdstuk 2**.

Het experimentele gedeelte begint met optimalisering van de meng-condities, met name om het effect na te gaan van de meng-temperatuur voor silica-versterkte NR met kleine hoeveelheden secundaire vulstoffen: **Hoofdstuk 3**. Variatie van de temperatuur-instelling van de interne menger in het begin van de mengcyclus wordt bestudeerd voor een combinatie van silica met CB N134, en een combinatie van silica met OC in een verhouding van 45/10 parts per hundred rubber (phr). Met toename van de initiële temperatuur- instelling van de menger leidt de verhoogde lossings-temperatuur voor de NR-mengsels gevuld met silica/secundaire

vulstoffen tot een betere silaniserings-reactie tussen de silica en de coupling agent TESPD. Echter, bij te hoge mengtemperatuur wordt een afname in mengsel-eigenschappen waargenomen ten gevolge van NR degradatie. De silica/CB- gevulde NR vertoont een hogere vulkanisatie-snelheid en trek-moduli, terwijl de trek-eigenschappen bij breuk en de tan delta bij 60°C vergelijkbaar blijven t.o.v. een zuiver silica-gevuld systeem. Silica/OC-gevulde NR vertoont een lager Payne effect, hogere vulkanisatiesnelheid, lagere moduli gecombineerd met trek-rek eigenschappen bij breuk vergelijkbaar met silica of silica/CB, een hogere tan delta bij -20°C en 0°C, als aanwijzingen voor betere ijs- en natte grip van bandenloopvlakken daarmee geproduceerd, respectievelijk een lager tan delta bij 60°C vergeleken met het silica-gevulde systeem, als indicatie voor verlaagde rolweerstand van banden. Het gebruik van hybride vulstoffen, kleine hoeveelheden secundaire vulstoffen zoals CB en OC in het bijzonder naast silica in NR biedt daarom de mogelijkheid van verdere verbetering in slijtage weerstand, natte tractie en rolweerstand van bandenloopvlakken.

Omdat de hybride vulstoffen als silica/CB N134 en silica/OC de mogelijkheid bieden om de mengsel-eigenschappen te verbeteren, in het bijzonder de belangrijkste banden-eigenschappen in vergelijking met zuivere silica-systemen, is een goede dispersie van de vulstof in de rubber matrix een belangrijke factor om goede versterking en mengsel-eigenschappen te verkrijgen. Aangezien de verwerkingscondities als mengtemperatuur en mengprocedure een invloed hebben op de dispersie en derhalve de eigenschappen, is het van doorslaggevend belang om een geoptimaliseerde mengtemperatuur voor silica-versterkte NR mengsels te benutten.

Hoofdstuk 4 vergelijkt drie verschillende mengvolgordes voor het toevoegen van secundaire vulstoffen aan de silica mengsels en optimaliseert de toevoeging van TESPD bij een verhouding van 45/10 phr voor silica/secundaire vulstof hybride systemen. De belading van CB N134 of OC samen met een eerste helft silica resulteert in optimale mengsel eigenschappen, zoals waar te nemen in een laag Payne effect, een hoger totaal Bound Rubber Content (BRC), hogere scheursterkte, lagere tan delta bij 60°C, en hogere tan delta bij -20°C vergeleken met zuivere silica als vulstof. Door variëren van de TESPD belading vertonen beide vulstof systemen een afname in Payne effect en de mengsel viscositeiten, toename van de vulkameter torsie, schijnbare crosslink dichtheid, modulus en treksterkte met toenemende TESPD-dosering, terwijl de scheursterkte en de dynamische eigenschappen een optimum laten zien. Op basis van deze gezamenlijke eigenschappen wordt het optimum in TESPD gehalte vastgelegd op 2,3 phr voor silica/OC en 4,1 phr voor silica/CB hybride vulstofsystemen, wat een verlaging inhoudt van de hoeveelheid coupling agent en derhalve lagere kosten van de rubber producten.

Silica-silaan technologie is geïmplementeerd om conventionele CB in banden loopvlak mengsels te vervangen, met name voor personenwagenbanden om rubberen loopvlakken te verkrijgen met lagere rolweerstand, hogere natte tractie en vergelijkbare slijtageweerstand. Die technologie kan ook worden toegepast voor op NR vrachtwagen banden loopvlak mengsels. Omdat de slijtageweersstand echter de levensduur beïnvloedt en omdat dit een probleem is voor silica-versterkte banden loopvlak mengsels, richt **Hoofdstuk 5** zich op het effect van lage hoeveelheden CB als secundaire vulstof op de eigenschappen van hoog-dispergeerbare silica-gevulde NR mengsels. De gedeeltelijke vervanging van silica door CB N134 met hoog specifiek oppervlak en hoge structuur levert een duidelijk synergistisch effect op voor het algehele eigenschappenpatroon. Verschillende hoeveelheden CB N134 worden gebruikt ter vervanging van silica in de mengsel formulering teneinde het totale vulstof gehalte gelijk te houden op 55 phr. Een toenemende verhouding CB in de hybride vulstoffen verhoogt op gelijkmatige wijze de mengsel viscositeiten, vulkanisatiesnelheid index, 300% modulus en DIN slijtage index. Bij laag gehalte aan CB, d.w.z. bij 0-36 gew% CB ten opzichte van het totale vulstofgehalte, veranderen het Payne effect en de tan delta bij 0°C en 60°C als indicatief voor natte tractie en rolweerstand maar marginaal, maar nemen daarboven gestaag toe. Aanvulkanisatie- en vulkanisatie-tijden worden korter in aanwezigheid van CB, hetgeen een toename in productiviteit mogelijk maakt. Het Bound Rubber gehalte en de mechanische eigenschappen als treksterkte, breukrek, scheursterkte en tan delta bij -20°C als indicatie voor ijs-tractie, vertonen een optimum bij 18 gew% CB betrokken op het totale vulstofgehalte, ofwel bij een verhouding silica/CB van 45/10 phr. Betrokken op banden eigenschappen als ingegeven door de laboratorium test resultaten, kunnen de slijtage weerstand, de natte grip en ijs tractie daarom worden verbeterd terwijl de banden rolweerstand kan worden gehandhaafd op het optimum niveau voor deze silica/CB verhouding.

Het gebruik van OC in combinatie met silica of als hybride vulstof geeft de mogelijkheid de eigenschappen van silica banden te verbeteren als ingegeven door een lager Payne effect, hogere tan deltas bij -20°C en 0°C, aanwijzingen voor betere ijs- en natte grip eigenschappen, respectievelijk een lagere tan delta bij 60°C vergeleken met het zuivere silica-gevulde systeem, aanwijzing voor verlaagde rolweerstand. **Hoofdstuk 6** betreft onderzoek naar het effect van dosering van OC als secundaire vulstof in hoeveelheden van 0-36 gew% betrokken op het totale gehalte vulstof of anders 0-20 phr, in combinatie met silica en TESPD als silaan coupling agent. Bij verhoging van de dosering OC in de silica-gevulde NR mengsels gaat het Payne effect en de mengsel viscositeiten omlaag, hetgeen aanwijzingen geeft voor lagere vulstof-vulstof

interactie en verbeterde verwerkbaarheid. De resultaten geven kortere aanvulkanisatie- en vulkanisatie-tijden, wat de mogelijkheid biedt om de productiviteit te verbeteren doordat de cyclustijden verkort kunnen worden. Ook worden verhoogde tan delta bij -20°C en bij 0°C waargenomen. De optimale hoeveelheid OC ligt bij 9 gew% t.o.v. het totale vulstof-gehalte of bij een verhouding van 50/5 phr silica/OC, en geeft een goede balans in mengsel eigenschappen zoals Payne effect, vulkanisatiesnelheids index, tan delta bij -20°C, tan delta bij 60°C en DIN slijtage weerstand. De resultaten laten zien dat het gebruik van hybride vulstof banden kan opleveren met beter natte tractie, lagere rolweerstand en verbeterde slijtage weerstand vergeleken met het puur silica-gevulde systeem.

De Organoclay in het huidige proefschrift bevat 47 gew% oppervlakte-modificatiemiddel, een type dimethyl dihydrogenated tallow ammonium chloride (2HT). **Hoofdstuk 7** beoogt het effect te onderzoeken van dit oppervlakte-modificatiemiddel op de eigenschappen van silica-versterkte NR vrachtwagenbanden loopvlak mengsels, door gebruik te maken van silica/2HT, silica/OC en silica/MontMorilloniTe (MMT)/2HT. De doseringen van 2HT zijn gevarieerd van 0-9,5 phr, deze hoeveelheden berekend op basis van de 2HT-gehaltes in de OC zelf. Door het gehalte 2HT te verhogen nemen de mengselviscositeit, het Payne effect en de aanvulkanisatietijd significant af. Op basis van de eigenschappen van zowel ongevulkaniseerde mengsels als vulkanisaten ten aanzien van het Payne effect, trek-rek eigenschappen, DIN slijtage weerstandsindex, schijnbare crosslink dichtheid, tan delta bij -20°C en tan delta bij 60°C, werd een overall beste balans in eigenschappen waargenomen bij 4,7 phr modificatie-middel voor een silica-gevuld en een silica/MMT-gevuld mengsel, en anderzijds bij 5,0 phr OC wat van zichzelf 2,4 phr modificatiemiddel bevat, voor een silica/OC-gevuld systeem. Bij het optimale gehalte 2HT als oppervlakte modificatie-middel van de vulstof konden een lager Payne effect, hogere vulkanisatiesnelheids-index, hogere tan delta bij -20°C en lagere tan delta bij 60°C worden verkregen, hetgeen de mogelijkheid aantoont van het gebruik van het zuivere modificatiemiddel op zich om de verwerkbaarheid te verbeteren, evenals de rolweerstand, natte tractie en slijtageweerstand van op silica gebaseerde mengsels voor bandenloopvlakken.

Om de eigenschappen van silica vrachtwagenbanden loopvlak mengsels te verbeteren, en in het bijzonder de slijtageweerstand, is het effect van doseringen van hoog-cis-gehalte BR, of met hoog-vinyl-gehalte in oplossing gepolymeriseerde SBR (SSBR) als secundaire polymeren in silica-gevulde NR mengsels onderzocht in vergelijking met pure silica-versterkte NR mengsels: **Hoofdstuk 8**. Doseringen van BR of SSBR in hoeveelheden van 0-30 phr in

combinatie met NR bij 100-70 phr leiden tot langere aanvulkanisatie- en optimum vulkanisatie-tijden, en lagere mechanische eigenschappen. Bij toenemende hoog-cis BR hoeveelheden wordt een betere tan delta bij 60°C verkregen als aanwijzing voor verlaagde rolweerstand van bandenloopvlakken daarop gebaseerd, en betere schijnbare crosslink dichtheid en DIN slijtageweerstand index, respectievelijk betere tan delta bij -20°C en 0°C als aanwijzingen voor de ijs- en natte tractie. De resultaten laten ook een optimum dosering zien van NR in combinatie met BR of SSBR bij een verhouding van 80/20 phr zoals blijkt uit de Bound Rubber gehalten en 300% modulus. Bij silica-gevulde mengsels met optimale verhouding van NR/BR, kan 56% verbetering van de DIN slijtageweerstand worden bereikt.

Om de eigenschappen van silica vrachtwagen banden loopvlak mengsels verder te bestuderen wordt het effect van de vinyl-gehalten in BR en SSBR als secundaire polymeren nader onderzocht in silica-gevulde NR mengsels bij optimale verhouding van 80/20 en in combinatie met een optimale hoeveelheid secundaire vulstoffen en polymeren in silica-gevulde NR mengsels in **Hoofdstuk 9**. Met toenemend vinyl-gehalte in BR in combinatie met NR worden een verbeterd Payne effect, betere 300% modulus, versterkingsindex, tan delta bij -20°C en 0°C verkregen, terwijl de treksterkte, rek bij breuk en DIN slijtage weerstandsindex afnemen met toenemend vinyl-gehalte. Verhoging van het vinyl-gehalte in SSBR laat verbetering zien in het Payne effect, de 300% modulus, tan delta bij -20°C en 0°C en een klein beetje in DIN slijtage-weerstand index. Silica/CB N134-gevulde NR/BR en NR/SSBR, respectievelijk silica/OC Dellite 67G-gevulde NR/BR en NR/SSBR geven positieve effecten te zien in aanvulkanisatie- en optimale vulkanisatie-tijd, met lichtelijk veranderd Payne effect, trek-rek eigenschappen, tan delta bij -20°C en 0°C, resp. DIN slijtageweerstand in vergelijking met het mengsel op basis van CB. Het gebruik van OC geeft verbetering in Payne effect en tan delta bij 60°C, aanwijzingen voor een verlaagd vulstof-vulstof netwerk en diensgevolge lagere rolweerstand van het bandenloopvlak-mengsel in vergelijking met het mengsel zonder OC.

Ofschoon zuivere silica-gevulde rubber mengsels zelfs betere hoofdeigenschappen van banden opleveren, zoals lagere rolweerstand en natte tractie, is de slijtage-weerstand nog altijd lager dan voor CB-gevulde rubber mengsels. Om de hoofd band-eigenschappen van silica-gevulde rubber mengsels verder te verbeteren door gebruikmaking van secundaire vulstoffen als CB N134 of OC met verschillende vulstof-karakteristieken, is het gebruik hiervan in combinatie met silica of hybride vulstof systemen onderzocht. Over het geheel genomen richt dit proefschrift zich voornamelijk op de hoofd band-eigenschappen als weergegeven door de tan delta bij -20°C en 0°C voor ijs- en natte tractie respectievelijk, en tan delta bij 60°C voor

rolweerstand en DIN slijtageweerstand index op laboratorium schaal. Een optimum verhouding van silica/CB N134 hybride vulstoffen van 45/10 phr leidt tot beter ijs en natte tractie, resp. slijtage weerstand, bij gelijkblijvende banden rolweerstand. Bij optimum verhouding silica/OC bij 50/5 phr worden betere ijs-tractie, lagere rolweerstand en ook lichtelijk verbeterde natte tractie en slijtage weerstand verkregen in vergelijking met het zuivere silica-gevulde NR systeem. Verder onderzoek betreft de invloed van secundaire polymeren als BR of SSBR met verschillende glas-overgangstemperaturen en/of verschillende microstructuren, in samenspel met NR of als hybride polymeersystemen op de eigenschappen van de mengsels. De optimum verhouding NR/hoog-vinyl BR bij 80/20 phr vertoont een grote verbetering in ijs-en natte tractie, resp. slijtageweerstand, bij gelijkblijvende rolweerstand. Aan de andere kant gaf de optimum verhouding NR/hoog-vinyl SSBR bij 80/20 phr betere ijs- en natte tractie, resp. slijtageweerstand, maar slechtere rolweerstand van banden. Het laatste deel van dit proefschrift betreft de combinatie van optimale dosering secundaire vulstoffen en polymeren in silica-gevulde NR mengsels. Silica/CB-gevulde NR/BR en NR/SSBR resulteren in positieve effecten op ijs- en natte tractie, respectievelijk slijtageweerstand, maar slechtere rolweerstand. Daarentegen leveren silica/OC-gevulde NR/BR en NR/SSBR ook positieve resultaten betreffende ijs- en natte tractie, respectievelijk slijtageweerstand, maar houden de goede rolweerstand op pijl. Over het geheel genomen gaf de combinatie OC en BR met silica-gevulde NR daarom de beste hoofdeigenschappen van banden, in het bijzonder slijtageweerstand, hetgeen het hoofddoel was van dit proefschrift.

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Curriculum Vitae

Suppachai Sattayanurak was born in Songkhla, Thailand on the 21st of June 1984. He obtained his Bachelor of Science in Rubber Technology at the Faculty of Science and Technology, Prince of Songkla University (PSU), Pattani Campus, Thailand in 2007. The project topic was “Preparation of Thermoplastic Polyolefins Based on Natural Rubber and Polypropylene Blends”. After he got his bachelor degree, he started working at RPS Technologies. Co., Ltd., Pathumthani, Thailand in 2007-2008 and later changed job to Thai Bridgestone. Co., Ltd., (Nong Khae Plant), Saraburi, Thailand in 2008-2013, at the Compounding Section, Technical Department. He obtained his Master of Science in Petrochemistry and Polymer Science at the Faculty of Science, Chulalongkorn University, Bangkok, Thailand in 2012. The master thesis topic was “Properties of Styrene Butadiene Rubber Compounded with Devulcanized Waste Spew Rubber from Tire Manufacturing”. From 2013-2015 he worked at Bridgestone Asia Pacific Technical Center. Co., Ltd., Pathumthani, Thailand in the Product Process Development Section. In January 2016, he started studying his PhD under the joint program between the Prince of Songkla University (PSU), in the Faculty of Science and Technology, Pattani Campus, Thailand and the University of Twente (UT) in the Elastomer Technology & Engineering (ETE) group, Faculty of Engineering Technology. He studied and worked at both Universities, 2 years at the UT under supervision of Prof. Dr. Jacques W.M. Noordermeer and Prof. Dr. Anke Blume, and another 2 years at PSU under supervision of Asst. Prof. Dr. Kannika Sahakaro, on a project titled “Silica-Reinforced Natural Rubber: Shifting Tire Performance by Hybridization with Secondary Fillers and Polymers”. His PhD research was supported by the Netherlands Natural Rubber Foundation (Rubber Stichting, the Netherlands), Apollo Tyres Global R&D B.V. (the Netherlands) and the Prince of Songkla University (Thailand) PhD Scholarship.