Silica-Reinforced Natural Rubber for Low Rolling Resistance, Energy-Saving Tires

Aspects of Mixing, Formulation and Compatibilization

Wisut Kaewsakul

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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.

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Silica-reinforced natural rubber for low rolling resistance, energy-saving tires: aspects of mixing, formulation and compatibilization

By Wisut Kaewsakul

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SILICA-REINFORCED NATURAL RUBBER FOR LOW ROLLING RESISTANCE, ENERGY-SAVING TIRES

ASPECTS OF MIXING, FORMULATION AND COMPATIBILIZATION

DISSERTATION

to obtain
the degree of doctor at the University of Twente,
on the authority of the rector magnificus,
Prof. Dr. H. Brinksma,
on account of the decision of the graduation committee,
to be publicly defended
on Thursday, April 18th, 2013 at 14:45

by
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This dissertation has been approved by:

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To my beloved parents

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CHAPTER 1

INTRODUCTION

1.1 DEVELOPMENT OF NATURAL RUBBER TECHNOLOGY

The exudation of the white milky sap or latex obtained from the tree of *Hevea Brasiliensis* which is classified in the genus of Euphorbiaceae,[1] is practically the only important commercial source of natural rubber nowadays. Natural Rubber (NR) has a very long history after it has firstly been observed by Christopher Columbus during the American voyage in 1493–1496. He recorded that the natives of Haiti used the sap from some plants to make balls, water proof cloths and shoes. The tree which produces the white milky fluid was called in dialect: “caa-o-cahu”, meaning weeping tree.[2] After the discovery, the information of this material spread all over Europe, and contributed to the start of rubber technology and consequent polymer development.

In the beginning, use of NR encountered difficulties caused by its intrinsic thermoplastic behavior, i.e. melted (adhered to everything) and froze (cracked easily) in hot and cold weather, respectively. In 1839, Charles Goodyear[3] discovered a successful solution which essentially led to the fundaments of the up-to-date rubber industry. He invented that sulfur could react with NR under heated conditions leading to better rubber products which had properties far superior to those of the raw form. This procedure was named “vulcanization”. The considerable improvement in resistance to temperature changes and the unique properties of this elastic material resulted in an immediate increase in the use of NR for a variety of applications.

However, in those early days the amount of NR produced was not enough for the global demand. In the early 1930s, synthetic rubbers were first produced in Germany and consequently replaced natural rubber in many applications.[4] Out of 24.9 million tonnes of world-wide rubber consumption in 2010, 43.4 % is NR.[5] It is produced on plantations mainly located in Asia (approximately 90%), particularly in southeast countries: Thailand, Indonesia, and Malaysia. The other part is the synthetic rubbers, both commodity and specialty types, which are produced in a number of industrial countries, spread over the world. Raw materials for producing those synthetic rubbers are mostly obtained from petroleum or crude oils.

The introduction of a pneumatic bicycle tire made from natural rubber by John Dunlop in 1888 led to a large consumption of NR which greatly expanded the rubber industry also towards automotive applications.[6] Nowadays, more than half of NR is consumed in commercial vehicle tires including trucks, bus, aircraft, tractor, racing car, and off-the-road applications, since it provides an excellent flexibility and good resistance to blow-out (low heat-build up). In addition, a growing field for NR is in engineering applications, due to its outstanding dynamic properties, in particular its fatigue resistance, i.e. cycles to failure. As such, it is applied in the production of bridge bearings, commercial building pads, motor mounts, suspension systems, vibration isolators and rail pads. Another key advantage is its high resistance to tearing and cut growth, so that catastrophic failure of rubber articles can be avoided.

The properties of rubber goods depend significantly on the choice of rubber type, the compound compositions: fillers, curing agents, and other additives, the production process, as well as the shape and design of the products. In these respects, there has continuously been research in order to obtain products with superior properties, more environmentally friendly and cost effective. Due to the depletion of petroleum oils and more stringent environmental and safety concerns, the use of renewable materials and less toxic substances, to produce rubber products under more efficient energy use is one of the key directions at present and for the future. NR is a renewable material and a carbon dioxide (CO_2) sequester. Carbon dioxide is taken from the air to produce this natural polymer, and the rubber trees after their service life are normally used for furniture production. Therefore, the useful features of NR which enable benefits to human and environmental needs should be further implemented to extend its use as a sustainable material.

1.2 BACKGROUND AND RATIONALE

NR is a renewable material, which combines excellent mechanical and dynamic properties. It has been and still is in use in a variety of applications, mostly in the form of filled vulcanizates. Silica as a reinforcing filler in compounds has been used less than carbon black, but is growing tremendously in use, especially in the tire industry. The full replacement of carbon black by silica as reinforcing filler in passenger tire treads was firstly introduced by Michelin in 1992, since it significantly reduces rolling resistance and improves wet traction of tires.[7] The use of silica reduced tire rolling resistance by approximately 20% relative to carbon black.[8] Assuming correct tire pressures are maintained and making allowance for varying speeds and different driving conditions, a 20% reduction in rolling resistance corresponds to 3 – 4% fuel savings.[8] In addition, silica provides substantial benefits in winter tires and all-season tires as the silica-reinforced compounds are more elastic and flexible at lower temperatures leading to better grip and braking under winter conditions.[8]

A main drawback of silica comes from strong interparticle forces, making it difficult to obtain a good dispersion within the rubber matrix. The surface of precipitated silica exhibits a hydrophilic character with a number of silanol (Si-OH) groups which cause the formation of hydrogen bonds between aggregates and agglomerates. The hydrophilic nature of the silica surface and the tendency to form hydrogen bonds lead to a high filler-filler interaction which prevents easy dispersion during mixing and a poor compatibility between silica and hydrocarbon rubbers. As a consequence, inferior final vulcanizate properties are usually obtained. These difficulties can be overcome by use of silane coupling agents, which are able to react chemically with silica and rubber during the mixing and vulcanization stages, respectively.[9-11] Therefore, the mixing of silica filled compounds is basically different from that of carbon black.

The present research studies the role of silane coupling agent and then focuses on the utilization of modified NR in order to enhance the compatibility between silica and NR or silica-rubber interaction, which could lead to a reduction or a possible replacement of conventional silane coupling agents. Efficient use of silane coupling agents in silica-filled rubber compounds is rather difficult, caused by involvement of the silanization reaction. Various mixing-processing conditions need to be optimized for silanized silica-filled compounds. The use of modified NR could therefore give several advantages including cost savings, material availability and environmental benefits.

1.3 AIM OF THE PROJECT

The present project is designed to investigate an alternative route to enhance silica-NR interaction by the use of chemically modified NR, possessing some functional groups to react with the silanol groups on the silica surface. In order to thoroughly investigate the use of Epoxidized Natural Rubber (ENR) as raw materials, there are several factors to be taken into considerations. First, processing conditions as well as rubber formulation which influence mixing quality and silanization efficiency of silica-reinforced NR compounds are optimized. Interactions or reactions between rubber and silica, cure characteristics, mechanical and dynamic properties of the rubber compounds are investigated, to compare the use of modified NR versus unmodified NR with silane coupling agent. The mechanistic aspects of compatibilization are also studied through a variety of characterization tools.

1.4 CONCEPT OF THE THESIS

Chapter 1 — This thesis starts with an introduction of the history and development of NR technology, followed by a description of the background and aim of the project.

Chapter 2 — The use of silica in rubber compounds is reviewed. For better understanding of the silica technology developed for rubber applications, the history and literature are discussed with special emphasis on the improvement of silica reinforcement. In addition, the motivation and scope of the project are also given.

Chapter 3 — An experimental study first focuses on optimization of the mixing conditions which are to be used for further investigations. Because the mixing conditions are key parameters for silica reinforcement and have not yet been fully explored for NR compounds, an attempt to understand these factors which influence the properties of silica-filled NR compounds is carried out and discussed.

Chapter 4 — This section discusses the rubber recipe which plays a significant role on silica-reinforced rubber properties. Type and amount of silica, silane coupling agent, and diphenylguanidine are optimized. The surface area and structure of silica are taken into account, and correlated with the physical properties of the rubber compounds and vulcanizates.

Chapter 5 — Different types of modifying agents are employed to check the effect of various functionalities contained in the modifying chemicals, on the properties of NR compounds. A mechanism of the reactions that take place during processing the silica-based NR compounds, is defined.

Chapter 6 — With regard to the scorch safety of silica-filled compounds, bis-triethoxysilylpropyl tetrasulfide (TESPT) which is the most widely used silane coupling agent for silica-reinforced rubber systems is studied in comparison with bis-triethoxysilylpropyl disulfide (TESPD). Because of the different levels of the sulfur moiety in the structure of these two types of coupling agents, an investigation of sulfur compensation for the TESPD-added compounds is carried out, compared to the compound plus TESPT as a reference.

Chapter 7 — Diphenylguanidine (DPG) as a secondary curing accelerator for silica compounds is suspect for its toxicity, therefore alternative substances such as dithiophosphate (DTP) have been developed to replace DPG. In this chapter, a comparative study between DPG and DTP used in a silica-filled NR compound is performed.

Chapters 8 — This chapter focuses on the influence of epoxide functionality in ENR on the compatibility of silica-filled ENR compounds. Parallel studies with respect to various levels of epoxidation degree in ENR in the absence of TESPT, as well as a combination of ENRs with different loadings of TESPT are carried out. Physical/mechanical and dynamic properties of the compounds and vulcanizates are assessed to verify the reinforcing efficiency of silica.

Appendix — The experiments in this part are executed to confirm the linkage type of filler-to-rubber interactions in silica-filled NR and ENR compounds in the presence and absence of TESPT silane coupling agent. Unmodified squalene (Sq) and epoxidized squalene (ESq) are used as model compounds for NR and ENR, respectively. The reactions between silica and model squalenes are carried out at temperatures to resemble the optimum rubber compound dump temperature. The bound silicas in the mixtures are extracted and analyzed for their compositions by using the Fourier-transform infrared spectroscopy (FT-IR) technique.

Summary — The knowledge and insight derived from every experimental study are finally summarized in this section.

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CHAPTER 2

SILICA-REINFORCED RUBBERS WITH PARTICULAR EMPHASIS ON IMPROVING REINFORCEMENT EFFICIENCY

2.1 INTRODUCTION

To date, rubber products are vastly used in daily life because they serve various important functions. A variety of rubber products for different applications require differences in properties and performances which depend significantly on the right compounding ingredient combinations, including rubbers, additives, and reinforcing agents.

Reinforcement of rubbers by fillers is of practical and technical importance to improve product performance, and so has continuously been in research focus. The development of reinforcing fillers for tires, which involve the largest rubber consumption worldwide, is an obvious example. In the early nineteenth century, carbon black was the first commercial reinforcing filler developed for tires to improve modulus, tensile strength, abrasion resistance, skid resistance and other physical properties.[1,2] After that, all types of tires were reinforced by carbon black, until the observation of further improved tire performance with other filler systems was revealed in the 1990s. In 1992, Michelin introduced the "Green Tire" which employs silica as reinforcing filler.[3] The right combination of silica and silane coupling agent not only provides a comparable reinforcing efficiency compared to carbon black, but a silica-reinforced tire gives benefits in terms of vehicle fuel economy due to a lower tire rolling resistance compared to that of carbon black filled tires.[4,5]

In spite of the above mentioned success of silica used in tire compounds, difficulties are principally caused by the surface chemistry of this filler and its poor ability to interact with the rubbers. In the beginning, use of silica was very difficult because of its highly polar nature, and hence low compatibility with general purpose rubbers, leading to weak cohesive bonding forces.[6,7] However, today's situation is that silane coupling agents can overcome this major problem and therefore they are commonly used in industry. In addition to silane, the utilization of polar rubbers for further improvement in silica reinforcing efficiency is becoming a subject of interest.

In this chapter, the basis of reinforcing filler technology is described. This includes the history and development of silica. Special attention is paid to the mixing of silica, regarding the reactions that take place in the presence of coupling agents as well as of polar polymers. The scope of the project is also described.

2.2 REINFORCING FILLERS

Among the ingredients formulated in rubber compounds, fillers commonly have a significant effect on both compound and vulcanizate properties. Fillers used to modify the properties of rubbers normally possess an essential functionality which is able to bond to the rubber matrix and consequently improve the processability and final product performance. These active fillers are classified as reinforcing fillers. On the other side, the fillers which exhibit intermediate or a low ability of property improvement are identified as semi- and non-reinforcing types, respectively. The basic characteristics which determine these categories of fillers are not only particle surface activity, but also particle size, particle surface area and particle structure.

2.2.1 Factors influencing filler reinforcement

2.2.1.1 Particle surface activity. — Functional or active fillers can give a strong interaction between filler and rubber matrix when compared to inactive fillers, which relates to the affinity for and ability to react with the rubber.[8] Chemical interaction between filler and rubber depends significantly on the type or form of the functionality on the filler surface. Some fillers need to be modified in order to match the surface chemistry to a specific rubber. Silica, for example, is one of the active fillers which require a surface modification as will be described later.

2.2.1.2 Particle size. — Particle size of a filler is one of the key parameters which strongly affect rubber properties. Figure 2.1 shows a diagram of filler classification based on their particle size. Silica and carbon black have very small primary particle sizes in the range of 10 – 100 nm and are classified as reinforcing fillers which can significantly improve rubber performance. Fillers with particle size in the range of 100 – 1,000 nm and 1,000 – 10,000 nm are classified as semi- and non-reinforcing fillers (diluents), respectively. When the particle size is greater than 10,000 nm which greatly exceeds the polymer interchain distance already, the filler causes an area of localized stress, leading to elastomer chain rupture on flexing or stretching, and hence deterioration in rubber properties.[9]

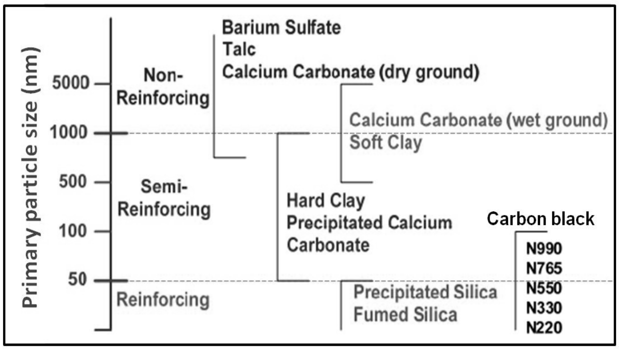

Figure 2.1 *Classification of fillers based on the size of the primary filler particle.*[9]

2.2.1.3 Particle surface area. — In the case of reinforcing fillers, they have a high surface area which provides more active contact sites, which provide a higher potential to contribute to strong filler-rubber interactions in rubber compounds. There are three methods used to measure the particle surface area of fillers; 1) the nitrogen surface area (NSA); 2) the statistical thickness surface area (STSA); both methods based on the BET (Brunauer-Emmett-Teller) nitrogen-adsorption theory according to ASTM D6556; and 3) the CTAB-adsorption (cetyl-trimethyl-ammoniumbromide) method. Recently, the measurement of carbon black surface area by the CTAB method according to ASTM D3765 has been withdrawn and replaced by the STSA technique, because the CTAB method is labor-intensive of nature and has poor testing precision.[10] However, the CTAB method is still applicable for silica in accordance with ASTM D6845. Basically, the NSA or BET method measures the overall surface area of the particles including micropores: pore diameters less than 2 nm (20 Å). The STSA and CTAB-adsorption methods estimate only the external surface area of the carbon black and silica particles, respectively. So, the values obtained from these two methods are defined as the specific surface area that is accessible to rubber molecules.[10] It is acknowledged that the physical properties of filled rubbers strongly correlate with the specific external surface area rather than with the BET values, where the specific surface area also shows a good correlation with the primary particle size.

2.2.1.4 Particle structure. – The primary particles of reinforcing fillers; silica and carbon black, are generally spherical. However, these particles are not stable during their production, but form aggregates/agglomerates or bundles because of self-association of the active functionalities on their surface.[11] The anisometry of these fillers is described in terms of "structure", which includes aggregate shape, density and size. The higher the structure, the better the reinforcement efficiency.[4,5,12] The measurement of this structure is based on the oil-adsorption technique according to ASTM D6854 since the former DBP-adsorption (dibutylphthalate) method is no longer accepted because of toxicity.

2.2.2 Black and non-black reinforcing fillers

Reinforcement of rubbers can be achieved by the addition of fillers which are generally classified into reinforcing and non-reinforcing fillers. In some cases, they are divided into black and non-black types. The efficiency of reinforcement depends on particle size, structure and surface area of the filler.[12-15]

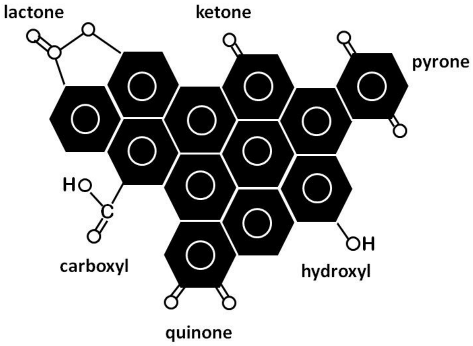

Figure 2.2 *Chemical surface of carbon black in the form of graphitic basal planes with various functional groups.*[15]

2.2.2.1 Carbon black. – Carbon black is most commonly used as reinforcing filler in the rubber industry because of its high capability for reinforcement. Figure 2.2 illustrates the surface chemistry of carbon black. It is primarily composed of carbon with presence of a low percentage of other hydrocarbon or oxygen-containing groups on its surface, e.g. phenol, carboxyl, ketone, quinine, lactone, pyrole, and lactone.[15] The relatively non-polar surface is compatible with hydrocarbon rubbers that are widely used in rubber compounding. The black has a limited number of chemically active sites (less than 5% of total surface) which arise from broken carbon-carbon bonds because of the methods used to manufacture the black. However, the presence of oxygen complexes is not essential for reinforcement in most general purpose rubbers. The reinforcing activity is mainly attributed to mechanical interlocking of the rubber onto the carbon black surface, the chemisorption of the rubber onto the filler surface due to free radical interactions between carbon atoms in the filler and in the rubber, and the Van der Waal forces between carbon black and rubber.[15]

2.2.2.2 Silica. — As carbon black can only be used in black rubber articles, a search for alternative active fillers which permit the production of highly durable colored products led to the development of non-black fillers. In the beginning, the use of silica as non-black reinforcing filler instead of carbon black caused various problems such as higher compound viscosity and more difficult processing. This is due to a major difference in polarity between the silica surface and rubber hydrocarbons. Figure 2.3 shows the surface chemistry of precipitated silica. The surface of silica aggregates or particles is virtually covered by silanol groups (-Si-OH) that are very polar and considerably chemically active.[16,17] This feature leads to low compatibility with general purpose rubbers, and hence weak filler-rubber interaction.[6,7]

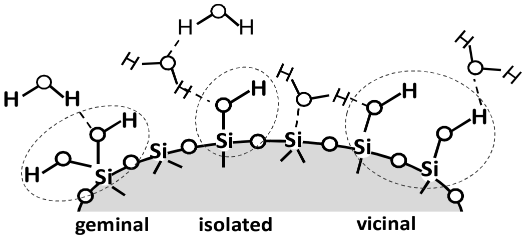

Figure 2.3 *Surface structure of silica with three different forms of silanol groups: geminal, isolated, and vicinal.*[16]

However, with the aid of coupling agents, properties of silica-filled rubber such as physical/mechanical properties or elasticity can be successfully improved.[3-7,18-20] Thus, silica is currently used next to carbon black as a main reinforcing filler to increase the usefulness of rubbers in various applications. Particulate fillers like carbon black and silica are able to increase the strength of vulcanized amorphous rubbers more than tenfold.[7] Thus, relatively few applications of elastomers are used in the unfilled or gum state. Styrene-butadiene rubber, for instance, has virtually no commercial use as an unfilled compound.

2.3 REINFORCING EFFECT

Reinforcement of rubber is often defined as the improvement in properties which generally means an increase in modulus, hardness, tensile strength, abrasion resistance, tear resistance or other properties. Accordingly, a practical definition of reinforcement is the improvement in service life of rubber articles that could fail in a variety of ways. One of the most important being rupture failure accelerated by fatigue, a process that occurs during the wear of a tire tread.[21]

2.3.1 Reinforcement concept

The reinforcement mechanism of filled rubber is better understood after the study on the strain dependence of filler-reinforced rubber by Payne (1965).[22,23] He studied the relation between the three-dimensional filler aggregates and the dependence of the storage and loss moduli on strain. It was concluded that the network of aggregates could easily be ruptured even at small strain. Subsequently, the Payne concept has been widely used to characterize the interaction between filler and filler as well as filler and rubber interaction, as illustrated in Figure 2.4.[24]

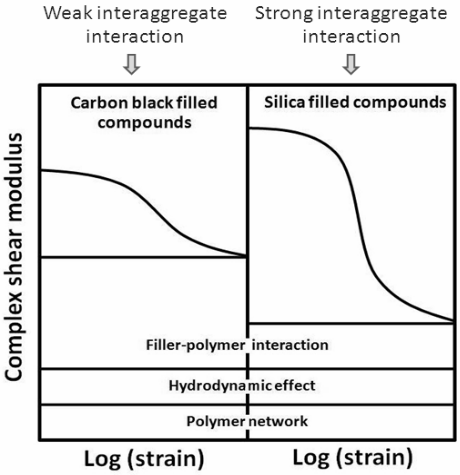

Figure 2.4 *The Payne concept of reinforcing filler-filled rubber compounds.*[24]

2.3.1.1 Filler-filler interaction: Payne effect. — The filler-filler interaction in reinforced rubber causes a strain-dependent contribution to the modulus. A drastic decrease of the storage modulus under variable strain amplitudes, from small to large deformations, was observed by Payne (see Figure 2.4). He explained that this behavior is the result of breakage of physical bonds (i.e. van der Waals forces and hydrogen bonds) among filler particles. The effect is strongly reversible when the strain is released and does not depend on the type of rubber, but is significantly dependent on the type of filler. The Payne-effect is stronger for silica when compared with that of carbon black (see Figure 2.4), as a consequence of the strong interparticle forces between the silica particles.[6,22-25]

2.3.1.2 Filler-rubber interaction. — Several models have been postulated regarding the filler-rubber interactions in carbon black filled compounds. Rubber chains can be trapped in the voids of the filler aggregates, and so they are immobilized and shielded from deformation.[26,27] In addition, the rubber layer attached on the surface of filler particles also exhibits an immobilized or glassy state character.[28-30] The immobilized rubber is attributed to physical interactions or chemical reactions as the case of a silica-coupling agent filled system, and is called "in-rubber structure" which means the strong filler-rubber interaction. The bundles of filler aggregates including trapped/bound rubber do not contribute to the elastic behavior of the rubber matrix, but act as rigid filler particles. Therefore, the in-rubber structure increases the effective filler loading and hence the strain independent contribution to the modulus.[26-29]

2.3.1.3 Hydrodynamic effect. — This parameter is another strain-independent contribution to the modulus. It is described as an increment in moduli of rubber compounds caused by the addition of filler particles. The Einstein-Guth-Gold relation,[29] as shown in Equation (2.1), is used to interpret the modulus of elastomers filled with poorly-reinforcing fillers, when the volume fraction of filler (Ø) is small (Ø<0.3);

$$G' = G_0'(1 + 2.5\phi + 14.1\phi^2) \qquad (2.1)$$

where G' and G_0' represent the moduli of the filled and unfilled elastomers, respectively. The ratio of G'/G_0' is called the strain amplification factor which indicates the magnitude of the local strain generated by the presence of the fillers. However, it is noteworthy that Equation (2.1) is not applicable for elastomer filled with well-reinforcing fillers like carbon black and silica, wherein the modulus becomes much larger than given by Equation (2.1). The formation of a three-dimensional network of linked carbon black aggregate particles resulting in the increased modulus is thought to be the cause of this discrepancy. Taking into account that the dispersed particles interact at practical concentrations and including the influence of an adjustable form factor (f) of the aggregates, Equation (2.2) has been proposed.[31]

$$G' = G_0'(1 + 0.67 f\phi + 1.62 f^2 \phi^2) \qquad (2.2)$$

2.3.1.4 Polymer network. **—** Before vulcanization, a small amount of polymer networking is formed by physical crosslinks of entangled chains and some chemical crosslinks occurred during polymerization with e.g. vinyl structures. However, the network of rubber is mainly generated during vulcanization by crosslinking chemicals. This crosslinking is also one of the strain-independent contributions to the modulus. The modulus of vulcanized rubber is proportional to the crosslink density of the networks, which depend significantly on the vulcanization system.

2.3.2 Postulated models for bound rubber in reinforcing filled systems

With regard to filler-rubber interaction in filled rubber compounds, several models of bound rubber, i.e. rubber partly bonded to filler particles, have been proposed. Medalia (1970)[26] and Kraus (1971)[27] proposed bound rubber in the form of occluded rubber: the aggregates or agglomerates of active fillers can form a filler-filler network by self-association in the rubber matrix, and trap some part of rubber in the void of their structure, as shown in Figure 2.5(a). It was proposed that the filler aggregates with occluded rubber behave as large filler particles, as the trapped rubber does not contribute to the elastic behavior of the rubber matrix at lower strain. Smith (1968)[28] as well as Pliskin and Tokita (1972)[29] suggested that rubber molecules are able to attach on the filler surface by chemical adsorption and then the model of shell rubber was proposed, as shown in Figure 2.5(b). Further, the glassy rubber shell model has been proposed[32] to support the idea of in-elastic behavior (glassy state) of the chemically bound rubber layer on the carbon black surface, as shown in Figure 2.5(c).

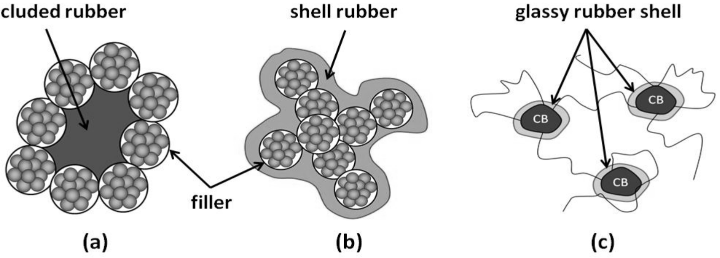

Figure 2.5 *Bound rubber models proposed by various researchers; (a): occluded rubber;[26,27] (b): shell rubber;[28,29] and (c): glassy rubber shell.[32]*

Several researchers[30,32-36] used proton nuclear magnetic resonance (^{1}H-NMR) to study the molecular flexibility of polymers when they are modified by filler particles, as reviewed by LeBlanc.[37] ^{1}H-NMR results have demonstrated that bound rubber composes of two bound layers with different levels of molecular mobility, as presented in Figure 2.6.[30,32-36]

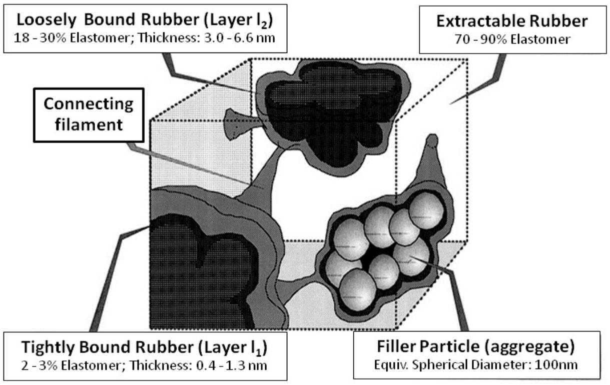

Figure 2.6 *Arrangement of layers of rubber around carbon black particle.*[37]

In the tightly bound layer (layer l_1) directly surrounding the filler surface, molecular motion is strictly constrained, that is the rubber polymer is in the glassy state. On the other side, molecules in the loosely bound layer (layer l_2) have much higher mobility, although they are more constrained relative to the molecular mobility of unfilled rubber vulcanizate. The thickness of the tightly bound layer is estimated to be 0.4-1.3 nm. This means that the bound rubber constitutes a substantial increase in the diameter of carbon black aggregates. However, the molecular mobility and glass transition temperature (T_g) of the rubber matrix in the filled system are shown to be hardly affected by the carbon black.[30,32-36] So as a whole, it is still a small amount.

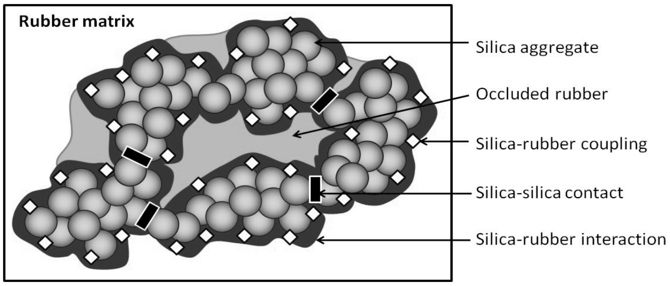

Figure 2.7 *Bound rubber model of a silica/coupling agent–filled rubber compound.*[38]

The model of rubber reinforcement with silica modified by a silane coupling agent is shown in Figure 2.7. The silica aggregates form a network by strong hydrogen bonding. Apart from the occluded rubber, there is a layer of bound rubber chemically bonded to the silica surface by the organosilane coupling agent. In addition, some rubber chains are probably also loosely adsorbed on the modified surface which also contribute to bound rubber, but silica-rubber interaction is very weak in this latter case. Under high deformation, the filler network partially breaks open leading to the reduction of occluded rubber and hence the deformation of the matrix. However, with the aid of coupling agent, the rubber polymers chemically attached to the silica surface and occluded rubber remain grossly immobilized, and therefore still contribute to the modulus.[38]

2.4 TECHNICAL DIFFICULTIES IN USING SILICA

The problems of using silica come from its polar nature, which affects the vulcanization/cure characteristics and compatibility with non-polar elastomers. Because the silica surface is acidic and has a number of hydroxyl groups as illustrated in Figure 2.3, it forms strong hydrogen bonds with either basic or polar materials such as cure accelerators. The adsorption of curatives by silica and H-bonds with itself results in tight aggregation of silica and causes an adverse effect on cure behavior and a poor dispersion of silica in rubber compounds.[6,7,39,40]

The filler dispersion of silica-filled rubber compounds is generally worse than carbon black-filled ones. It is known that good dispersability of filler in a rubber compound is very important, as the mechanical properties are controlled by the degree of filler dispersion.[6,7] Moreover, when a large amount of silica is added, the viscosity increases substantially, making the rubber compounds more difficult to process, and causing excessive wear of the processing equipment.[41,42] In order to solve these problems, various coupling agents are in use when mixing silica into rubber compounds.[18,38-40,43]

The temperature window for mixing of silica compounds is rather limited by the decreasing silanization rate at low temperature and risk of scorch at high temperature. High temperatures improve the silanization rate and reduce sterical hindrance of the silylpropyl group of the coupling agent by increased thermal mobility.[41,42,44] Reuvekamp (2003)[45] studied the mixing of silica-filled SBR/BR with the use of bis-triethoxysilylpropyl tetrasulfide or TESPT as silane coupling agent, and found the results as shown in Figure 2.8.

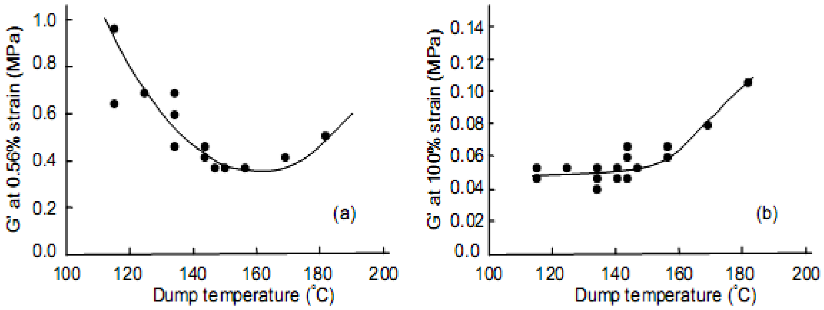

Figure 2.8 *Influence of mixing dump temperature on storage modulus (G') at; (a): 0.56% strain (Payne effect); and (b): 100% strain.*[45]

The Payne effect decreases with increasing mixing dump temperature up to 150°C and then slightly increases. On the other hand, the storage modulus at 100% strain starts to increase at more than 150°C dump temperature, resulting from premature scorch during the mixing process. Therefore, the final mixing temperature should be in the range of 145°C to 155°C to achieve a good silanization reaction and to avoid pre-crosslinking or scorch.[45] The reaction rate is increased with increasing concentration of silane, but finally reaches a plateau, i.e. the rate is limited by the limited amount of accessible silanol groups on the silica surface.[18,46]

2.5 IMPROVEMENT OF SILICA REINFORCING EFFICIENCY

Utilization of silica for rubber reinforcement differs from the use of carbon black since the polarity of the silica surface makes it incompatible with rubbers, particularly non-polar rubbers, resulting in agglomeration of silica in the rubber matrix. Moreover, the silanol groups are acids and cause adsorption of curatives, resulting in delay of the vulcanization reaction and, thus reduction of crosslink density. Therefore, modification of the silica surface as well as the use of polar rubbers are used in order to improve adhesion between rubber and filler, and to enhance the properties of the rubber vulcanizates.[18,39,40,43,47]

2.5.1 Modification of silica surface by using silane coupling agents

2.5.1.1 Properties of compounds and vulcanizates. — The chemical treatment of silica surfaces has become the most successful method to improve rubber-filler interaction and reduce filler-filler interaction. Among those chemical treatments, coupling agents are widely used to improve filler dispersion, and to prevent chemical adsorption of curatives on the silica surface. This involves an increase in adhesion between rubber and silica, improvement in wetting of silica, rheology and other handling properties.[39,40] The coupling agent also modifies the interface region to strengthen the organic and inorganic boundary layers. Silica coupling agents or X_3SiRY are characterized by dual functionalities. RY represents an organofunctional group and X represents a hydrolyzable alkoxy group attached to the silicium atom. The organofunctional groups are chosen for reactivity or compatibility with the polymer, while the hydrolyzable alkoxy groups are to react with silanol groups forming a chemical bond to the silica surface.[48]

When a silane is incorporated in silica-filled rubber compounds, it produces some remarkable property enhancements. For example, a mercaptosilane added to a silica-filled SBR formulation, produces a threefold increase in 300 % modulus, a 30 % increase in tensile strength and a significant reduction in heat build up and compression set.[7] This is because silanes have functionalities capable of chemical reactivity with both the silica and the rubber network. For the mercaptosilane in sulfur vulcanization, the alkoxysilyl groups react with silanol-groups on the silica surface to form a stable siloxane linkage, while the organic functionality can participate in reactions that lead to a linkage with the rubber. Thus, it appears that silanes with the appropriate functionality provide a chemical bond between the silica particles and the rubber network. This coupling, then, is apparently responsible for the full reinforcing action of the silica. This indicates that a maximum reinforcement by filler requires strong attachments to the rubber, as well as a small ultimate particle size.[7]

Furthermore, an increase in crosslink density of the silica/rubber vulcanizates in the presence of a silane coupling agent is observed. This leads to an increase in the final thermal stability of the composites. The results can be explained by the fact that there is a development of organic functional groups on silica surfaces treated by coupling agents, resulting in an increase of the adhesion at the interface between silica and rubber matrix.[49] Ansarifar and coworkers[50] studied the reinforcing effect of silica and silane coupling agent on the properties of NR vulcanizates. They found an improvement in crosslink density and bound rubber as a function of bis-(3-triethoxysilylpropyl) tetrasulfide (TESPT) loading. The tensile strength, elongation at break, stored energy density at rupture and cohesive tear strength deteriorated at low loading of TESPT, but they subsequently increased after sufficient amount of TESPT was introduced into the compound. The better filler dispersion in the rubber matrix was accounted for the improvement in properties of the vulcanizates. Nevertheless, the cyclic fatigue life was adversely affected, and the hardness hardly changed as a result of adding TESPT to the rubber.

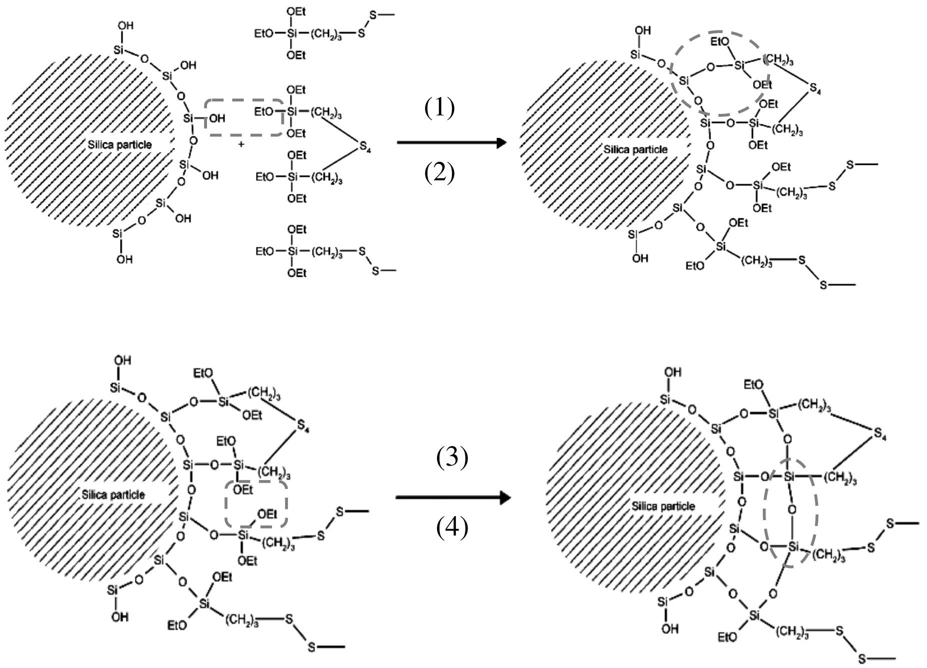

Figure 2.9 *Silanization mechanism of silica and TESPT.*[53]

2.5.1.2 Mechanism of silanization and coupling reactions. — The reactions between silica, silane coupling agent and rubber have been extensively reviewed.[41,45,51] The reactions of TESPT as a coupling agent for rubber and silica are illustrated in Figure 2.9. During mixing, one of the ethoxy-silyl groups of the coupling agent reacts with a silanol group of the silica by either (1) direct condensation or (2) hydrolysis then condensation. This is followed by a condensation reaction between pairs of neighboring silane molecules which can also occur by either (3) hydrolysis then condensation or (4) homocondensation.[18,52,53] During vulcanization, the reaction between the coupling agent and the rubber takes place through added sulfur in the compound or that generated by disproportionation of TESPT, as schematically shown in Figure 2.10. The reaction between the silane and rubber that occurs during vulcanization completes the silica-silane-rubber coupling and gives rise to better filler-polymer interactions, resulting in maximum reinforcement.[53-55]

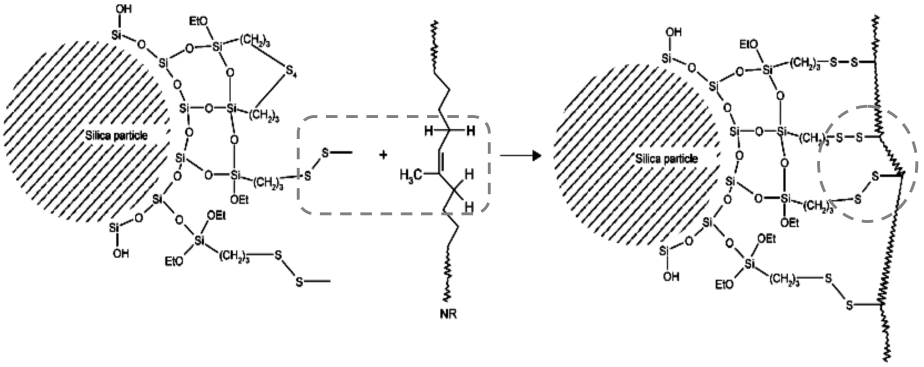

Figure 2.10 *Reaction between rubber and TESPT.*[53]

2.5.2 Use of polar elastomers in silica-filled compounds

Beside various coupling agents, polar elastomers are known to improve the properties of silica-filled rubber vulcanizates. The interaction between silica and rubber and its influences on properties of rubber have been studied extensively for decades. Several published papers have revealed that precipitated silica could interact strongly *via* primary chemical bonds with functionalized polymers such as chlorosulfonated polyethylene (CSM)[56], epoxidized natural rubber (ENR)[57-60] and carboxylated nitrile rubber (XNBR).[61]

Recently, it has been reported that the properties of silica-filled natural rubber (NR) and silica-filled ethylene-propylene-diene rubber (EPDM) could be improved by adding small amount of polychloroprene rubber (CR).[62,63] Improvement of the modulus and delta torque ($M_H - M_L$) of the vulcanizates was obtained. However, the Mooney scorch time increased with increasing CR content, because the chloroprene unit of CR has less allylic carbons and less reactive double bonds than the isoprene unit of NR. The tensile strength and elongation at break increased by adding CR. This was attributed to the improvement in filler dispersion as a result of the occurrence of hydrogen bonding between chlorine on CR and silica, as schematically shown in Figure 2.11. The optimum properties were obtained when the CR content was about 6 phr.[62] Das and coworkers[63] investigated the effect of CR addition on the dispersion of silica in ethylene-propylene-diene rubber (EPDM). The results revealed that the optimum physical properties were achieved when the blend ratio of EPDM:CR equaled to 92.5:7.5 by weight.

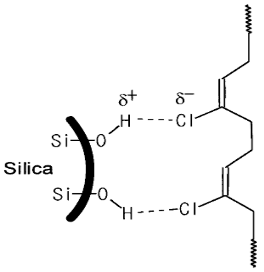

Figure 2.11 *Interaction between polychloroprene rubber and silica.*[62]

Sun and coworkers[64] studied the effect of nitrile rubber (NBR) on the properties of silica-filled NR vulcanizates. They observed a decrease in the rheometer torques of compounds at optimum vulcanization times with increasing NBR content. The scorch time and optimum cure time became shorter as NBR content increased. The mechanical properties such as modulus and hardness were improved by adding NBR. This was attributed to the polar nitrile groups in NBR which could form hydrogen bonds with silanol groups of silica and result in strong silica-NBR interaction. As a consequence, the dispersion is enhanced. In another report, Choi and coworkers[65] found improvements in crosslink density, modulus, heat build up and wear properties of silica-filled styrene-butadiene rubber (SBR) vulcanizates containing acrylonitrile-styrene butadiene rubber (NSBR). By increasing the NSBR content, the bound rubber content increased and the cure time and cure rate became faster. Since NSBR has basic nitrile groups as well as the SBR structure, it is compatible with both silica and SBR leading to the enhancement of silica dispersion.

Manna *et al.*[58] indicated that epoxidized natural rubber (ENR) could interact chemically with precipitated silica when the mix of the two was extruded at 150 – 170°C. The extent of interaction between the rubber and silica depended on the extrusion time, volume fraction of filler, shear rate and the addition of silane coupling agent. In this work, N-3-(N-vinylbenzylamino) ethyl-γ-amino propyl trimethoxy silane monohydrochloride was used as coupling agent. The activation energy of the chemical interaction between ENR and silica decreased on the addition of the silane. The authors suggested a probable mechanism of chemical interaction between ENR and silica, illustrating the role of coupling agent in the chemical interaction as shown in Figures 2.12 and 2.13. During high temperature molding of the rubber-filler mixture, the silanol groups on the silica filler surface directly react with the epoxy groups of ENR (see Figure 2.12) and with $-OCH_3$ group of the coupling agent, while $-NH_2^+-$ reacts with the epoxy groups of ENR (Figure 2.13) leading to the coupling bond formation.

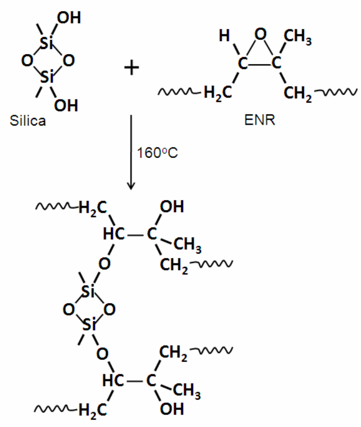

Figure 2.12 *Proposed mechanism of the reaction between ENR and silica in the absence of silane coupling agent.*[58]

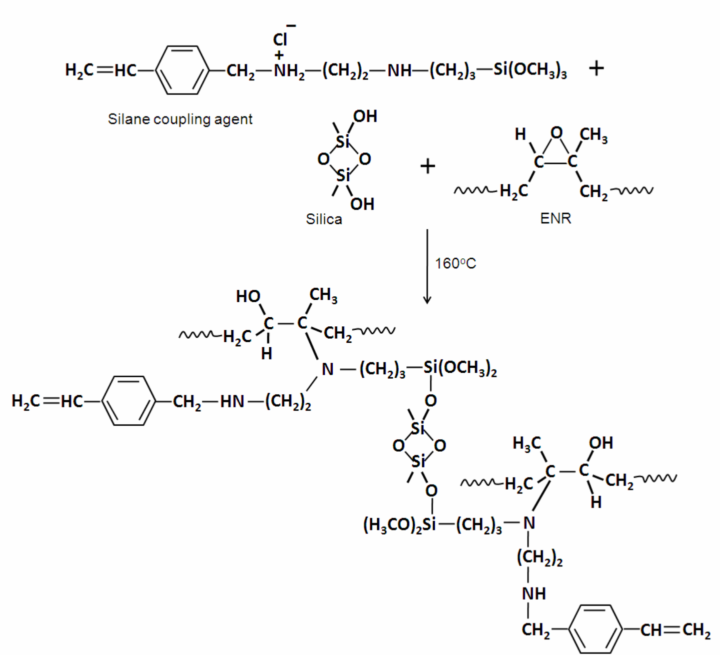

Figure 2.13 *Proposed mechanism of the reaction between ENR and silica in the presence of silane coupling agent.*[58]

Cataldo[66] reported improved mechanical properties of silica-filled NR compounds through the use of epoxidized natural rubber (ENR) without using a silane coupling agent. He suggested that the reason for these improvements lies in the polar nature of ENR which interacts strongly with the silica surface by the hydrogen bonding mechanism. George and coworkers[67] also found that incorporation of ENR in nitrile rubber (NBR)-silica composites could also modify the technological properties. Observations from bound rubber, rheometric studies and gel fraction also supported these results. They suggested that NBR and ENR can form self-crosslinked structures (I) and ENR could also link with silica particles (II) at the vulcanization temperature, thus functioning as a coupling agent as depicted in Figure 2.14.

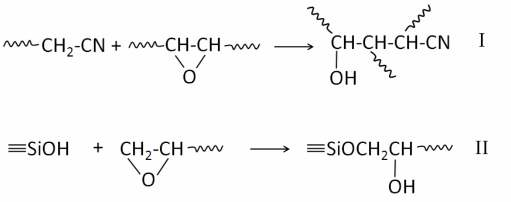

Figure 2.14 *ENR Functioning as coupling agent for silica-filled NBR.*[67]

Enhancement of silica-polymer interaction can also be obtained through some functional groups such as maleic anhydride (MA). Bikiaris *et al.* [68] utilized maleic anhydride grafted polypropylene (PP-*g*-MA) to compatibilize between polypropylene and nanosilica. It was demonstrated that the use of PP-*g*-MA resulted in a reduction of silica agglomerates and hence finer dispersion. This was attributed to a reaction between the hydroxyl groups on the silica surface and the maleic anhydride groups of the modified polymer. Interaction between hydroxyl groups of a paper sludge and maleic anhydride groups of maleated natural rubber (MNR) has also been proposed.[69] Additionally, Sahakaro and Beraheng[70] investigated silica-filled MNRs in comparison with unmodified natural rubber, both with and without silane coupling agent. It was found that, for the compounds without silane, the MNR with 6 phr of maleic anhydride showed the lowest filler-filler network interaction as indicated by a decrease of storage modulus upon increase of strain in the filled compound, i.e., the Payne effect. This MNR compound also yielded optimum mechanical and dynamic properties due to an improved silica dispersion, as confirmed by SEM micrographs. They discussed that the maleic anhydride groups grafted onto natural rubber molecules of the MNRs enhance the polarity of rubber and thus an interaction between the anhydride groups and the hydroxyl groups on the silica surface, as postulated in Figure 2.15. Moreover, the addition of silane into the MNR compounds could further increase filler-rubber interaction and decrease filler-filler interaction.

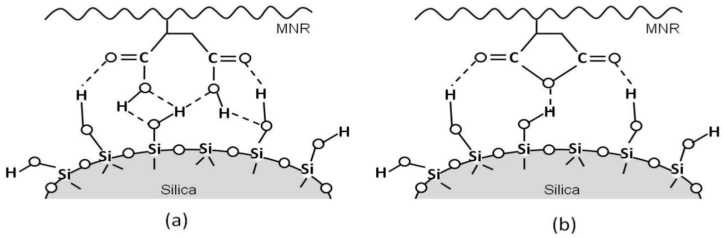

Figure 2.15 *Postulated interactions between the maleic anhydride groups of MNR and the hydroxyl groups on the silica surface.*[70]

2.6 MOTIVATION AND FOCUS OF THE PROJECT

Natural rubber is an attractive polymer as it combines unique mechanical and elastic properties. In addition, it is a renewable material which is produced from rubber trees and hence does not require petroleum oil for its production. So, natural rubber offers profound importance for both human development and environmental conservation.

Silica technology used for rubber has long been developed, since silica can reinforce rubber and gives high performance of articles, particularly in tires. The major problem of this combination is that silica has a relatively high polarity by nature and can not easily be mixed with natural rubber which is a non-polar material. Furthermore, NR is more susceptible to degradation under excessive mixing conditions, compared to its synthetic counterparts. To date, bifunctional organosilane type coupling agents effectively solve the incompatibility drawback as it is able to hydrophobize silica to become more compatible with hydrocarbon rubber and to additionally strengthen the interaction between silica and rubber.

However, silane chemistry is rather complicated because of the necessary *in-situ* reactions during rubber processing. The mixing temperature for silica/silane coupling agent filled rubber needs to be approximately 140-150°C which quite requires a high energy input. Alternative routes for improving processability and utility of silica-rubber mixes is therefore to be searched for. Polar-modified natural rubber is of interest because it may lead to a reduction or a possible replacement of conventional silane coupling agents. This material may also give several advantages, like production cost savings, material availability, environmental benefits and a market expansion of modified natural rubber.

In this thesis, the effect of silica used in normal natural rubber (unmodified) is a priority to be well understood, prior to switching to modified natural rubber. Therefore, the thesis is divided into two main parts; 1) silica-filled unmodified natural rubber; and 2) silica-filled modified natural rubber. In the first part, mixing conditions, rubber formulation, effect of various modifying agents, the use of a disulfane-containing bifunctional organosilane instead of the tetrasulfane type, and the replacement of diphenylguanidine by dithiophosphate, are investigated. In the second part, the influence of functionalities grafted onto natural rubber in the form of epoxidized natural rubber is evaluated, in comparison with the use of conventional silane in silica filled compounds cured with a sulfur vulcanization system. Reinforcing efficiency is monitored by measuring silica dispersion ability, i.e. reinforcement parameter, flocculation kinetics, and the Payne effect or filler-filler interaction, filler-rubber interaction, i.e. bound rubber measurements, as well as other compound properties, i.e. cure characteristics and Mooney viscosity. All the compound properties are analyzed in parallel with the mechanical and dynamic properties of the vulcanizates.

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CHAPTER 3

OPTIMIZATION OF MIXING CONDITIONS FOR SILICA-REINFORCED NATURAL RUBBER COMPOUNDS

The dump temperature and mixing interval between rubber, silica and silane coupling agent for silica-filled natural rubber (NR) tire tread compounds using bis-(triethoxysilylpropyl) tetrasulfide (TESPT) as silane are optimized. The dump temperature turns out to be the key parameter governing the properties of the silica-filled NR compounds. The increase in viscosity of the compounds by changing the dump temperature from 100-150 °C indicates that inevitably some cross-linking of NR occurs by sulfur contained in TESPT, simultaneous with the silanization reaction between silica and silane. However, the viscosity decreases again when dump temperatures above 150 °C are applied, indicating a dominant occurrence of degradation of the NR-molecules. The results are in good agreement with bound rubber contents. The overall properties indicate that a dump temperature in the range of 135-150 °C and a silica-silane-rubber mixing interval of 10 minutes are the most appropriate mixing conditions for silica-filled NR compounds with TESPT as coupling agent.

3.1 INTRODUCTION

Natural rubber (NR) is a renewable material which combines excellent mechanical and dynamic properties, and its use covers a wide variety of applications, mostly in the form of filler-reinforced vulcanizates. The commonly used reinforcing fillers in rubber compounds are carbon black and silica. Replacement of carbon black by silica is growing, especially in the tire industry since the introduction of the "Green Tire Technology" by Michelin in 1992.[1] Silica significantly reduces rolling resistance and improves wet traction of tire tread compounds compared to carbon black.[2] However, a major drawback of using silica are difficulties in processing which come from the polarity difference between silica and rubber.

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The polar nature of silica negatively affects its compatibility with non-polar elastomers. The silica surface is acidic with a number of silanol groups. Hence, it forms strong hydrogen bonds or reacts with either basic or polar materials such as accelerators resulting in the adsorption of curatives by silica. In addition, strong hydrogen-bonds between the silica particles themselves result in tight silica aggregates and agglomerates causing poor dispersion of silica in rubber compounds.[3] A good dispersion of filler in a rubber compound is very important for the mechanical and dynamic properties.[3,4] The dispersion of silica-filled rubber compounds is generally worse compared to that of carbon black-filled ones. Moreover, when a large amount of silica is added, the viscosity substantially increases making the rubber compounds more difficult to process, and causing wear of the processing equipment. These difficulties can be overcome by use of silane coupling agents, which are able to combine chemically with silica and rubber during the mixing and vulcanization stages, respectively.[5-7] As a consequence, mixing of silica-filled compounds is basically different from that of carbon black-filled ones.

Mixing of rubber and silica with a silane coupling agent involves the reaction between silanol groups on the silica and ethoxy or hydroxyl groups of the silane, i.e. the silanization reaction. However, the efficient use of silanes as coupling agents in silica-filled rubber compounds is rather limited, caused by side-reactions. Various mixing-processing conditions need to be optimized for silanized silica-filled compounds.[8] The temperature window for mixing silica compounds is rather limited by a too low silanization rate versus the risk of scorch. High temperatures improve the silanization rate due to the temperature dependence of the reaction[5] and reduction of steric hindrance of the silylpropyl groups of the coupling agent by increased thermal mobility.[9] Based on a study with SBR/BR compounds,[10] the dump temperature should be in the range of 145°C to 155°C to achieve good silanization and to avoid pre-crosslinking. Furthermore, a mixing time of at least 10 minutes is needed for the silanization reaction during the first mixing step.

Most of the work in this area was focused on synthetic rubbers, in particular SBR/BR based-compounds for passenger tires. There are only a few studies dealing with silica-filled NR. The optimization of mixing conditions for silanized conventional silica-filled NR compounds was studied by Wolff.[11] The author concluded that an increase of mixing temperature and time for silica modification with silane enhances the compatibility between silica and NR through a chemical coupling bond of TESPT with the rubber. The overall properties are dependent on the extent of this interaction. However, it was stated that the *in-situ* modification reaction of silica with TESPT should not be considered as an optimum reaction, since the recipe was composed of only 20 phr of silica in combination with 40 phr of carbon black.

This chapter presents the optimization of mixing conditions, i.e. mixing temperature and silica-silane-rubber mixing interval, which may have an influence on mixing quality and silanization efficiency of silica-filled natural rubber compounds. Mooney viscosity, cure characteristics, filler-filler and rubber-filler interactions, as well as mechanical and dynamic properties of the rubber compounds and vulcanizates are evaluated.

3.2 EXPERIMENTAL

3.2.1 Materials

The natural rubber used was Ribbed Smoked Sheet 3 (RSS3), locally produced in Pattani (Thailand). The solution SBR (Buna VSL 5025-0 HM, Lanxess GmbH, Germany) contains 25% styrene and 75% butadiene, of which 50% in the vinyl configuration. The compounding ingredients were highly dispersible silica with a cetyl trimethylammonium bromide (CTAB) specific surface area[12] of 171 m^2/g (Ultrasil 7005, Evonik GmbH, Germany), bis-(triethoxysilylpropyl) tetrasulfide (TESPT) with sulfur content of approximately 22 wt% (Zhenjiang Wholemark Fine Chemicals, China), treated distillate aromatic extract or TDAE oil (Vivatec 500, Hansen & Rosenthal, Germany), zinc oxide (Global Chemical, Thailand), stearic acid (Imperial Chemical, Thailand), polymerized 2,2,4-trimethyl-1,2-dihydroquinoline or TMQ, diphenylguanidine or DPG and N-cyclohexyl-2-benzothiazolesulfenamide or CBS (all from Flexsys, Belgium), and sulfur (Siam Chemical, Thailand).

3.2.2 Compound preparation

The compound recipe used for this study is shown in Table 3.1. The amounts of TESPT and DPG applied in this recipe were based on the CTAB specific surface area of the silica according to Equations (3.1) and (3.2) as suggested by Guy *et al.*[13]:

$$\text{Amount of TESPT (phr)} = 0.00053 \times Q \times CTAB \qquad (3.1)$$

$$\text{Amount of DPG (phr)} = 0.00012 \times Q \times CTAB \qquad (3.2)$$

where Q is the silica content (phr) and CTAB is specific surface area of the silica used (m^2/g).

Table 3.1 *Compound formulation*

Ingredients	Amount (phr)
NR (RSS3)	100.0
Silica (Ultrasil 7005)	55.0
Silane (TESPT)	5.0
Process oil (TDAE)	8.0
Zinc oxide	3.0
Stearic acid	1.0
TMQ	1.0
DPG	1.1
CBS	1.5
Sulfur	1.5

Mixing was performed using an internal mixer with a mixing chamber of 500 cm^3 (Chareon Tut Co., Ltd., Thailand). The mixer was operated at a fill factor of 70 % and a rotor speed of 60 rpm. Initial temperature settings of the mixer were adjusted in the range of 50-140°C: Table 3.2. NR was initially masticated for 2 mins. Then, half of the silica and silane were added and mixed for half the duration of the silica-silane-rubber mixing interval, i.e.: 2.5, 5, 7.5 and 10 mins, prior to adding the second half of silica and silane together with TDAE oil. The mixing was then continued to the full intervals, i.e.: 5, 10, 15 and 20 mins. Subsequently, the other ingredients: ZnO, Stearic acid, TMQ and DPG, except CBS and sulfur, were added and mixed for 3 mins. The compounds were then dumped, sheeted out on a two-roll mill, and kept overnight prior to incorporation of CBS and sulfur on a luke-warm two-roll mill.

Mixer temperature settings and silica-silane-rubber mixing intervals prior to adding other chemicals were varied following the experimental design as shown in Table 3.2. Gum or unfilled compounds were also included in this study in order to determine the reinforcement parameter (α_F) from the cure characteristics; see below.

Table 3.2 *Experimental design for optimizing mixer temperature and mixing interval for silica-filled NR compounds*

Mixer temperature setting (°C)	**Mixing interval (mins.)**			
	5	**10**	**15**	**20**
50	x	x	x	x
60	x	x	x	x
70	x	x	x	x
80 - 140	-	x	-	-

x is assigned to the conditions for which both gum and filled compounds were prepared.

3.2.3 Mooney viscosity and cure characteristics

The compounds were tested for their Mooney viscosities by using a Mooney viscometer (ViscTech+, TechPro, USA) at 100°C with large rotor according to ASTM D1646. The value is represented as ML(1+4)100°C.

The cure characteristics were determined using a Moving Die Processability Tester or MDPt (TechPro, USA). The increase in torque (S') at a temperature of 150°C, a frequency of 0.833 Hz and 2.79 % strain was measured for 30 minutes. The optimum vulcanization time ($t_{c,90}$) was determined and used for press-curing of the samples.

3.2.4 Characterization of filler-filler and filler-rubber interactions

3.2.4.1 Reinforcement parameter. — The reinforcement parameter (α_F) was calculated by using the data from the cure characteristics according to Equation (3.3)[14]:

$$\frac{S'_{\max} - S'_{\min}}{S'^{0}_{\max} - S'^{0}_{\min}} - 1 = \alpha_F \left(\frac{m_F}{m_P} \right) \qquad (3.3)$$

where $S'_{max} - S'_{min}$ = torque difference of the silica filled rubber; $S'^{0}_{max} - S'^{0}_{min}$ = torque difference of the corresponding gum or unfilled compound; m_F/m_P = filler loading, where m_F and m_P correspond to the mass fractions of filler and polymer, respectively. The reinforcement parameter, α_F turns out to be a filler specific feature, independent of the cure system, and closely related to the morphology of the filler in the compound.[14]

3.2.4.2 Flocculation rate constant. — Silica flocculation can be observed by following the changes of the storage modulus of uncured compounds without curatives at low strain amplitude during thermal annealing.[15] In order to calculate the flocculation kinetics of the silica, the storage modulus at 0.56 % strain amplitude can be monitored during heating at 100°C for 12 mins by using the Moving Die Processability Tester, according to Mihara *et al.*[16] The degree of flocculation (x) can be expressed by the ratio of the Payne effect at time t and at infinite time:

$$x = \frac{G'(t) - G'(i)}{G'(f) - G'(i)} \qquad (3.4)$$

where $G'(t)$ is the storage modulus at 0.56% strain amplitude after heating time t; $G'(i)$ is the storage modulus after preheating for 1 minute; $G'(f)$ is the storage modulus at infinite time, taken as 12 minutes in order to reduce measuring time.

As mentioned by Böhm and Nguyen,[15] silica flocculation can be experimentally described as a first order reaction for which the kinetics can be described by a simple model equation. Mihara *et al.*[16] take this information and apply the following equation to calculate the flocculation rate constant (k_a):

$$k_a = \frac{\ln(1 - x_1) - \ln(1 - x_2)}{t_2 - t_1} \quad [\mathrm{s}^{-1}] \qquad (3.5)$$

where k_a is the rate constant; t is the heating time; x is the degree of flocculation; 1 and 2 refer to different heating times t.

3.2.4.3 Payne effect. — Storage shear moduli (G′) of compounds cured to their $t_{c,95}$ at 150°C were measured under shear deformation using a Rubber Process Analyzer (RPA, Alpha Technologies, USA). A strain sweep test was done in the range of 0.56 - 100 % strain at 0.50 Hz and 100°C.

3.2.4.4 Bound rubber content. — Bound rubber measurements were carried out both with and without ammonia treatment. The ammonia treatment was done in order to cleave the physical linkages between rubber and silica, so that the true chemically bound rubber could be determined.[17] The procedure adopted for the bound rubber measurement was as follows:

- 0.2 g of sample, i.e. uncured masterbatch (without curatives), was put into a metal cage and immersed in 20 ml of toluene for 72 h at room temperature. Toluene was renewed every 24 h.

- The sample was removed from the toluene, dried at 105°C for 24 h.

- The sample was immersed again in 20 ml of toluene for 72 h at room temperature in either a normal or an ammonia atmosphere in order to cleave the physical linkages. Toluene was renewed every 24 h.

- The sample was dried at 105°C for 24 h and weighed.

The bound rubber content was calculated according to Equation (3.6)[17]:

$$Bound\ \ rubber\ \ content\ \ (\%) \quad = \quad \frac{W_{fg} - W_f}{W_p}\ x\ 100 \qquad (3.6)$$

where W_{fg} is the weight of silica with the bound rubber attached; W_f is the weight of silica in the specimen; W_p is the weight of polymer in the specimen. W_f and W_p are calculated with reference to the compound formulation and initial sample weight.

3.2.5 Vulcanization and measurement of tensile and tear properties

The compounds were press vulcanized at 150°C to $t_{c,90}$. The vulcanized sheets having a thickness of about 2 mm were die-cut to dumbbell shaped specimens for tensile tests and to angle shape specimens (die type C) for tear tests. The tests were performed at a crosshead speed of 500 mm/mins according to ASTM D412 and ASTM D624, respectively, using a Hounsfield Tensile Tester. The mean values of tensile and tear properties taken from five specimens are reported.

3.2.6 Determination of dynamic mechanical properties

The vulcanizates cured to their $t_{c,95}$ at 150°C in the RPA were tested for dynamic mechanical properties using a frequency sweep test. The frequencies were varied in a range of 0.05 - 33 Hz at a fixed strain and temperature of 3.49 % and 60°C, respectively.

3.2.7 Cure characteristics of NR and SBR compounds in the presence of TESPT and DPG (without CBS and sulfur)

In order to explain the difference in change of Mooney viscosities with dump temperature of silica-filled NR compounds in comparison with previous experience with

SBR compounds,[10] two additional compounds were prepared. These compounds were composed of rubber with only TESPT and DPG at amounts of 5.0 and 1.5 phr, respectively. The compounds were prepared using a two-roll mill; rubber was milled for 6 mins, then DPG was added and mixed for 2 mins, and TESPT was subsequently incorporated and mixed for 2 mins. The compounds were sheeted out to a thickness of about 0.5 cm, and kept overnight prior to testing.

The cure characteristics of these compounds were analyzed by using the RPA with a frequency of 0.833 Hz and strain 2.79 % for 12 mins. The testing temperature was varied from 120-180°C with an increment of 10°C for each separate test.

3.3 RESULTS AND DISCUSSION

3.3.1 Processing properties

3.3.1.1 Mixing temperatures and torques. — The initial mixer temperatures settings and silica-silane-rubber mixing intervals prior to the addition of other chemicals were varied so that the influence of different dump (end) temperatures on the silica-filled NR compounds could be evaluated. The dump temperatures as function of initial temperature settings and silica-silane-rubber mixing intervals of the silica-filled NR compounds, in comparison with those of gum compounds, are shown in Figures 3.1 and 3.2, respectively.

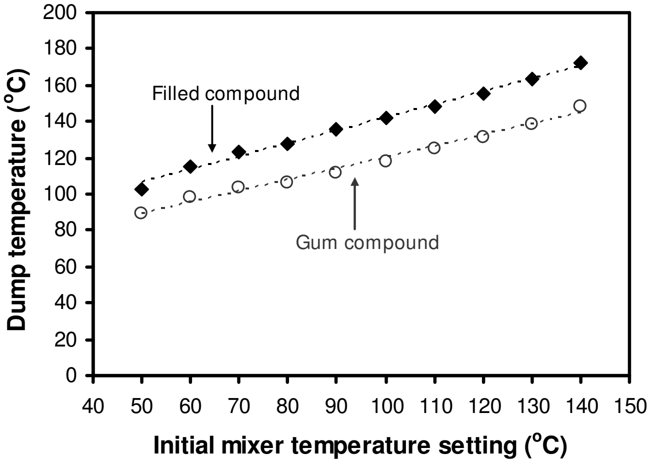

Figure 3.1 *Dump temperature as a function of initial mixer temperature setting for gum and silica-filled NR compounds, with 10 mins. mixing interval for silica+silane and rubber.*

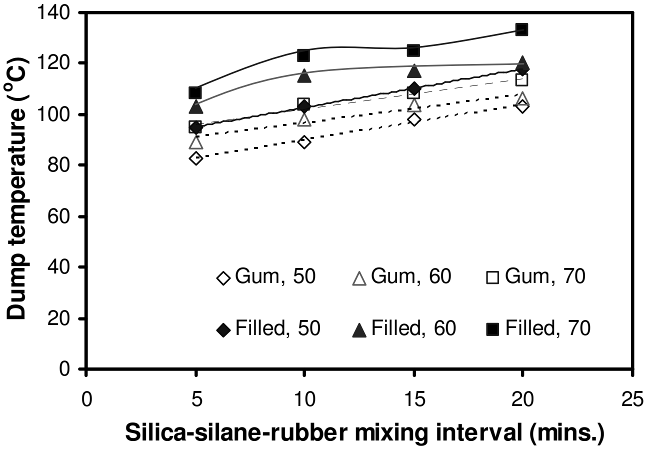

Figure 3.2 *Dump temperature as a function of silica-silane-rubber mixing interval for gum and silica-filled NR compounds. The initial mixer temperature settings were varied from 50 to 70°C, as indicated.*

By increasing the initial mixer temperature setting, the dump temperatures of both filled and gum compounds increase linearly. The filled compound shows a significantly higher dump temperature than that of the gum compound, attributed to the influence of hydrodynamic effects of the silica filler leading to higher shear forces generated during mixing. By choosing the initial mixer temperature settings in the range of 50 – 140°C, dump temperatures in the range of 90 – 170°C could be obtained. Considering the different silica-silane-rubber mixing intervals of filled and gum compounds, longer periods clearly give higher dump temperatures for both compounds, and the filled compounds, have again higher dump temperatures than the gum compounds.

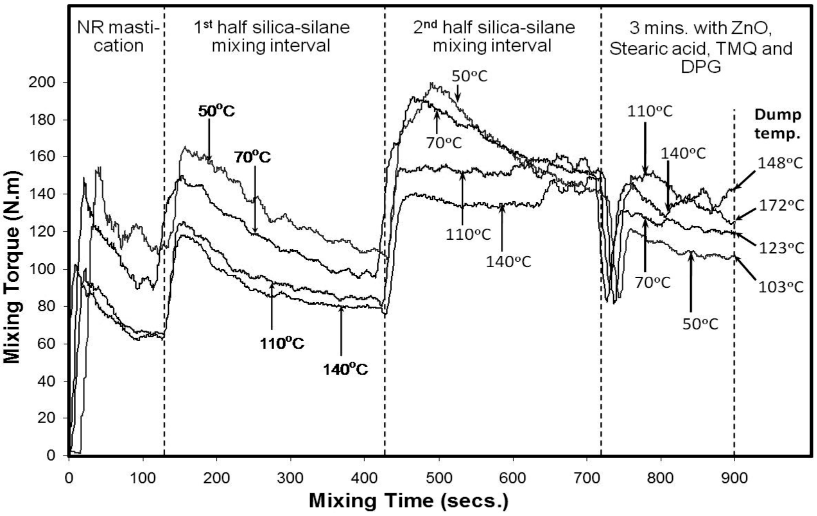

Figure 3.3 *Mixing torques for silica-filled NR compounds prepared with various mixer temperature settings, as indicated for each line. The silica-silane-rubber total mixing interval was 10 mins.*

Figure 3.3 shows typical mixer torque curves during mixing of silica-filled NR compounds prepared by adjusting the initial temperature setting in order to reach different dump temperatures, as they are indicated in the figure. The torque curves show quite different behaviors at different mixing times. Higher mixer temperature settings correspond to lower mixing torques in the range of 0 – 600 s mixing time, as depicted also in Figure 3.4: the torque average at 300 s in the first non-productive stage substantially decreases with increasing mixer temperature setting. This is commonly the result of lower mixture viscosity due to the higher temperature. However, in the second non-productive stage, the compounds with low initial mixer temperature settings (i.e. 50 and 70 °C) again show a decrease of mixing torque, while the compounds with high initial mixer temperature settings (i.e. 110 and 140 °C) display rather constant mixing torque with a slight increase at the end of this mixing stage. In this latter case, the lower mixture viscosity due to a higher temperature is balanced by the higher mixture viscosity due to a better silanization reaction and some premature crosslinking caused by sulfur in TESPT. For mixing times larger than 600 s, a crossover of the curves can be observed in Figure 3.3.

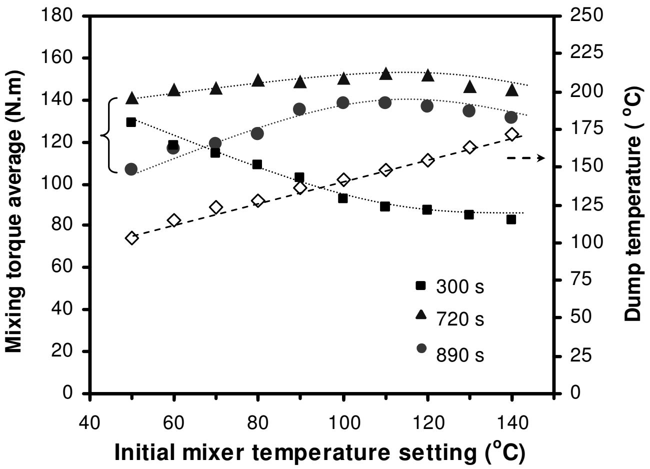

Figure 3.4 *Correlation between the mixer temperature setting, mixer torque and dump temperature of silica-filled NR compounds at 300, 720 and 890 seconds when a 10 mins. silica-silane-rubber mixing interval was used.*

Figure 3.4 shows that the mixing torque at 720 s increases with increasing mixer temperature setting to reach a maximum for a temperature setting of 110°C. At the end of mixing, i.e. 890 s, the torque also displays such a maximum. There are 3 possible reactions occurring during mixing: 1) silanization, 2) premature crosslinking due to sulfur in TESPT, and 3) rubber degradation. At dump temperatures lower than 150°C, silanization and some premature crosslinking are dominant so that the mixing torque increases at the later stage of mixing. However, at very high initial mixer temperature settings and consequent high compound dump temperatures, degradation of the natural rubber becomes dominant resulting in a decrease of torque. Some chemical ingredients (i.e. ZnO, stearic acid, TMQ and DPG) were added at the last stage of mixing. These chemicals, especially stearic acid, can provide an additional peptizing effect causing the mixing torque at 890 s to be lower than at 720 s, as shown in Figure 3.4. However, as every compound was mixed using the same quantities of ingredients and mixing procedure, this additional peptizing effect is presumed to be more or less the same. The change of torque as function of initial mixer temperature setting can therefore be explained using the three possible reactions as mentioned here before.

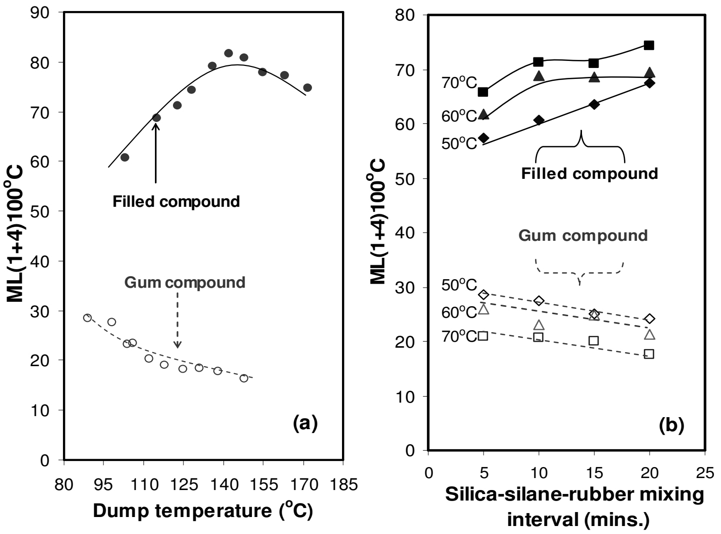

Figure 3.5 *Effect of (a): dump temperature and (b): silica-silane-rubber mixing interval on Mooney viscosity of gum and silica-filled NR compounds; parameter: initial temperature settings of mixer.*

3.3.1.2 Mooney viscosity of the compounds. — The Mooney viscosities of the silica-filled NR compounds prepared with the different mixer temperature settings and silica-silane-rubber mixing intervals in comparison with those of the gum compounds are shown in Figures 3.5(a) and 3.5(b), respectively. The filled compounds show much higher viscosities than the gum compounds, attributed to the hydrodynamic effect of the filler, filler-filler and filler-rubber interactions, and possibly some premature cross-linking of the rubber caused by sulfur in the TESPT in presence of DPG accelerator. For the silica-filled compounds, the Mooney viscosities initially increase with higher dump temperature, upon which the values gradually drop off when the dump temperature is over 150°C. This result corresponds with the change in mixing torque averages: Figure 3.4. Furthermore, the silica-filled compounds mixed with longer silica-silane-rubber mixing intervals, i.e. longer overall mixing times, give higher Mooney viscosities at a given an initial mixer temperature setting, as shown in Figure 3.5(b). On the other hand, the Mooney viscosities of the gum compounds show opposite trends, i.e. the values decrease with higher mixer temperature settings and with prolonged silica-silane-rubber mixing intervals. This is because a longer mixing time between silica, silane and NR results in a higher dump temperature, as displayed in Figure 3.2, giving an increase in degree of silanization of the silica and possibly some premature crosslinking of the rubber. Whereas the gum compound does not involve silica-silane-rubber reactions, the higher mixing temperatures can only lead to softening and destruction of the NR molecules. For these reasons, it is important to reconfirm that the mixer temperature setting has more of an effect than the time allocated for silanization of the silica-filled NR system, as already reported by Wolff.[11]

3.3.1.3 Cure characteristic of the compounds. — The cure characteristics of the silica-filled NR compounds: scorch time (t_{10}), cure time ($t_{c,90}$), cure rate index (CRI) as well as rheometer minimum torque (S'_{min}), are shown in Figure 3.6. With higher dump temperature the scorch time and cure rate index of the silica-filled compounds slightly increase, while the optimum cure time shows no significant change. The longer scorch time enhances processing safety while the higher cure rate leads to a similar optimum cure time, i.e. better scorch safety with the same curing cycle. Moreover, the rheometer minimum torques of the compounds reach a maximum value at a dump temperature in the range of 135 – 150 °C, which corresponds with a similar maximum in the mixing torque average at the end of compounding, i.e. 890 s of mixing time: Figure 3.4, and in the Mooney viscosity: Figure 3.5.

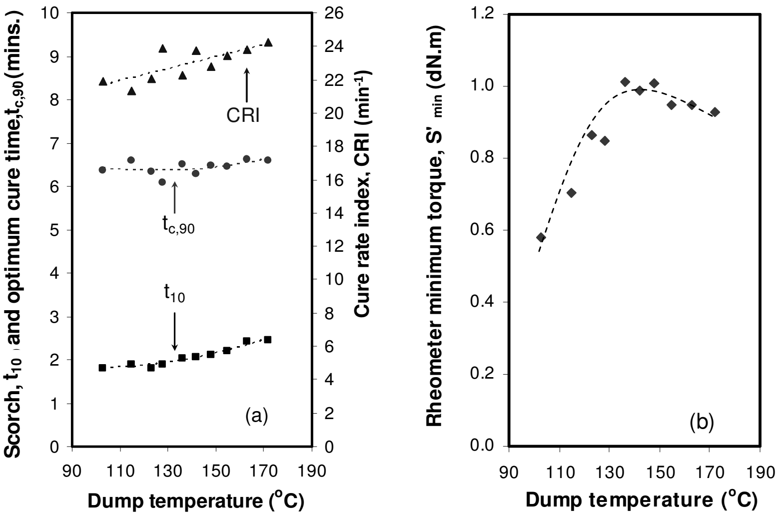

Figure 3.6 *Effect of dump temperature on (a): scorch time, optimum cure time, cure rate index and (b): rheometer minimum torque of silica-filled NR compounds.*

3.3.2 Silica dispersion

3.3.2.1 Reinforcement parameter of the compounds. — Basically, a lower reinforcement parameter indicates a better dispersion of a filler in a polymer.[14] In Figure 3.7, the reinforcement parameters of the silica-filled NR compounds are shown as function of dump temperature. The compounds prepared with higher dump temperature show a lower reinforcement parameter, indicating a better dispersion. However, a minimum α_F is observed in the dump temperature range of 135 – 170 °C, which agrees with the highest mixing torque average, Mooney viscosity, and minimum cure torque as displayed in Figures 3.4, 3.5 and 3.6(b), respectively.

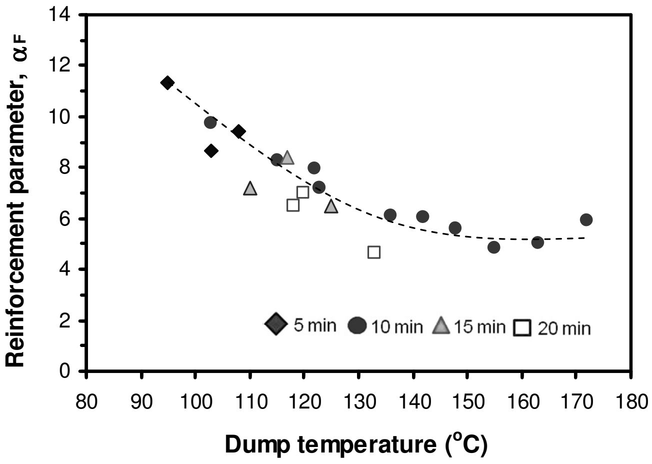

Figure 3.7 *Effect of dump temperature on reinforcement parameter of silica-filled NR compounds prepared with various silica-silane-rubber mixing intervals.*

3.3.2.2 Filler flocculation of the compounds. — Dispersion stability of the filler particles or filler aggregates in the rubber matrix influences the morphology of the filled rubber compounds. Reinforcing fillers, i.e. carbon black and silica, are able to flocculate caused by poor compatibility with the rubbers and their self-association, leading to a change in morphology and consequently deterioration in the physical properties of the vulcanizates.[15] It has been documented before that silica causes a greater degree of flocculation than carbon black, while silica is more polar and has a stronger self-association tendency through hydrogen bonding when compared to carbon black.[18] It is worth to mention that the flocculation process can occur during compound storage as well as directly prior to the onset of vulcanization in the absence of shear.[15] The kinetics of the flocculation process can be monitored by determination of the storage modulus during thermal annealing of a compound under a condition that represents vulcanization.

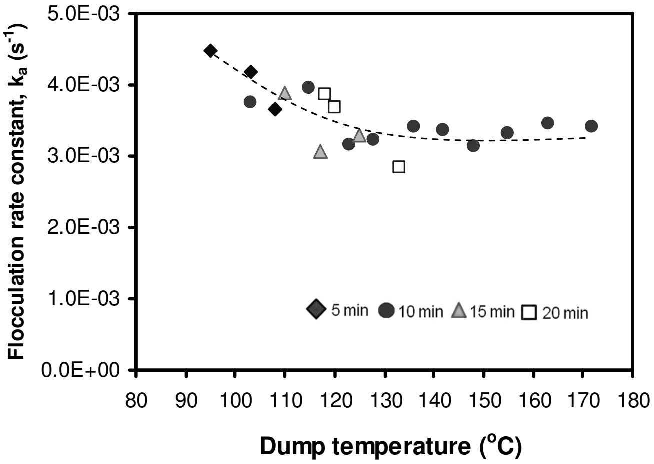

Figure 3.8 *Effect of dump temperature on flocculation rate constant of silica-filled NR compounds prepared with various silica-silane-rubber mixing intervals.*

The flocculation rate constant (k_a) of the silica-filled NR compounds as a function of dump temperature is shown in Figure 3.8. This value indicates how fast the silica flocculation process develops just before crosslinking, so that the parameter can be considered to represent silica dispersion stability as well as the degree of dispersion in silica-filled rubber compounds. Generally, a lower k_a value means a smaller tendency towards agglomeration in the rubber matrix. In other words, a lesser amount of silica flocculation corresponds to a better dispersion stability and finer morphology, presuming that the silica is well dispersed during mixing. As expected, mixing till elevated dump temperature and at longer mixing times enhances the dispersion stability of silica in the NR compounds, indicated by a decrease of the flocculation rate constant. This is in agreement with the degree of dispersion indicated by the reinforcement parameter: Figure 3.7. By increasing dump temperature, a better silica dispersion and distribution as well as a better homogenization of the distance between the silica aggregates is achieved. The plateau for the reinforcement parameter and the flocculation rate constant observed after the dump temperature of 135 °C indicates the best possible level of silica dispersion that we can obtain under the mixing conditions employed in this study.

3.3.3 Bound rubber content of the compounds

The bound rubber contents of the silica-filled compounds were evaluated under two conditions, i.e. with and without ammonia treatments. The ammonia treatment was used to cleave the physical linkages formed by physical adsorption, so that only the amount of chemically bound rubber, i.e. strong filler-rubber interactions and covalent bonds, were determined.

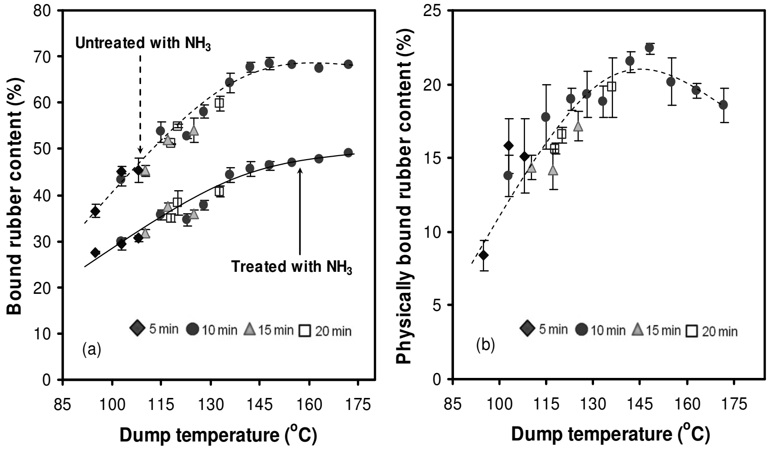

Figure 3.9 *Influence of dump temperature on bound rubber contents of silica-filled NR compounds; (a): total (untreated with* NH_3*) and chemically bound rubber (treated with* NH_3*); and (b): physically bound rubber content.*

Figure 3.9 shows the bound rubber contents as a function of dump temperature of the compounds measured without and with ammonia treatment. It is evident that the bound rubber content measured with ammonia treatment is lower than that measured without ammonia treatment. With increasing dump temperature and larger silica-silane-rubber mixing intervals, both total and chemically bound rubber contents in the compounds significantly increase, but level off when the dump temperature exceeds 135°C.

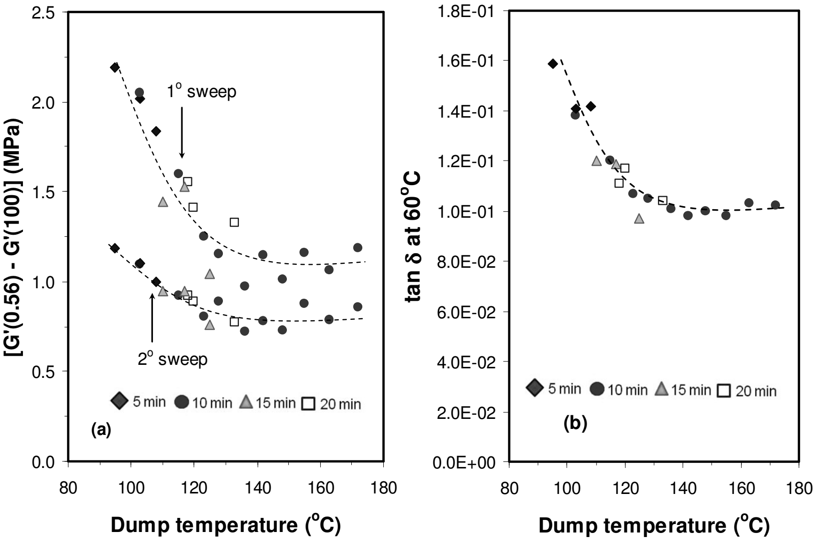

Figure 3.10 *Influence of dump temperature on dynamic properties; (a): Payne effect; and (b): tan δ at 60 °C (frequency 10 Hz) of silica-filled NR vulcanizates prepared with various silica-silane-rubber mixing intervals.*

Considering the physical linkages, obtained by subtracting the chemically bound rubber from the total bound rubber content: Figure 3.9b, the physically bound rubber of the compounds prepared at dump temperatures over 150°C starts to decrease, whereas the chemically bound rubber content remains unchanged. The decrease of physically bound rubber content might be attributed to the lower molecular weight of the NR-molecules after mixing. Basically, natural rubber molecules can easily be broken down by excessively high temperatures and shearing action, because it has reactive double bonds in every repeating unit along the rubber chain. Hence, under excessive mixing conditions, the NR chains are broken down leading to lower physical linkages in the compound. This phenomenon corresponds well with the decrease of Mooney viscosities at very high dump temperatures, as previously shown in Figure 3.5. Interestingly, the chemically bound rubber does not show any such dependence.

3.3.4 Dynamic properties of the compounds and vulcanizates

The Payne effect, i.e. the storage modulus difference between small (0.56 %) and large (100 %) strains, analyzed with a first and second sweep, and tan δ at 60°C of the silica-filled NR vulcanizates are shown as a function of dump temperature in Figure

3.10. By increasing the dump temperature and mixing time, the Payne effect as a measure of filler-filler interaction decreases, even in the second sweep test: Figure 3.10a. However, for dump temperatures above 135°C, there is no further change of the Payne effect. Regarding the tan δ at 60°C of the vulcanizates: Figure 3.10b, which is commonly used as an indication of rolling resistance of tires for which a lower value indicates a lower rolling resistance or less fuel consumption,[2] the compounds prepared with higher dump temperature and longer silica-silane-rubber mixing interval have lower tan δ at 60°C. The reduction of tan δ at 60°C levels off for dump temperatures above 135°C.

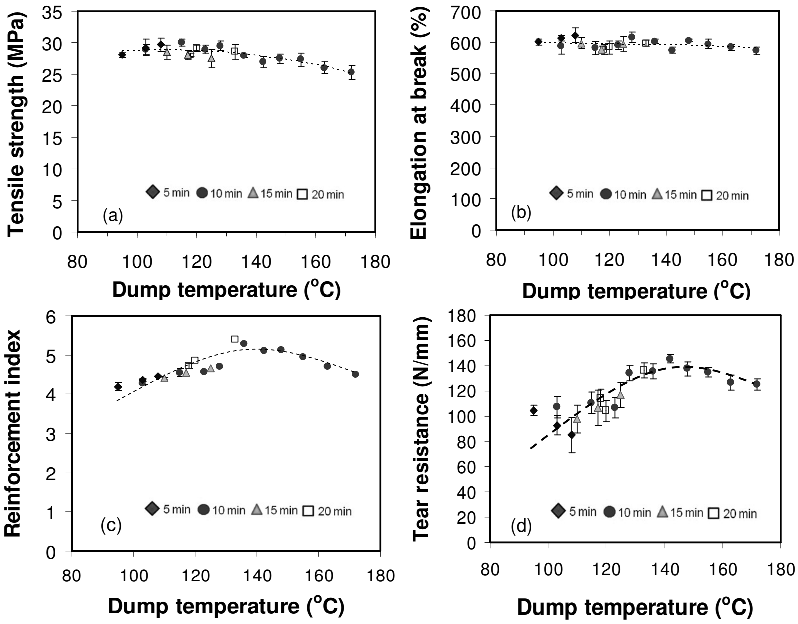

Figure 3.11 *Effect of dump temperature and silica-silane-rubber mixing interval on mechanical properties of silica-filled NR vulcanizates; (a): tensile strength; (b): elongation at break; (c): reinforcement index; and (d): tear resistance.*

3.3.5 Mechanical properties of the vulcanizates

Figure 3.11 shows the tensile strength, elongation at break, reinforcement index (i.e. the ratio of the moduli at 300% and 100% elongations or M300/M100) and tear resistance of the silica-filled NR vulcanizates prepared with varying dump temperatures and silica-silane-rubber mixing intervals. With varying dump temperatures and mixing times the elongation at break of the NR vulcanizates remains more or less the same, while the tensile strength slightly decreases with increasing dump temperature but shows no dependence on mixing times. The decrease of tensile strength, reinforcement index and tear resistance when the dump temperature exceeds 150°C is caused by the inevitable NR degradation under high temperature and shearing force. The degradation of NR with and without antioxidant after mixing in an internal mixer at 160°C and 180°C for 10 mins. was clearly demonstrated by Narathichat *et al.*[19] Considering the reinforcement index, an increasing dump temperature and silica-silane-rubber mixing interval lead to an optimum at 135°C; thereafter the values gradually decrease when the dump temperature exceeds 150°C. A change of tear resistance of the vulcanizates with varying dump temperatures and mixing times displays the same sort of dependence as that of the reinforcement index.

3.3.6 Competitive reactions between silanization, premature cross-linking and degradation in TESPT-silica-filled NR compounds

With respect to the change of the NR compound viscosities with dump temperature, as reflected in the final mixing torques, Mooney viscosities and rheometer minimum torques in Figures 3.4, 3.5 and 3.6(b) respectively, each separate property reveals the same trend. With increasing mixing temperatures, the compound viscosities initially increase, then reach a maximum for a dump temperature range of 135-150°C. For dump temperatures above 150°C, the compound viscosity drops. This phenomenon is different from the work reported by Wolff,[11] in which a steady decrease of viscosity with increasing dump temperature from 110 to 170°C for silica-filled NR compounds was observed. However, it should be noted that only 20 phr of silica was used in combination with 40 phr of carbon black in that work. In the case of silica-TESPT filled SBR/BR compounds, Reuvekamp *et al.*[10] reported a rather constant viscosity with increasing dump temperatures from 120-150°C, but an increased Mooney viscosity when dump temperatures above 150°C were obtained, caused by premature scorch of the rubber by sulfur contained in the TESPT. It is clear that the NR and SBR/BR compounds display remarkably opposite trends of compound viscosities with varying mixing conditions.

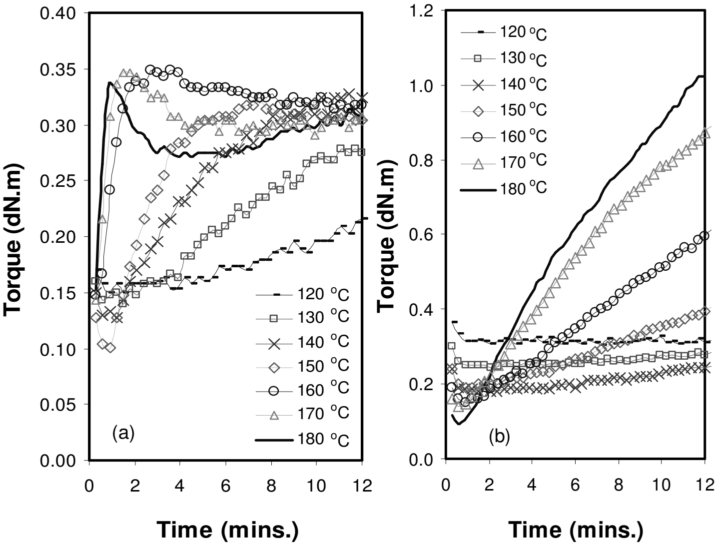

Figure 3.12 *Cure characteristics of (a): NR and (b): SBR compounds, in the presence of TESPT (5.0 phr) and DPG (1.5 phr) at different cure temperatures.*

The mixing torque can be used as an indication for what is happening. During mixing times of 120-720 s in Figure 3.3, which represent the first and second incorporations of silica, silane and processing oil, the decrease in the mixing torques with increasing temperature, especially after the first incorporation, is due to several factors. These include softening of the rubber at high temperature, and the breakdown of NR chains and silica structures by the mixing due to mechanical energy input, in combination with the hydrophobation effect of the TESPT silica surface modification. However, interestingly, a crossover of mixing torques is noticed at the final stage of mixing. It demonstrates that, besides the silanization reaction between silica and silane, a crosslinking or scorch reaction of NR with sulfur released from TESPT is simultaneously taking place, i.e. a bond between silica-silane-rubber and rubber-rubber is created in the compound and consequently causes a rise in the compound viscosity. In order to prove this, the cure characteristics of NR and TESPT were investigated in comparison with that of SBR as shown in Figure 3.12. The test was performed with compounds without CBS and elemental sulfur. It is clearly seen that NR readily reacts with TESPT at a temperature as low as 120°C and the reaction rate increases rapidly at higher temperatures, as seen from a change of the cure curves. SBR shows a different behavior since it starts to react with TESPT only at a higher temperature, i.e. 150°C.

The rheometer torque differences, commonly used to indicate the extent of crosslinking of both compounds are shown in Figure 3.13. The value for the NR+TESPT compound substantially increases from a test temperature of 120°C up to 150°C, and then gradually decreases at higher temperatures: a sort of reversion. On the other hand, the torque difference for the SBR+TESPT compound remains constant till a temperature of 140°C, and then increases rapidly when the cure temperature exceeds 150°C. These results indicate that the viscosity of silica-TESPT filled rubber compounds significantly depends on a premature crosslinking reaction which takes place during the mixing process due to available sulfur in TESPT, in addition to the silanization reaction and the thermo-mechanical shearing action. The large difference between the torque scale variation for SBR and NR in Figures 3.12 and 3.13 arises from the difference in molecular structures of NR and SBR. The torque increases observed in these rheometer curves are due to the light crosslinks caused by sulfur in TESPT only. A combination of partial crosslinking and bulky phenyl groups in the styrene part of SBR causes a larger restriction for movement of molecular chains under shear and hence a larger torque increase for SBR, compared to NR. In this context it is worth to mention that TESPT was first developed as a sulfur-cure accelerator with sulfur-donor properties, before it became commonly accepted as a coupling agent.[20,21] Therefore, the increase of the silica-filled NR compound viscosities for dump temperatures in the range of 100-145°C: Figure 3.5, is to a large extent due to the silica-silane-NR coupling reaction that occurs during the mixing process, and this reaction reaches its maximum at a dump temperature around 135-150°C. This premature crosslinking reaction dominates over the breakdown of rubber chains and silica structures.

As seen from Figure 3.5, the viscosities of the silanized silica-filled NR compounds tend to decrease again at dump temperatures above 150°C. This may be attributed to an optimum degree of silica-rubber and rubber-rubber interactions/reactions induced by the TESPT. Furthermore, degradation of rubber chains and/or polysulfide linkages becomes prominent. This observation can be also confirmed by the change of bound rubber content in the compounds: Figure 3.9. The chemically bound rubber reaches a plateau at a dump temperature of approximately 135°C, indicating that the silica-silane-rubber and rubber-rubber interactions/ reactions remain intact at higher temperature and shear force. Meanwhile, the physically bound rubber content in the compounds prepared at dump temperatures over 150°C decreases somewhat, suggesting a reduction of chain entanglements or the physical network of rubber molecules due to a chain shortening by the degradation reaction.

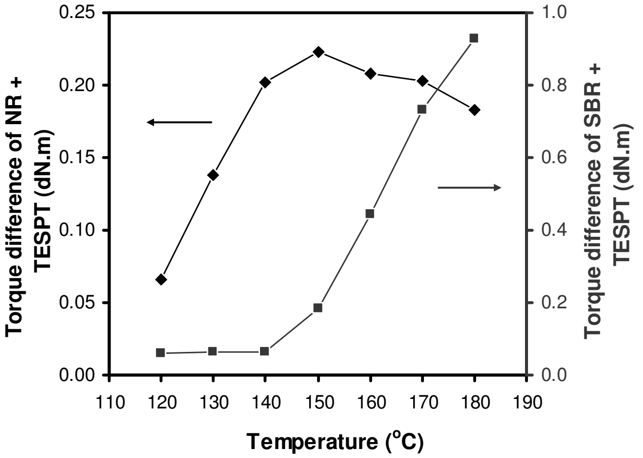

Figure 3.13 *Rheometer torque difference of NR and SBR compounds as a function of cure temperature in the presence of TESPT (5.0 phr) and DPG (1.5 phr).*

The mixing of silica-silane and NR can not avoid this premature crosslinking when TESPT is used as coupling agent, as the NR starts to react with sulfur present in TESPT at a temperature as low as 120°C: Figure 3.13. The increased Mooney viscosity is normally an undesired processing property since it leads to processing difficulties in extrusion and calendering. Surprisingly, this phenomenon does not have an adverse effect on other properties of the compounds and vulcanizates. As illustrated in Figure 3.6, even better cure characteristics are obtained for compounds prepared with higher dump temperature, as indicated by the faster cure rate and longer scorch time. The improvement in cure behavior could be the result of better silanization so that all silica surfaces are well covered with silane resulting in less acidity and polarity, which in turn prevents accelerator adsorption and cure retardation. Furthermore, when DPG is used in the recipe to enhance the silanization reaction[22] as well as to act as a secondary accelerator, the higher level of silanization could also mean that a smaller portion of CBS is adsorbed on the still uncovered silica surface, so that this accelerator is more efficiently used for the curing. The improvement of the mechanical properties with increasing dump temperature to the optimum point, i.e. in the range of 135-150°C, especially in terms of reinforcement index (M300/M100) and tear resistance: Figure 3.11, is accounted for by a better silica dispersion in the NR as indicated by the reinforcement parameter (α_F), flocculation rate constant (k_a) and Payne effect of the compounds in Figures 3.7, 3.8 and 3.10, respectively. This also corresponds with the higher bound rubber content which indicates a better filler-rubber interaction. The lightly crosslinked network formed at the later stage of mixing restricts the movement of dispersed silica particles. As a consequence, the re-agglomeration of silica is reduced, as depicted by a decrease of the flocculation rate constant: Figure 3.8. The results of this present work show a good agreement with the work reported by Lin *et al.*,[23] in which the compounds comprising of TESPT showed a reduction of silica flocculation when they were mixed at higher dump temperature. Based on the present results, re-agglomeration of silica/TESPT-filled NR compounds can be effectively suppressed when a sufficiently high mixing temperature is used. This is not only due to better silica dispersion, higher degree of hydrophobation, greater extent of polymer-filler interaction, but also due to the lightly crosslinked network as a result of a small amount of crosslinking during mixing.

The tan δ at 60°C, a measure of rolling resistance of tires based on silica-filled NR, is shown to improve when the compound dump temperatures are increased and the optimum temperature is in a range of 135-150°C, in agreement with all other properties.

Based on our investigations on the reinforcement parameter, flocculation rate constant, bound rubber content, Payne effect, loss tangent at 60°C (indication for rolling resistance), and mechanical properties, the optimal mixing conditions for silica-filled NR with TESPT as a coupling agent are a dump temperature in the range of 135-150°C, and 10 mins mixing interval of silica-silane-rubber after mastication and before the addition of the other ingredients: ZnO, Stearic acid, TMQ and DPG. The decrease of reinforcement parameter, flocculation rate constant and Payne effect combined with the increase of bound rubber content can be taken as a proof for proper silanization. However, it is worth to emphasize that the change of Mooney viscosity with dump temperature is different for the NR and SBR cases when TESPT is used. The Mooney viscosity of silica-filled NR compound increases due to sulfur in the TESPT to the maximum and thereafter decreases at higher temperatures as NR degradation starts to take place.

3.4 CONCLUSIONS

Varying initial mixer temperature settings from 50-140°C and mixing intervals from 5 to 20 minutes for the silica-filled NR compounds lead to dump (end) temperatures in a range of 90-170°C. The properties of both compounds and vulcanizates show a strong dependence on dump temperature, since the silanization reaction and silica dispersion are key parameters in this system. The optimal mixing conditions for silica-filled NR compounds with TESPT as a coupling agent are a dump temperature in the range of 135-150°C, and 10 mins mixing interval of silica-silane-rubber prior to addition of the other ingredients: ZnO, Stearic acid, TMQ and DPG. Mixing performed till dump temperatures above 150°C leads to a decrease in vulcanizate properties as a result of NR degradation. During mixing of silica-filled NR compounds with TESPT as coupling agent, it is evident that, in addition to the silanization reaction, premature crosslinking reactions take place since NR can start to react with sulfur coming from TESPT molecules at a temperature as low as 120°C. However, this phenomenon does not have an adverse effect on the vulcanizate properties.

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CHAPTER 4

OPTIMIZATION OF RUBBER FORMULATION FOR SILICA-REINFORCED NATURAL RUBBER COMPOUNDS

The rubber formulation plays a significant role in the properties of NR compounds filled with silica. In this work, the influences of various silicas, silane coupling agents and diphenylguanidine (DPG) on the properties of compounds and vulcanizates, i.e. cure characteristics, Mooney viscosity, flocculation kinetics, bound rubber content, Payne effect, tan δ at 60 ^{o}C, tensile and tear properties are investigated. The results demonstrate that compound viscosity and curing behavior, as well as vulcanizate properties of the silica-filled NR are much improved by incorporating silane coupling agents. Bis-(triethoxysilylpropyl) tetrasulfide (TESPT) clearly gives better overall properties than the disulfide-based silane (TESPD), except for scorch safety. DPG acts as a synergist to sulfenamide primary accelerators, as well as activator for the silanization reaction. Highly dispersible (HD) silicas can significantly enhance the degree of dispersion, and so lead to higher filler-rubber interaction. As a consequence, the HD silicas provide better dynamic and mechanical properties for filled-NR vulcanizates compared to conventional (CV) counterparts. The optimal quantities of both silane coupling agent and DPG required in the formulation are correlated to the cetyl trimethylammonium bromide (CTAB) specific surface area of the silicas. Furthermore, the results reveal that the silica structure as characterized by the dibutylphthalate (DBP) adsorption also strongly influences the reinforcing efficiency.

4.1 INTRODUCTION

Silica is one of the most commonly used reinforcing fillers nowadays, as it enhances the performance of technical rubber products, especially tires and mechanical rubber goods. It has become a strong alternative for carbon black fillers in tires after it was reported that silica provides a better balance in tire properties, in particular rolling resistance, heat build-up and wet grip, compared to those for carbon

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black.[1,2] However, the introduction of silica into rubber compounds also brought some disadvantages, generally with regard to processing and vulcanization aspects.

The key fundamental characteristics of the filler which determine the properties of silica-filled rubber compounds are surface chemistry, as well as particle size and structure. Silica is a hydrophilic substance, highly polar in nature due to the presence of silanol groups on its surface.[3] In addition, acidity of silica attributed to these same silanol groups plays a role.[4] A very high surface area and high structure of silica are required to increase the active sites for their interactions towards the modifying coupling agent and rubber phase.[1,2,5,6] However, these factors generally lead to difficulties in rubber processing.

The properties of silica-reinforced rubber compounds strongly depend on the silica dispersion as affected by the mixing process.[3-6] Due to the self-associated hydrogen bonds among silica particles/aggregates, and the relatively low compatibility between silica and generally non-polar rubbers, the utilization of mixing procedures as applied for carbon black-filled compounds generally results in poor silica dispersion.[3,4] Excessive mixing energy input must be applied for distributing the particles or aggregates.[7,8] In addition, despite a good dispersion after mixing, the phenomenon of silica re-agglomeration or so-called flocculation can take place during compound storage. This leads to the reformation of silica agglomerates in the rubber matrix, and as a consequence, deterioration in rubber properties.[9-12]

Silica surface reactivity plays a significant role, not only on the dispersibility but also on the adsorption effect. In a rubber formulation, silica comes in contact with several compounding ingredients competing for adsorption on its surface through either hydrogen bonding or Van der Waals forces. Polar chemicals, for instance zinc compounds, fatty acids, amine antioxidants, glycols and accelerators in particular, have rather strong adsorptive interactions with the silica surface. Apart from lowering the crosslink density caused by the acidity of the silica surface and by adsorption of accelerators that affect the cure behavior, the adsorbed layer of chemicals prevents direct wetting between silica and rubber, and then lessens the extent of silica-rubber interactions.[4,7,13] To minimize the accelerator adsorption on the silica surface and hence to improve cure characteristics, either glycols or amines are normally added into the rubber compounds. In addition to diethylene glycol (DEG), the commonly used amine for this purpose is diphenylguanidine (DPG) which itself is also acting as a synergistic secondary accelerator for sulfenamide accelerated sulfur vulcanization.[4,14] Furthermore, DPG facilitates as a catalyst the silanization reaction between silica and silane coupling agent.[15,16]

To overcome the intrinsic problems associated with the nature of silica, bifunctional organosilanes or silane coupling agents are available since 1971 to essentially modify the hydrophilic silica via a chemical reaction on the surface. The coupling agents contain two different active sites; one is to react with the silanol groups on the silica surface and the other with the rubber molecules.[1,17,18] The bridge formation between silica and rubber through silane chemistry results in a considerable improvement in reinforcement of rubbers filled with silica. The effective use of silane coupling agents improves filler-rubber interaction, degree of silica dispersion, and cure characteristics. The most commonly used silane coupling agent in rubber compounds cured with a sulfur system is bis-(triethoxysilylpropyl) tetrasulfide (TESPT). However, the use of TESPT under high temperature mixing conditions encounters the problem of premature scorch during mixing, causing undesired high compound viscosities.[19] The scorch originates from free sulfur released from TESPT at the high mixing temperature, i.e. 140-150°C, required for the silanization reaction.[18-20] To overcome this drawback, alternative silanes have been introduced such as bis-(triethoxysilylpropyl) disulfide (TESPD)[21], and octanoylthiopropyltriethoxysilane (NXT silane).[22] Therefore, the properties of silica-filled rubber products significantly depend on the right combination of the key ingredients employed in the system.

This present work aims to optimize the rubber formulations for silica-filled NR compounds. Silane coupling agents, i.e. TESPT and TESPD, DPG as well as silicas, i.e. conventional and highly dispersible types, are taken into consideration. The effects of silica types, of silane and DPG loading on the compound and vulcanizate properties, i.e. Mooney viscosity, cure characteristics, Payne effect, flocculation tendency, bound rubber content and dynamic and mechanical properties are evaluated. The optimization of the compound formulation specifically for NR is an absolute necessity, because it does not compare with synthetic rubbers which have previously been investigated mainly for passenger car tires.

4.2 EXPERIMENTAL

4.2.1 Materials

In this study, some of compounding ingredients used, i.e. natural rubber (RSS3), zinc oxide, stearic acid, TDAE oil, TMQ, CBS, DPG, and sulfur, are as described in Chapter 3. Two types of silane coupling agents were used: bis-(triethoxysilylpropyl) tetrasulfide or TESPT (Zhenjiang Wholemark Fine Chemicals, China), and bis-(triethoxysilylpropyl) disulfide or TESPD (Si-266, Evonik GmbH, Germany) with sulfur contents of approximately 22.0 and 14.4 wt%, respectively. Five grades of silica classified as conventional (CV), i.e. Ultrasil VN3 and Ultrasil VN2, as well as highly dispersible (HD) types, i.e. Ultrasil 7005, Zeosil 1165MP and Hi-Sil EZ160 were employed in this work. Suppliers and technical data of the silicas are detailed in Table 4.1.

Table 4.1 *Types, suppliers and technical data of silicas.*

Silica	Supplier	Type	BET (m^2/g)	CTAB (m^2/g)	DBP (g/100g)
Ultrasil VN3	Evonik Degussa, Germany	CV	175	165	176
Ultrasil VN2	Evonik Degussa, Germany	CV	127	125	185
Ultrasil 7005	Evonik Industries, Germany	HD	180	171	217
Zeosil 1165MP	Rhodia Silices, France	HD	160	150	202
Hi-Sil EZ160	PPG Industries, Netherlands	HD	160	150	192

4.2.2 Rubber formulations

The quantities of TESPT and DPG applied for silica-filled rubber compounds were based on the CTAB specific surface area of the silica, and calculated by using the equations[6] as displayed in Chapter 3.

Table 4.2 *Compound formulations.*

Ingredient	Dosage (phr)
Natural rubber	100.0
ZnO	3.0
Stearic acid	1.0
TMQ	1.0
Ultrasil 7005 (or other)[a]	55.0
TESPT (or TESPD)	5.0 (or variable)[b]
TDAE oil	8.0
DPG	1.1 (or variable)[b]
CBS	1.5
Sulfur	1.5 (or variable)[c]

[a] *Five types of silica were studied, as detailed in Table 4.1.*

[b] *The variable amounts of silane coupling agents and DPG are shown in Table 4.3.*

[c] *Adjusted so that with the sulfur contained in the coupling agent all compounds had the same total amount of sulfur.*

The compound formulation containing the calculated amount of TESPT and DPG was considered as reference formulation, as detailed in Table 4.2. To investigate the influence of variable contents of silane coupling agents and DPG, a series of tests was done with Ultrasil 7005 with the quantities of both chemicals varied at lower and higher loadings compared to the calculated values based on its CTAB specific surface area. Either the silane or the DPG was varied at a time, the other was kept constant. Table 4.3 shows the variable amounts of silane and DPG applied in this work.

Table 4.3 *Variable quantities of silane (TESPT or TESPD) and DPG in the Ultrasil 7005 filled rubber formulations.*

Set I	**varying silane content; DPG was fixed at 1.1 phr**						
Silane	wt% relative to silica	0	6.0	7.5	**9.0**	10.5	12.0
	phr	0	3.3	4.1	**5.0**	5.8	6.6
Set II	**varying DPG content; TESPT was fixed at 5.0 phr**						
DPG	wt% relative to silica	0	0.51	1.20	**2.05**	2.82	3.53
	phr	0	0.28	0.66	**1.13**	1.55	1.94

With regard to the silica types, the compound formulation was the same as in Table 4.2, but owing to the difference in CTAB specific surface areas among the five silica grades the quantities of TESPT calculated for those silicas were different. These different amounts of TESPT lead to varied amounts of sulfur available in the compound. Therefore, the amounts of total sulfur were corrected by addition of elemental sulfur in the vulcanization package to ensure that every compound contained the same overall sulfur content during curing.

4.2.3 Mixing procedure

The mixing was performed using an internal mixer with a chamber of 500 cm^3 (Chareon Tut Co., Ltd., Thailand). The mixer was operated at a fill factor of 70 % and a rotor speed of 60 rpm. The initial temperature setting of the mixer was at 100°C in order to reach dump temperatures of approximately 140 – 145°C. NR was initially masticated for 2 mins. Then, half of the silica and silane was added and mixed for 5 mins, prior to adding the second half of silica and silane together with TDAE oil and mixed for another 5 mins. Subsequently, ZnO, stearic acid, TMQ and DPG, were added and mixed for 3 mins. The compounds were then dumped, sheeted out on a two-roll mill, and kept overnight prior to the incorporation of CBS and sulfur on a luke-warm two-roll mill.

4.2.4 Property analysis and testing

Mooney viscosity, cure characteristic, flocculation kinetics, Payne effect, bound rubber content, tensile/tear and dynamic mechanical properties of the compounds were investigated according to the methods as described in Chapter 3.

4.3 RESULTS AND DISCUSSION

4.3.1 Effect of silane coupling agents

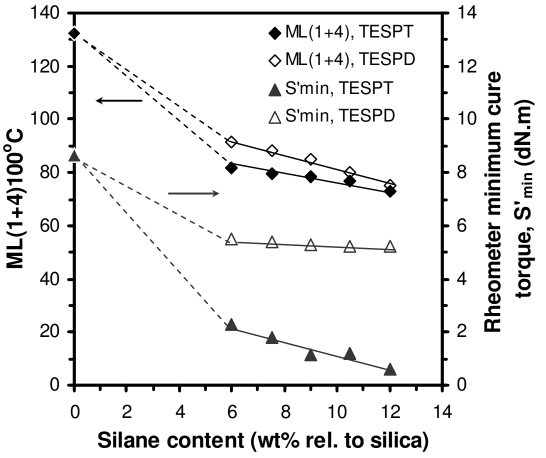

Figure 4.1 *Effect of quantity of TESPT and TESPD on compound Mooney viscosity and rheometer minimum cure torque of the Ultrasil 7005 silica-filled NR compounds.*

4.3.1.1 Hydrophobation and lubrication effects. — This part of the study was executed with one type of silica: highly dispersible Ultrasil 7005. Figure 4.1 shows Mooney viscosities and rheometer minimum cure torques of the silica-filled NR compounds as function of the quantities of TESPT and TESPD. The results display a large difference in both Mooney viscosities and the minimum cure torques of the compounds with and without silane coupling agents. The incorporation of coupling agents at 6 wt% relative to the silica loading (3.3 phr) leads to a strong reduction in the compound viscosity already, and the values further decrease with increasing the silane contents. This behavior can be mainly described by the hydrophobation and lubrication effects of silane coupling agents. TESPT and TESPD can effectively modify the hydrophilic silica surface to become more hydrophobic, and as a consequence result in a better compatibility between silica and NR matrix. The chemical mechanism involved during the mixing of silica, silane and rubber has been explicitly described by the reaction between the alkoxy groups of silane coupling agent and the silanol groups on silica surface through either a direct condensation reaction or hydrolysis prior to condensation at the appropriate temperature, resulting in the formation of covalent bonds.[17] The reaction is the so-called silanization reaction. Besides hydrophobation, a lubrication effect also plays a role. Owing to the fact that these silane coupling agents are in liquid form with rather low molecular weight, they can function as a processing aid which potentially assists the rubber molecules to flow. With respect to these effects, the NR compounds filled with silica in presence of silane coupling agents have much better compatibility between silica and rubber, and improved processibility, compared to the compound without coupling agent.

Comparing the TESPT- and TESPD-containing compounds, the ones with TESPT show lower Mooney viscosities and minimum cure torques than the TESPD-based mixes. As the viscosities of silica-filled compounds depend strongly on the degrees of hydrophobation and lubrication of the silica as mentioned earlier, addition of these two types of silane coupling agents at the same amounts should lead to similar degrees of silanization or hydrophobation in both compounds. Based on equal weight, TESPD with lower molecular weight even represents a higher molar content compared to TESPT. However, as seen in Figure 4.1, the compounds containing TESPD show higher Mooney viscosities and much larger values of minimum cure torque than those with TESPT. The large difference in minimum cure torques possibly provides an indication that the compounds with TESPT and TESPD experience different levels of silica flocculation (re-agglomeration of silica aggregates) taking place at the beginning of vulcanization, i.e. under thermal treatment. Therefore, the silica dispersion stability may play an important role in the difference in viscosities between these two types of compounds.

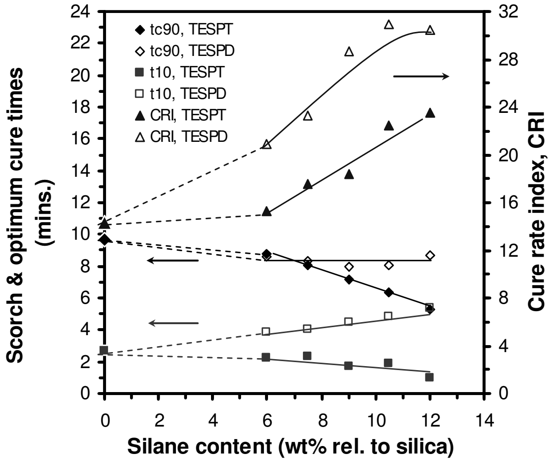

***Figure 4.2** Effect of quantity of TESPT and TESPD on scorch time (t_{10}), optimum cure time ($t_{c,90}$) and cure rate index of the silica-filled NR compounds.*

The natural rubber compounds containing TESPT and TESPD display different cure characteristics. Increasing the TESPT content decreases both scorch (t_{10}) and optimum vulcanization times ($t_{c,90}$) of the compounds. Quite a different behavior is observed in the case of TESPD, as seen in Figure 4.2. Increasing TESPD loading increases the scorch time, while the optimum cure time remains more or less constant. Increase of the TESPT content also increases the amount of sulfur available in the compounds for the crosslinking reaction and so lowers the scorch and cure times. In the case of TESPD, during the induction period, some of the elemental sulfur added into the compound to compensate for the reduced total sulfur level vs. TESPT is inserted into the disulfane to activate the TESPD for the coupling reaction[18], leading to the prolonged induction period. Higher amounts of TESPD used in the formulation reduce the overall active sulfur available at the beginning of the vulcanization process, and so prolong the scorch time even more. The different reactivity of the sulfur moieties of the tetrasulfane of TESPT and the disulfane of TESPD, as well as the insertion of sulfur into the disulfane to result in the reactive polysulfane in the case of TESPD was previously described by Luginsland.[18]

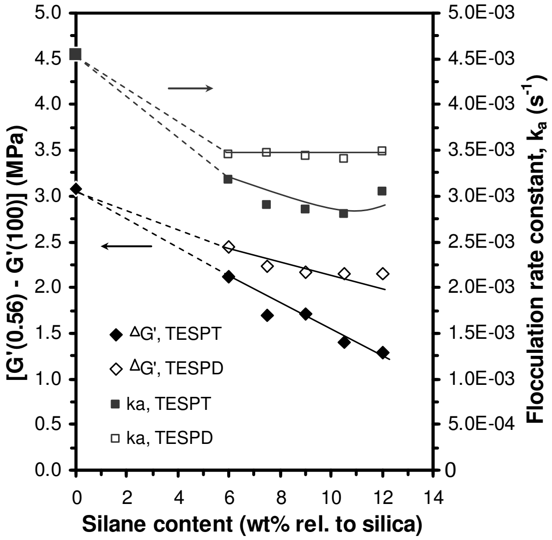

Figure 4.3 *Influence of quantity of TESPT and TESPD on Payne effect and flocculation rate constant for silica-filled NR compounds.*

4.3.1.2 Silica dispersion stability and filler-filler interaction. — The results of compound viscosities suggest that the use of TESPT and TESPD may give different levels of silica dispersion and/or flocculation. In order to obtain evidence for silica-silica interactions and silica flocculation in the compounds with the different silane types, the flocculation kinetics and Payne effects were evaluated. Figure 4.3 depicts the Payne effect and flocculation rate constant of the silica-filled NR compounds containing various amounts of TESPT and TESPD. The Payne effect, as determined by the difference in the storage modulus at small and large deformations (0.56 and 100 % strain, respectively) is a measure of the extent of filler-filler interaction. It can be seen that silane coupling agents can greatly reduce the Payne effect. TESPT containing compounds show a much smaller Payne effect than those with TESPD, and the reduction of this storage modulus difference becomes even more pronounced when the amount of TESPT coupling agent is increased. The change of Payne effect corresponds well with a change of the flocculation rate constant with silane contents. It indicates how fast the re-agglomeration or flocculation process of silica aggregates can develop in the compounds.[12,20] In general, a lower flocculation rate constant indicates a better silica dispersion stability. In addition, this parameter can be used to assess the extent of filler-filler interaction at the beginning of vulcanization. From the results observed in Figure 4.3, the incorporation of coupling agents into the compounds abruptly reduces the flocculation process. The silica-filled NR compounds with TESPT coupling agent show better silica dispersion stability compared to the ones with TESPD. This result corresponds with the difference in minimum cure torques as observed in Figure 4.1. The compound with TESPT clearly has a lower flocculation rate constant (k_a) indicating that the flocculation process is prominently suppressed during thermal treatment at the onset of vulcanization, thereby keeping the viscosity at a low level.

4.3.1.3 Network contributions. — From previous studies,[19,20] the mobility of silica particles or aggregates dispersed in the rubber matrix can be significantly restricted by the network resulting from filler-rubber interactions and rubber-rubber crosslinks. In Figure 4.4, the chemically bound rubber content of the compound without silane coupling agent is very low while the compounds with silane coupling agents show much higher values of chemically bound rubber content. The bound rubber contents gradually increase with increasing TESPT and TESPD up to their optimum contents in the range of 9.0-10.5 wt% relative to the amount of silica. TESPT clearly gives higher chemically bound rubber contents, contributed by both filler-rubber interaction and rubber-rubber crosslinks caused by the sulfur in the polysulfide moiety of TESPT itself, because TESPT can act as a sulfur donor. TESPT was actually originally developed as a sulfur-donor accelerator.[24] The released free sulfur can cause some crosslinking of NR molecules at elevated temperature. As demonstrated in Chapter 3,[20] TESPT already begins a crosslinking reaction in NR at a temperature as low as 120°C.

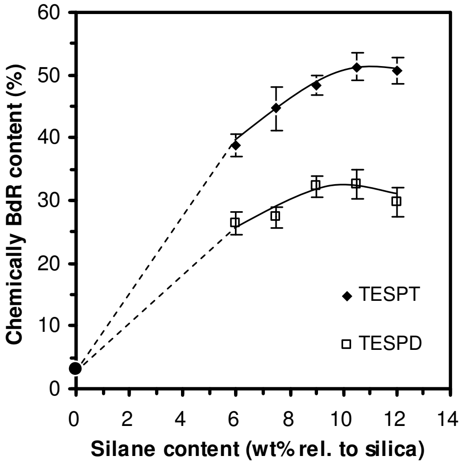

Figure 4.4 *Influence of quantity of TESPT and TESPD on chemically bound rubber (BdR) content of the silica-filled NR compounds.*

With regard to the different chemically bound rubber contents in the silica-silane-NR compounds with TESPT and TESPD, it is worth to discuss the chemical bonds and interactions formed during the non-productive mixing stage. While the ethoxy groups of the silanes react with silanol groups on the silica surface, the tetrasulfide ($-S_4-$) moiety in TESPT splits off reactive sulfur radicals which can link to rubber molecules under shearing at high mixing temperature. On the other side, TESPD does not or only little release free sulfur since it consists merely of a disulfide ($-S_2-$) which at best provides only one reactive mono-sulfur after splitting off to couple with a reactive NR molecule. So, only bonds of silica-TESPD and silica-TESPD-NR (without rubber-rubber crosslinks) are presumed to occur during mixing in that case. Based on a study of Luginsland[18] regarding the reactions of TESPT and TESPD with a model compound for NR: squalene, the disulfane moiety in TESPD is unable to react directly with double bonds in the NR even in the presence of accelerator. Only if sulfur is added in the second productive mixing step, it can be inserted in the disulfane to become a reactive polysulfane where the coupling reaction can take place. However, this is not fully the case for the silica-TESPD filled NR in this study, because the increase of bound rubber content with increasing TESPD loading as shown in Figure 4.4, suggests that TESPD can yet react with NR molecules during mixing. The difference in bound rubber content between TESPT- and TESPD-containing compounds is then mainly caused by the different extent of rubber-rubber crosslinks originating from free sulfur available particularly in the compounds with TESPT.

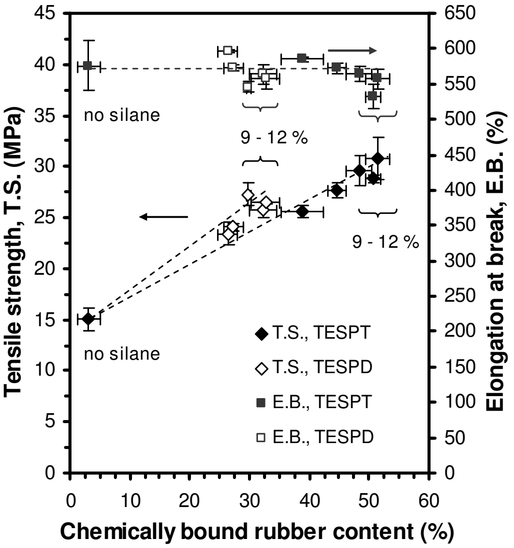

Figure 4.5 *Correlation between tensile strength and elongation at break with chemically bound rubber content of silica-filled NR compounds with various amounts of TESPT and TESPD. 9-12% indicates the amount of silane in weight percentage relative to silica.*

4.3.1.4 Mechanical properties. — To correlate the mechanical properties of silica-filled NR vulcanizates, prepared with varying contents of TESPT and TESPD, with the levels of filler-rubber interaction, the tensile strength and elongation at break, as well as tear resistance are plotted as function of chemically bound rubber contents, as shown in Figures 4.5 and 4.6, respectively. Linear correlations between tensile strength and tear resistance with the chemically bound rubber contents, i.e. filler-rubber interactions, are observed, while the strain at break does not significantly change with the increase of chemically bound rubber. These results provide clear evidence that the mechanical properties of silica-filled rubber vulcanizates are improved to a large extent by incorporating silane coupling agents. It is very surprising that the chemically bound rubber before vulcanization apparently determines mechanical properties throughout the vulcanization process, where the latter apparently has little impact anymore on the silica-silane coupling. It emphasizes the importance of a good silica-silane reaction in the mixing process. Both tensile and tear resistance show optimal values when TESPT and TESPD were incorporated at 9 – 12 wt % relative to the amount of silica. This corresponds to the recommended quantity according to Equation 3.1: i.e. 9.0 wt % of silica.

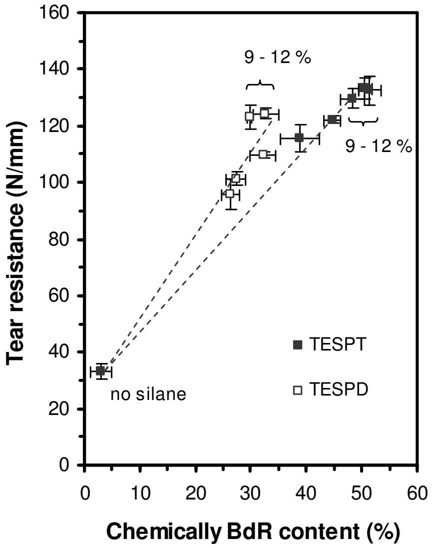

Figure 4.6 *Correlation between tear resistance with chemically bound rubber (BdR) content of silica-filled NR compounds with various amounts of TESPT and TESPD. 9-12% indicates the amount of silane in weight percentage relative to silica.*

4.3.2 Effect of diphenylguanidine

4.3.2.1 Mooney viscosities and cure characteristics. — Mooney viscosities and rheometer torques as function of DPG content are shown in Figure 4.7. With increasing DPG content in the compounds, the Mooney viscosity increases, whereas the minimum cure torque decreases. The viscosity of silica-filled natural rubber in presence of TESPT coupling agent is affected by several factors including filler-filler and filler-rubber interactions, eventual premature crosslinking, silica flocculation and the polymer chain length decreasing as a result of mixing shear. Under the same mixing procedure and temperature condition and with a fixed amount of TESPT, the increase in Mooney viscosity with increasing DPG content is an indication of higher filler-rubber interaction and possibly premature crosslinking. However, the minimum cure torque (S'_{min}) surprisingly does not follow this trend. At the vulcanization temperature, some silica flocculation may take place during the induction period,[12] and this phenomenon also affects the torque. The change of rheometer minimum torques therefore depends on competition between filler-rubber interaction, premature crosslinking and silica re-agglomeration. The reduction of the rheometer minimum cure torque with increasing DPG content suggests that the flocculation is largely suppressed when more DPG content is introduced, as the fast formation of a crosslinking network can prevent the re-agglomeration process of silica aggregates. The maximum cure torque (S'_{max}) also decreases with increasing DPG content. It again confirms that the extent of filler-filler interaction can be reduced by the use of DPG, as it lessens the flocculation tendency. In addition, the increase in rheometer torque difference ($\Delta S'$), i.e. the difference between maximum and minimum cure torques, reflects higher network contributions when DPG is increased, in correspondence with the change of Mooney viscosity.

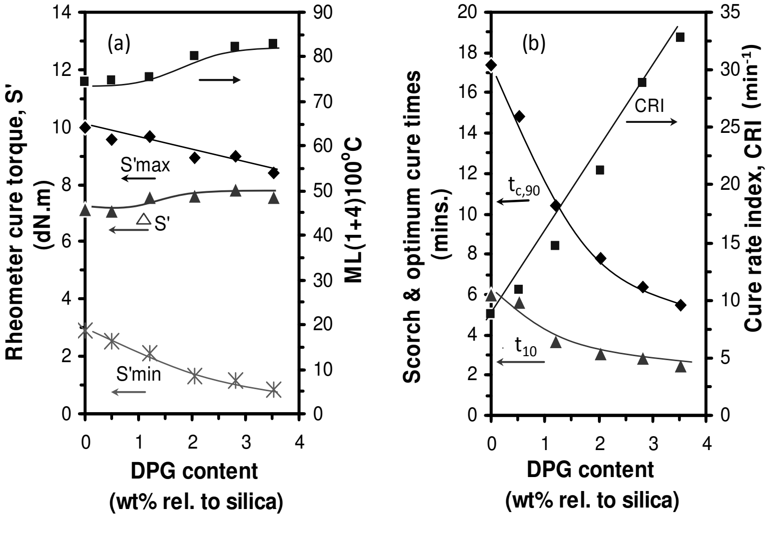

Figure 4.7 *Effect of DPG content on (a): Mooney viscosity and (b): cure characteristics of the silica-filled NR compounds.*

Cure characteristics of silica-filled NR compounds containing 9.0 wt% of TESPT relative to the silica amount and variable DPG contents are also shown in Figure 4.7. The results show that the scorch and optimum cure times of the compounds become shorter with increasing DPG content, corresponding to a steady increase of the cure rate index. Diphenylguanidine is generally used as a secondary accelerator which gives a synergistic effect with primary sulfenamide type accelerators. As the silica surface is acidic and highly polar in nature, which interferes with the performance of basic accelerators during sulfur vulcanization and causes delayed curing, the addition of DPG into the compounds improves the cure characteristics. In addition, DPG has been reported to act as a booster for the silanization reaction as amine can catalyze the condensation reaction.[16] The better silanization reaction results in more hydrophobicity of the silica surface and hence less interference with the vulcanization reaction.

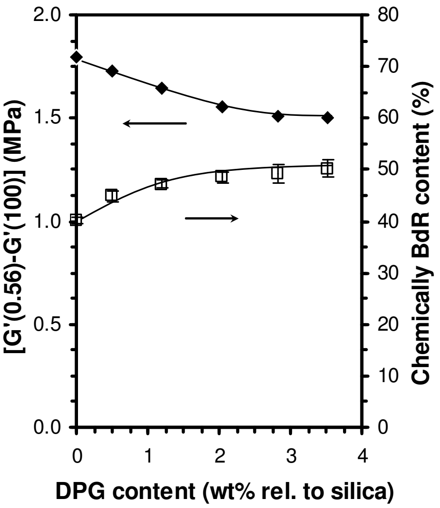

Figure 4.8 *Influence of DPG content on Payne effect and chemically bound rubber (BdR) content of the silica-filled NR compounds.*

4.3.2.2 Filler-filler and filler-rubber interactions. — Figure 4.8 shows that the chemically bound rubber content increases with increasing DPG content, while the Payne effect decreases. This observation supports that the incorporation of DPG enhances the hydrophobation of silica to result in less filler-filler interaction. In addition, DPG also functions as a silanization booster as mentioned earlier.[16] This greater efficiency of the silanization reaction leads to a better filler-rubber interaction. As a consequence, the decrease in Payne effect as well as the increase in chemically bound rubber content can be understood.

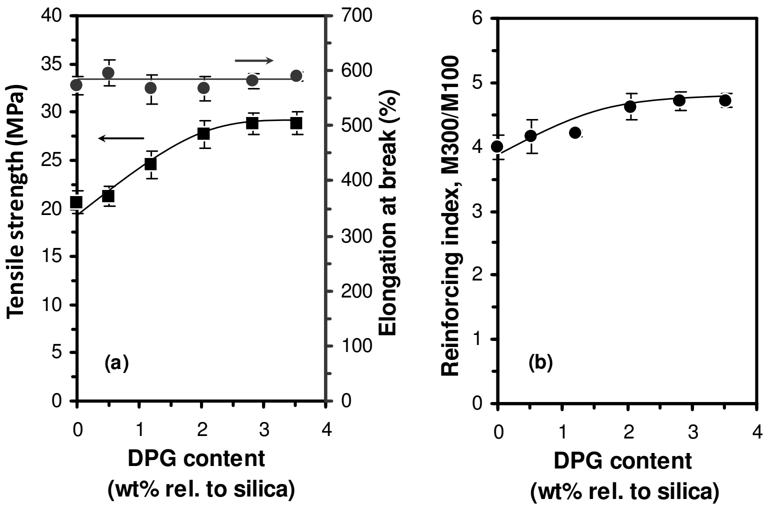

Figure 4.9 *Tensile properties of the silica-filled NR compounds adding various amounts of DPG.*

4.3.2.3 Mechanical properties. — Tensile properties of the silica-filled NR vulcanizates prepared using varying amount of DPG are shown in Figure 4.9. The tensile strength and reinforcement index M300/M100 gradually increase with DPG content up to 2 wt% of DPG relative to the silica amount, and thereafter level off when the DPG content is further increased. The elongation at break shows no significant change. The vulcanizate properties display a good agreement with the compound properties with regard to chemically bound rubber content and Payne effect. They indicate that the use of DPG at 2 wt% relative to silica is sufficient to obtain optimal properties of the silica-filled NR compounds. This optimal quantity determined experimentally here is in agreement with the calculated value according to Equation 3.2.

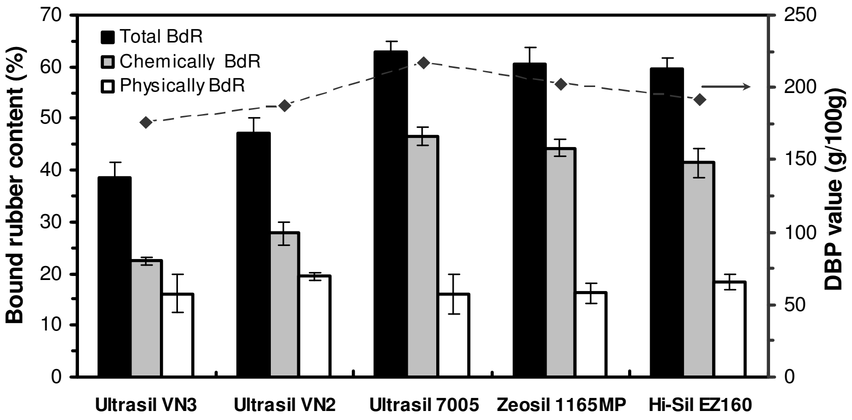

Figure 4.10 *Bound rubber content of the NR compounds filled with different types of silica, i.e. conventional and highly dispersible silicas, together with a plot of DBP value for each silica type.*

4.3.3 Effect of silica type

4.3.3.1 Filler-rubber and filler-filler interactions. — In this part of the study, two series of silica classified as (1) Conventional, i.e. Ultrasil VN2 and VN3, and (2) Highly Dispersible, i.e. Ultrasil 7005, Zeosil 1165MP and Hi-Sil EZ160, were employed to investigate their reinforcing efficiency in the NR compounds. Figure 4.10 shows the filler-rubber interaction as indicated by the total, chemically and physically bound rubber contents. Highly dispersible silicas clearly give higher total and chemically bound rubber contents, indicating a better dispersion and thus greater reinforcement power in comparison with conventional silicas. Highly dispersible silicas have been developed originally for synthetic rubbers like S-SBR and BR which develop lower shear forces than NR by lack of strain-induced crystallization so that this type of silica can be easily dispersed. The use of highly dispersible silica in rather highly viscous materials like natural rubber will surely lead to better dispersion, compared to conventional silica. Hence, the compounds filled with highly dispersible silica shall consist of smaller aggregates, corresponding to less filler-filler interaction, i.e. more filler-rubber interaction, compared to the conventional silicas, as indeed seen in the bound rubber contents in Figure 4.10. The greater extent of filler-rubber interactions leads to higher Mooney viscosities, as shown in Figure 4.11. The reduction of Payne effect when highly dispersible silicas are used instead of conventional silicas, as shown in Figure 4.12, supports their difference in levels of filler-rubber interactions.

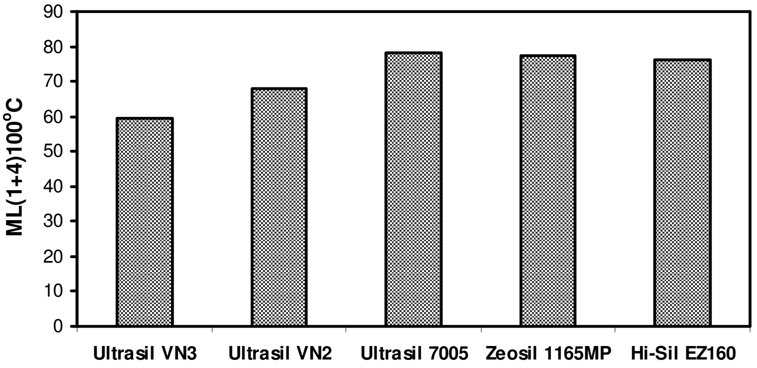

Figure 4.11 *Mooney viscosity of the NR compounds filled with different types of silica.*

Generally, in addition to the primary particle/aggregate sizes of the reinforcing fillers, filler structure also has an influence on reinforcing efficiency. The bound rubber content will depend not only on filler specific surface area and filler-rubber interaction but also on filler structure. At the optimum contents of TESPT silane coupling agent and DPG, all compounds are presumed to have relatively good filler dispersion when compared within the same group (either conventional or highly dispersible silicas). The difference in bound rubber content within each group can therefore be attributed to filler structure.

Considering the results shown in Figure 4.10, the bound rubber contents correspond well with the DBP-values as given in Table 4.1. In general, the DBP-value is a measure of reinforcing filler structures. The higher the DBP value, the higher the extent of bound rubber, in particular the chemically bound rubber. A high DBP-value indicates structures with high branching of aggregates[1,2,5] which provide a greater surface contact area between silica and rubber. For conventional silicas, Ultrasil VN2 with a lower CTAB-specific surface area but higher DBP value (Table 4.1), gives a higher bound rubber content compared to Ultrasil VN3. The highly dispersible silicas also show that filler-rubber interaction in the compound corresponds most clearly with filler structure, i.e. DBP-value and practically not with the BET or CTAB specific surface areas. As reported by Blume,[5] dispersion depends mainly on the DBP-value, where higher DBP-values lead to better filler dispersion. As the rubber molecular chains penetrate into the voids of silica aggregates during mixing, a higher structure with higher void volume allows more rubber molecules to penetrate into agglomerates, thus leading to breakdown of agglomerates into the smaller aggregates. This accounts for better dispersion of silica in the rubber, and hence higher filler-rubber interaction.

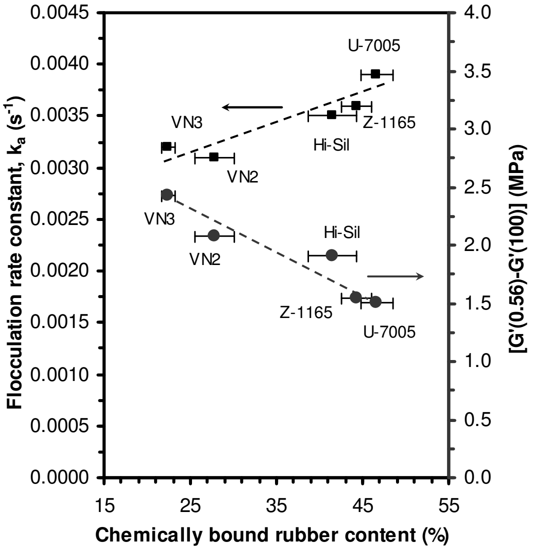

Figure 4.12 *Relationship between flocculation rate constant, Payne effect and chemically bound rubber content of the silica-filled NR compounds prepared with different types of silica.*

4.3.3.2 Silica dispersion stability. — Figure 4.12 shows that the compounds filled with highly dispersible silicas have poorer dispersion stability than the ones with conventional silicas, as faster flocculation can be observed in these compounds. Based on the bound rubber content depicted in Figure 4.10, highly dispersible silicas provide higher filler-rubber interaction. This should also provide better dispersion stability and suppress the flocculation process. However, this is not the case. A possible explanation may be in the diffusion of silica aggregates as it plays a role in flocculation kinetics. It is well known for colloidal systems that the diffusion constant depends on temperature, and inversely relates to viscosity and radius of the particles. This has empirically been proven to apply to filled rubber compounds, as demonstrated by a change of carbon black flocculation with matrix viscosity.[11] The increase of flocculation rate constant in spite of increasing compound viscosity and chemically bound rubber, as well as with increasing DBP-value: Figures 4.10-4.12, may therefore be attributed to a smaller size of the silica aggregates. The higher filler structure leads to a greater extent of agglomerate breakdown, resulting in smaller aggregates which can easier migrate through the unvulcanized compound under thermal conditions. The results do suggest however that even though highly dispersible silica is employed, the flocculation process in the compounds cannot be prevented. However, this feature does not give adverse effects on the Payne effect measured at 100 °C. The highly dispersible silicas still display less filler-filler interactions than the conventional counterparts.

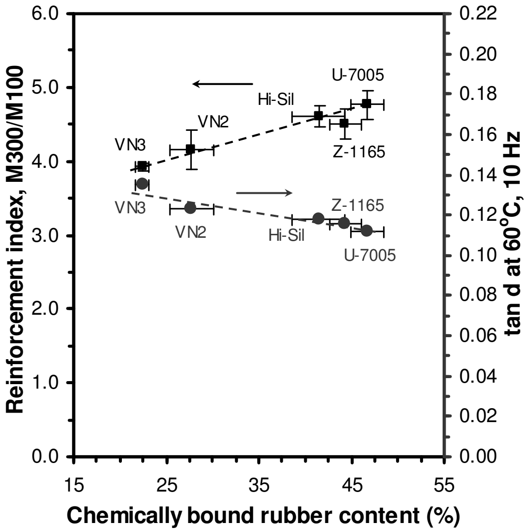

Figure 4.13 *Correlation between reinforcement index, tan δ at 60°C and chemically bound rubber content of the silica-filled NR compounds prepared with different types of silica.*

4.3.3.3 Mechanical and dynamic properties. — Reinforcement index M300/M100 and tan δ at 60°C correlate well with the chemically bound rubber content as depicted in Figure 4.13. Again, the chemically bound rubber content before vulcanization appears to be the governing factor for these mechanical properties after vulcanization. The use of highly dispersible silicas improves the mechanical and dynamic properties of filled NR vulcanizates. Generally, these two parameters reflect the rolling resistance of tires with treads made out of these rubbers. It is clearly indicated that the use of highly dispersible silica may provide lower rolling resistance compared to conventional silicas.

4.4 CONCLUSIONS

The addition of a silane coupling agent into silica-filled NR compounds significantly reduces Mooney viscosities and rheometer minimum cure torque (M_L) as result of hydrophobation and lubrication effects. Increasing TESPT contents decrease both scorch and cure times of the compounds while TESPD prolongs scorch time. The Payne effect and flocculation rate constant as indicative for filler-filler interactions decrease with more of these silane coupling agents used. The use of TESPT results in a greater extent of filler-rubber interactions, dispersion stability, tensile strength and tear resistance, when compared to the use of TESPD. Both types of silane show optimal loadings at approximately 9.0 wt% relative to the amount of silica. With incremental amounts of DPG, shorter scorch and cure times of the silica-TESPT filled NR compounds are observed. More DPG decreases the Payne effect and increases the bound rubber content as indicative for filler-rubber interactions. Tensile strength and reinforcement index M300/M100 increase with the addition of DPG up to its optimal amount of 2 wt% relative to the silica. Highly dispersible silicas provide higher bound rubber contents than conventional silicas and these values are in accordance with the DBP-values indicating higher silica structure. The use of higher structure silicas results in a lower Payne effect, i.e. better filler-rubber interaction, but also generates a faster flocculation process or less dispersion stability when compared with conventional silicas. A higher silica structure leads to better dispersion, smaller aggregate sizes and thus faster flocculation. The HD-silica reinforced-NR vulcanizates show better reinforcement index and lower tan δ at 60°C, indicative for lower rolling resistance if used in tire treads, compared to those of conventional silica filled compounds. The vulcanized properties linearly correlate with the chemically bound rubber contents before vulcanization.

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CHAPTER 5

ROLE OF DIFFERENT FUNCTIONALITIES IN SILANE COUPLING AGENTS ON REINFORCING EFFICIENCY OF SILICA-FILLED NATURAL RUBBER COMPOUNDS

The most commonly used silane coupling agents for optimizing overall properties of silica-filled rubber products are bifunctional organosilanes, in particular bis-(triethoxysilylpropyl) tetrasulfide (TESPT). In this chapter, different silane coupling agents are studied in order to gain better understanding of the role of TESPT used in silica-filled natural rubber (NR) compounds. Four silane coupling agents containing different functionalities, i.e. bis-(triethoxysilylpropyl) disulfide (TESPD), octyltriethoxysilane (OTES), vinyltrimethoxysilane (VTMS), and bis-(trimethylsilylmethyl) tetra-sulfide (TMSMT), are comparatively investigated using TESPT as a reference. The results reveal that alkoxy-based silanes (i.e. TESPT, TESPD, OTES and VTMS) can effectively reduce filler-filler interaction or Payne effect, leading to considerably improved silica dispersion and hence lower compound viscosity. This is attributed to the effect of silane-to-silica hydrophobation which contributes to better compatibility between silica and NR. The alkoxy-silanes with a sulfur moiety in their molecules, i.e. TESPT and TESPD, show more pronounced improvement in overall properties as a result of a strong and great extent of filler-rubber interaction generated in the compounds. However, TESPT gives superior efficiency than TESPD due to the effect of sulfur donation of TESPT itself. In addition, the use of TMSMT which has no alkoxy groups but contains only a sulfur moiety, elucidates that there are three reaction mechanisms involved in the system that utilizes sulfur-alkoxy-based silane coupling agents. These are: 1) silane-to-silica or silanization/hydrophobation reaction; 2) silane-to-rubber or coupling reaction; and 3) rubber-rubber crosslinking originating from the active sulfur released by the polysulfide-based silane TESPT. These simultaneous reactions are temperature dependent, and show an optimum level at a dump temperature of approximately 140-150 ^{o}C, as depicted by filler-filler and filler-rubber interaction, as well as mechanical properties of such compounds.

5.1 INTRODUCTION

A major drawback associated with the use of silica in rubber compounds are the processing difficulties derived from poor compatibility between highly polar silica and non-polar general purpose rubbers. Silica particles have a high surface energy due to a high concentration of silanol groups on their surface and tend to self-associate via hydrogen bonding, leading to the formation of a strong filler-filler network which results in a poor dispersion in the rubber matrix.[1,2] Mixing of silica-filled compounds needs to be optimized in combination with use of a silica surface modifying agent or coupling agent to ensure a good dispersion of silica in the rubber compounds.

Since the processability and properties of the silica-filled rubber compounds are strongly dependent on filler microdispersion and filler-rubber interaction, the self-association of the silica has to be minimized. There are several approaches towards improved silica dispersion and enhanced filler-rubber interactions, such as an optimization of the mixing procedure,[3] silica surface treatment,[4] newly developed silicas,[5,6] and the use of polar-functionalized rubbers as compatibilizers.[7] The most widely used method to maximize the reinforcing efficiency of silica is by use of bifunctional organosilanes as coupling agents. Under optimal conditions the silanes will chemically bond with silica during mixing and later couple with rubber during the vulcanization stage.[8,9]

Bis-(triethoxysilylpropyl) tetrasulfide (TESPT) is presently the most commonly used silane coupling agent. Studies on the coupling reaction mechanisms of TESPT towards silica and rubbers, have been extensively reviewed in Chapter 2 of this thesis.[8-13] In practical mixing procedures, the silica, TESPT and rubber are simultaneously introduced into a high thermo-mechanical internal mixer, in which various complicated reactions simultaneously take place. Within this mechanistic complexity, the extents of two important reactions need to be optimized: 1) the silanization or hydrophobation reaction between silane and silica; and 2) the coupling reaction between silane and rubber. Both reactions are dependent on time and temperature. The hydrophobation reaction is rather slow at moderate temperatures of e.g. 120°C.[8] Thus, a high compound mixing temperature which is often determined as the dump temperature is required in order to obtain a short processing cycle. At elevated temperatures, on the other hand, the coupling reaction between silane and rubber can be triggered resulting in premature scorch and hence an undesired high compound viscosity.[14-17] Based on a study with SBR/BR compounds,[14] the dump temperature should be in the range of 145-155°C to achieve good silanization and to avoid pre-crosslinking. In our work,[18] as presented in Chapter 3 of this thesis, the results indicate that in addition to the silanization reaction, pre-crosslinking reactions take place during NR compound mixing since NR can start to react with sulfur released from TESPT molecules at a temperature as low as 120°C. However, this phenomenon does not have an adverse effect on the NR vulcanizate properties. So, based on the overall properties, it was suggested that a dump temperature in the range of 135-150°C is still the most appropriate condition for silica-filled NR compounds with TESPT as coupling agent.

In the present chapter, the experiments are designed such as to render insight in the chemical mechanism of bifunctional organosilanes in reaction with NR, especially bis-(triethoxysilylpropyl) tetrasulfide. To observe the phenomena of the key functionalities, the quantities of silanes used in this study are based on equimolar concentrations of alkoxy- or sulfur-functionalities with reference to a certain amount of TESPT. Thereby, the number of alkoxy groups in alkoxy-based silanes is equalized so that the silanization or hydrophobation effect can be compared for each compound. A silane carrying only tetrasulfide groups (without alkoxy groups) is included comparable to the active sulfur content assumed to be available in the TESPT-added compound system. The effect of average sulfur chain length of silane coupling agents on the reinforcement efficiency is also studied to obtain information about whether the tetrasulfide group of TESPT is the optimal sulfur rank, or whether other (lower) sulfur ranks give comparable or even better performance. In addition, a vinyl type silane is included to investigate the effects of different alkoxy type functionalities, and whether the vinyl-site can also react with NR. The properties of silica-filled NR compounds and vulcanizates prepared with different silane agents are correlated with the phenomena of reinforcement. Various factors influencing the reinforcing ability of silanized silica in NR are discussed.

5.2 EXPERIMENTAL

5.2.1 Materials and compound recipes

In present experiments, the ingredients and compound recipe were the same as what has been described in Chapter 3, but only the type of silane coupling agents was varied as shown in Table 5.1.

***Table 5.1** Compound formulation.*

Ingredients	Amount (phr)
NR (RSS3)	100.0
Silica (Ultrasil 7005)	55.0
TESPT (or other)[a]	5.0 (or variable)[b]
Process oil (TDAE)	8.0
Zinc oxide	3.0
Stearic acid	1.0
TMQ	1.0
DPG	1.1
CBS	1.5
Sulfur	1.5

[a] *Five types of silane modifying agents were studied, as shown in Table 5.2.*

[b] *The variable amounts of other silanes were calculated, based on equimolar loadings of the alkoxy or sulfur functionalities compared to TESPT, as shown in Table 5.2.*

The five silanes employed include bis-(triethoxysilylpropyl) tetrasulfide (TESPT), bis-(triethoxysilylpropyl) disulfide (TESPD), (their technical details are given in section 4.2.1), octyltriethoxysilane (OTES), vinyltrimethoxysilane (VTMS), (both are from Merck KGaA, Germany), and bis-(trimethylsilylmethyl) tetrasulfide (TMSMT) which was synthesized in-house. The chemicals used for synthesizing TMSMT were chloromethyl-trimethylsilane (Merck KGaA, Germany), sodium sulfide (Alfa Aesar, USA), sublimed sulfur in powder form (Sigma-Aldrich, Germany), and absolute ethanol (Merck KGaA, Germany).

The quantities of silanes used in this study were based on equimolar concentrations of alkoxy- or sulfur-functionalities with reference to TESPT which was added at 5.0 phr or 9.0 wt% relative to the silica amount: Table 5.1. Thereby, the number of alkoxy groups in alkoxy-based silanes, i.e. TESPT, TESPD, OTES and VTMS, was equalized so that the silanization or hydrophobation effect can be compared for each compound. Meanwhile, the TMSMT amount was adjusted with respect to the active sulfur content assumed to be available in the system. Table 5.2 shows the amounts of silane agents used in this work. In order to clearly observe the effect of sulfur moiety in TESPT, the total sulfur amount present in the compound recipe was not corrected for the other silanes, different from the approach taken in Chapter 4.

Table 5.2 *Quantities of silanes applied into the formulation.*

Silane	Mw (g/mol)[a]	Epuimolar amount (mole)	Dose (wt%)[b]	Dose (phr)
TESPT	539	1.0[c]	9.0	5.0
TESPD	475	1.0[d]	7.9	4.4
OTES	276	2.0[d]	9.2	5.1
VTMS	148	2.0[d]	4.9	2.7
TMSMT	302	1.0[e]	5.0	2.8

[a] *corresponding to their chemical structures as shown in 5.2.3.*

[b] *wt% relative to 55 phr silica amount.*

[c] *reference.*

[d] *molar equivalent in alkoxy functionality.*

[e] *molar equivalent in sulfur functionality.*

5.2.2 Synthesis of bis-(trimethylsilylmethyl) tetrasulfide, TMSMT

The synthesis was carried out following the procedures described by Childress.[19]

5.2.2.1 Synthesis procedure. — The synthesis began with the reaction between sodium sulfide (Na_2S) and elemental sulfur, the so-called sulfur addition, in order to first obtain sodium polysulfide, preferably the tetrasulfide (Na_2S_4), as given in the following chemical equation (5.1):

$$Na_2S + 3S \rightarrow Na_2S_4 \qquad (5.1)$$

1 mole of Na_2S and absolute ethanol at about 80 wt% relative to the entire amount of the mixture were fed into a continuously stirred reactor, and stirred at a consistent speed, at 25°C under nitrogen atmosphere. Afterwards, 3 moles of sublimed sulfur in powder form were added. The reaction system was then heated to approximately 80°C within 13 mins to reflux, and subsequently the mixture turned dark in color. This reaction was continued over a period of 1 hour. After that the reactor was cooled down to 45°C and ready for subsequent addition of the halohydrocarbontrialkyl silane.

Chloromethyltrimethylsilane was filled into an additional funnel, and subsequently added dropwise into the reactor, which already contained Na_2S_4. The molar ratio of chloromethyltrimethylsilane to Na_2S_4 was 2:1, as demonstrated in Equation (5.2):

$$Na_2S_4 + 2Cl(CH_2)Si(CH_3)_3 \rightarrow (CH_3)_3Si(CH_2)S_4(CH_2)Si(CH_3)_3 + 2NaCl \quad (5.2)$$

The chloromethyltrimethylsilane was charged into the reactor in a time period of approximately 2 hours. After completing the addition, the reaction mixture was heated to about 80°C, and held under reflux for 3 hours. Then, the reactor was cooled to 25°C to obtain the product which was contaminated with sodium chloride salt.

The products obtained from the reaction include not only the bis-trimethylsilylmethyl tetrasulfide, TMSMT, but also the by-product of sodium chloride salt. It was suggested in the patent[19] that the salt particles produced in the chloromethyltrimethylsilane addition step are fairly large, and so filtration can be used for salt removal. Filtering paper with 5 micron pore size was therefore employed. The salt residue still contained residual TMSMT liquid product and was washed with ethanol to increase the overall product yield.

The ethanol was removed by using a rotary evaporator. After the evaporation process, the product was further dried in a vacuum oven at 80°C for 24 hours.

5.2.2.2 Characterization of product structure. — The chemical structure of the obtained product was characterized by using a 500 MHz Nuclear Magnetic Resonance (NMR) spectrometer (Unity Inova, Varian, Germany) with the ^{1}H-NMR technique. The sample was dissolved in deuterated chloroform $CDCl_3$. The ^{1}H-NMR spectrum of chloromethyltrimethyl silane which is a reagent for the reaction was also verified as a reference. The results obtained are depicted in Figure 5.1 and the proton type assignments for each absorption peak are shown in Table 5.3.

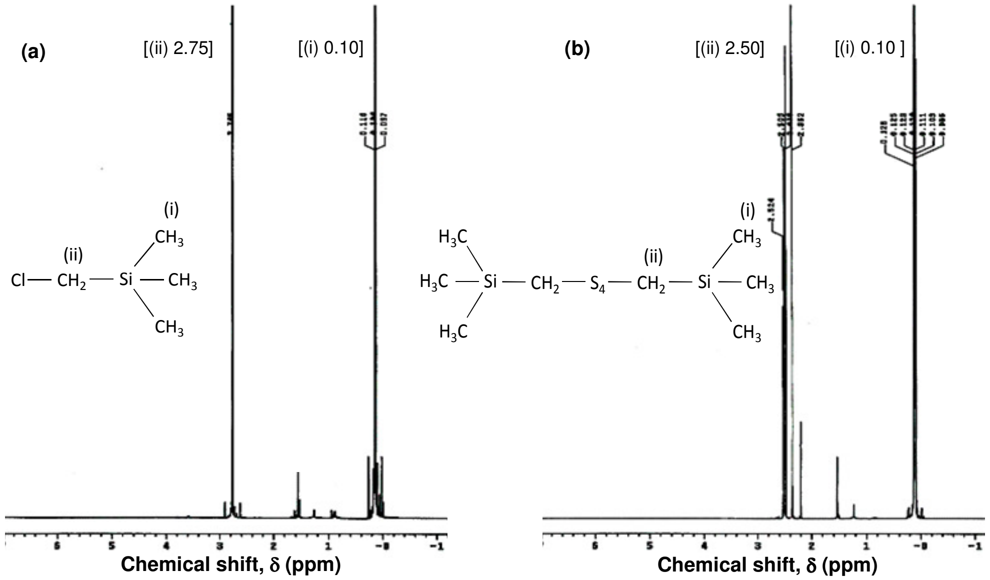


Figure 5.1 *^{1}H-NMR spectra of (a) chloromethyltrimethylsilane and (b) bis-(trimethylsilylmethyl) tetrasulfide TMSMT.*

Table 5.3 *Chemical shifts of different protons of chloromethyltrimethylsilane and bis-(trimethylsilylmethyl) tetrasulfide, TMSMT.*

Chemical shift (ppm)	Type	Description
0.10	Singlet	$-CH_3$
2.50	Singlet	$-CH_2-$, sulfur side
2.75	Singlet	$-CH_2-$, chloride side

The NMR spectra prove that the product obtained from the synthesis has the desired chemical structure, as evidenced in Figure 5.1. From Figure 5.1(a) and Table 5.3, the reagent chloromethyltrimethylsilane displays peaks at chemical shifts of 0.10 ppm assigned to the protons of the $-CH_3$ groups adjacent to the silicium atom, and at 2.75 ppm assigned to the protons of the $-CH_2-$ group adjoining the chloride atom. After the chloromethyltrimethylsilane has reacted with Na_2S_4 to obtain the desired product, the absorption peak of the methylene protons $-CH_2-$ has shifted from 2.75 ppm to about 2.50 ppm corresponding to the signal of methylene protons located next to a sulfur atom, as demonstrated in Figure 5.1(b). In addition, a few extra signals appearing close to 2.50 ppm indicate that the sulfur rank adjacent to the $-CH_2-$ group can be different. This refers to the mixture of sulfur chain lengths contained in this silane. Therefore, the ^{1}H-NMR technique provides a first indication for the successful synthesis of bis-(trimethylsilylmethyl) polysulfide.

In order to confirm the elemental composition in the molecular structure, elemental analysis was applied to quantitatively determine the percentages of carbon (C), hydrogen (H), and sulfur (S). Therefore, a CHNS-O analyzer (Thermo Quest, Italy) was employed with a dynamic flash combustion technique using the conditions as given in Table 5.4.

Table 5.4 *Test conditions of CHNS-O analyzer adjusted for the elemental analysis of the synthesized product.*

Condition	Detail
Furnace temperature	900°C
Oven temperature	65°C
Carrier flow	130 ml/min
Oxygen flow	250 ml/min
Reference flow	100 ml/min

The elemental analysis results are shown in Table 5.5, in which the percentages of each element correspond well with the values obtained based on a theoretical calculation. Therefore, it can be stated that bis-(trimethylsilylmethyl) tetrasulfide or TMSMT has been successfully synthesized and can be used for further study.

Table 5.5 *Theoretical and experimental concentrations of elements in the molecule of bis-(trimethylsilylmethyl) tetrasulfide TMSMT.*

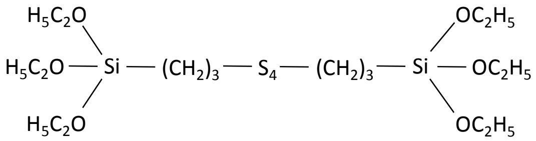
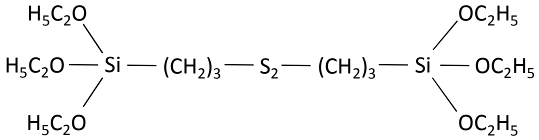
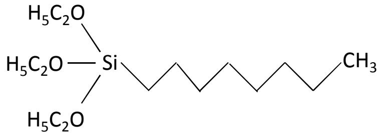
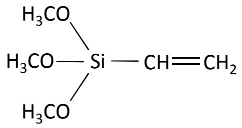
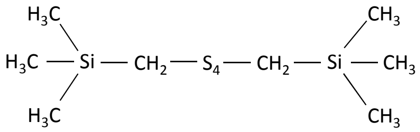
Product	wt% Elements[a]		
	Carbon	Hydrogen	Sulfur
Theory	31.8	7.3	42.4
Experiment	32.9 ± 0.2	7.5 ± 0.1	45.0 ± 0.3

[a] *The rest is the silicium content which is 18.5 wt% according to the theoretical calculation.*

5.2.3 Chemical structure of silane agents

The chemical structures of the five silane agents employed in this investigation are shown in Table 5.6.

Table 5.6 *Chemical structures of silane agents*

Chemical name	Abbreviation	Structure
Bis-triethoxysilylpropyl tetrasulfide	TESPT	
Bis-triethoxysilylpropyl disulfide	TESPD	
Octyltriethoxysilane	OTES	
Vinyltrimethoxysilane	VTMS	
Bis-trimethylsilylmethyl tetrasulfide	TMSMT	

5.2.4 Compound preparation

The equipments and procedures used for the compound mixing process were as previously described in Chapter 4.

5.2.5 Property analysis

Mooney viscosity, reinforcement parameter, Payne effect, bound rubber content and tensile properties, were tested according to the methods as described in Chapter 3.

5.3 RESULTS AND DISCUSSION

5.3.1 Mooney viscosity of the compounds as a function of mixing dump temperature

The initial mixer temperature setting was varied in order to reach different dump temperatures as illustrated in Figure 5.2.

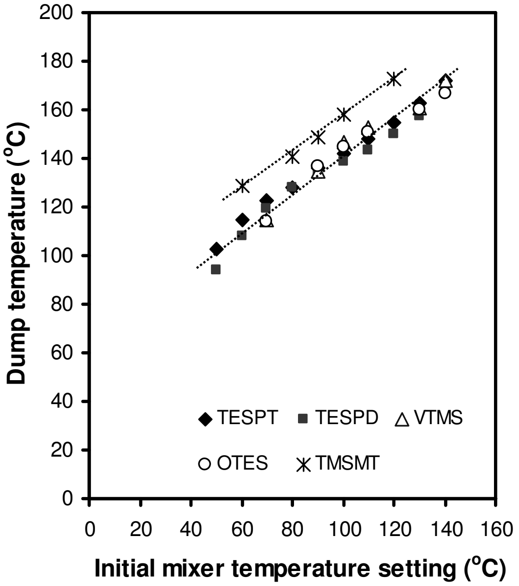


Figure 5.2 *The dump temperature of silica-filled NR compounds prepared with different silane agents as a function of initial mixer temperature setting.*

For all compound types studied, the dump temperature linearly increases with increasing initial mixer temperature setting. The compounds with alkoxy-based silanes, i.e. TESPT, TESPD, VTMS and OTES, show dump temperatures aligned on the same trend line, and which are lower compared to the dump temperatures of the compounds with the non-alkoxy based silane TMSMT. This may be attributed to the role of the alkoxy functionality, that can chemically hydrophobize the silica surface to become more compatible with the rubber phase and so improve silica dispersion, as discussed earlier in Chapter 4. With regard to the non-alkoxy type silane containing compound, due to the absence of the silanization/hydrophobation effect, silica agglomerates are difficult to break and distribute into the rubber matrix. So, the compound viscosity remains high: Figure 5.3, and extra heat is generated under the excessive shearing action.

Mooney viscosity is one of the indications for the processing properties of rubber compounds. The use of silica in rubber without proper surface modifying agent will normally result in an undesired high compound viscosity caused by the silica-rubber incompatibility. Today, various modifying agents, especially silane coupling agents, are used to effectively overcome this limitation.[8,15,20]

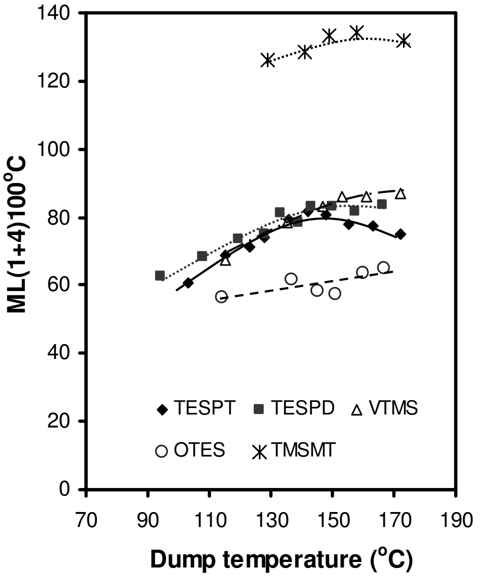


Figure 5.3 *Relationship between Mooney viscosity and dump temperature of silica-filled NR compounds prepared with different silane agents.*

As shown in Figure 5.3, the alkoxy-based organosilanes substantially reduce the compound viscosity, when compared to the non-alkoxy TMSMT, because of their hydrophobation power through the reaction of the alkoxy with the silanol groups of the silica, as already mentioned. In addition to the influence of the alkoxy groups, the sulfur moiety in the silane agents also plays a significant role. With increasing mixing dump temperature, the Mooney viscosity of the compounds prepared with TMSMT, a sulfidic (non-alkoxy)-silane, gradually increases and reaches an optimum at dump temperatures in the range of 140 - 150°C. TESPT and TESPD, which are sulfidic alkoxy-type silanes, show a similar trend, but at lower values. After the Mooney viscosities have reached the maximum value, the compounds show some sort of reversion which could be linked to a change within the polysulfide linkages. According to the conclusion given in Chapter 3, this result is in good agreement with the fact that, apart from the silanization reaction, a certain amount of coupling and cross-linking reactions of active sulfur towards natural rubber also takes place during mixing in the mixer, which results in a rise of the Mooney viscosity. Basically, all these reactions are temperature dependent. Higher mixing temperatures lead to a higher potential for silanization as well as for crosslinking.[8,11,14] In general, an increase of the degree of silanization should lead to a decrease in compound viscosity as a consequence of improvement in silica dispersion.[5,9,14] However, this is apparently not the case for NR, for which the Mooney viscosity initially increases with increasing dump temperature, and then either levels off or decreases a little after reaching a certain dump temperature. This points to a dominant effect of network contributions towards the compound viscosity. These network contributions originate from premature crosslinking that mainly includes two possible features: (1) silica-silane-rubber linkages; and (2) rubber-rubber cross-links. For the sulfide based silanes, i.e. TESPT, TESPD and TMSMT, the crosslinks are formed *via* sulfur that is released and activated at the high temperature. For vinyl silane, i.e. VTMS, the crosslinks can also occur via C=C and active radicals generated during mixing. Surprisingly, for OTES which has alkoxy groups with an alkyl chain, there is also a slight increase of the compound viscosity with increasing dump temperature. Nonetheless, the OTES silane gives the lowest compound viscosity, as this system can generate only a silanization or hydrophobation reaction and no real crosslinks.

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5.3.2 Dispersion degree and filler-filler interaction

The reinforcement parameter correlates with the degree of dispersion or morphology of the silica in the rubber matrix.[21] In Figure 5.4, TESPT gives the lowest reinforcement parameter compared to the others, indicating the highest degree of silica dispersion or smallest average size of the silica aggregates/agglomerates. TESPD shows the same trend as TESPT, but some higher values which means that TESPD provides a larger average size of the silica structures in the compounds and reflecting an inferior silica dispersion when compared with TESPT. Among the alkoxy-based silanes, the modifying agents containing sulfur, i.e. TESPT and TESPD, give better silica dispersion than the non-sulfide silanes, i.e. OTES and VTMS. The worst dispersions are observed for the compounds with TMSMT or the non-alkoxy-based silane.

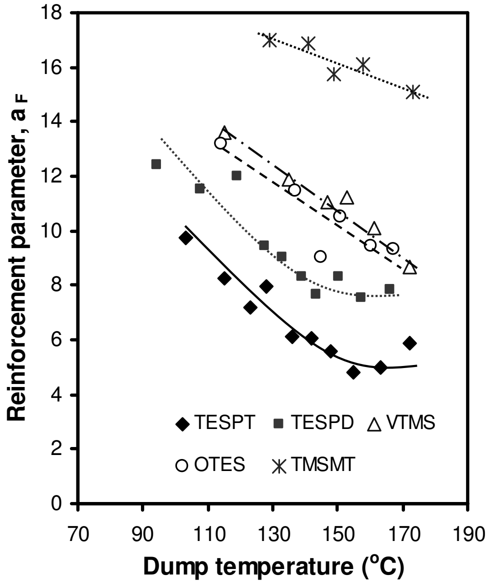

Figure 5.4 *Reinforcement parameter of silica-filled NR compounds prepared with different modifying agents as a function of dump temperature.*

In order to provide further evidence for the filler-filler networks in the compounds, the Payne effect was determined and the results shown in Figure 5.5. The change of the Payne effect with dump temperature of the different compounds shows a good agreement with the Mooney viscosities and reinforcement parameters: Figures 5.3 and 5.4, respectively. The lowest filler-filler interactions or Payne effects are achieved by using TESPT and TESPD as silica surface modifying agent. OTES and VTMS show higher levels but a similar extent of filler-filler interaction, whilst TMSMT gives the highest level of Payne effect in accordance with the poorest filler dispersion as already displayed in Figure 5.4.

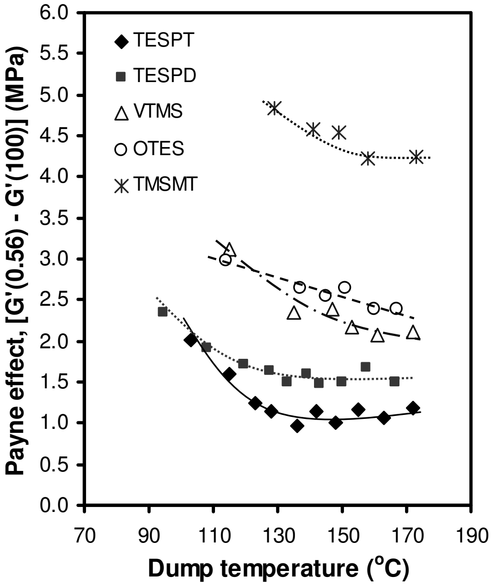

Figure 5.5 *Payne effect of silica-filled NR compounds prepared with different silane agents as a function of dump temperature.*

5.3.3 Network contributions in the compounds

Based on the results of the reinforcement parameters and Payne effects, it is clear that the alkoxy-based organosilanes reduce filler-filler interaction for silica-filled natural rubber compounds, indicating that they can effectively transform the hydrophilic into a more hydrophobic silica surface to provide better compatibility between the silica and natural rubber. This leads to improved silica dispersion. However, the different alkoxy-silanes show variable efficiency because of their differences in functionalities on the other side of the silane molecules, as depicted in Table 5.6. TESPT and TESPD possess sulfur functionalities that can create crosslinks during mixing at high temperature and so strongly affect the compound viscosity, silica dispersion, and filler-filler interaction. The alkoxy non-sulfur silanes, i.e. OETS and VTMS, show somewhat less reactivity compared to the sulfide types. Free sulfur released from TESPT can produce lightly crosslinked rubber during the non-productive mixing process.[18] These network contributions result in a better stability of the dispersed silica aggregates as the chemical linkages restrict the silica mobility in the rubber matrix, and hence suppress the re-agglomeration of silica. The explanation was already elaborated in terms of the correlation between flocculation and network contributions in Chapters 3 and 4. The sulfur moiety contained in the silanes provides additional aid for the improvement of the silica dispersion stability and Payne effect of silica-filled rubber systems. The use of TMSMT which has no alkoxy groups but only a sulfur functionality clearly demonstrates the ineffectiveness of this silane type, as it provides only a poor silica dispersion and very high extent of filler-filler interaction in the NR compounds. Not being able to silanize, TMSMT cannot chemically hydrophobize the silica surface and so the large difference in polarity between silica and NR is not overcome. The results demonstrate that it is necessary to utilize bifunctional organosilanes for silica-filled compounds.

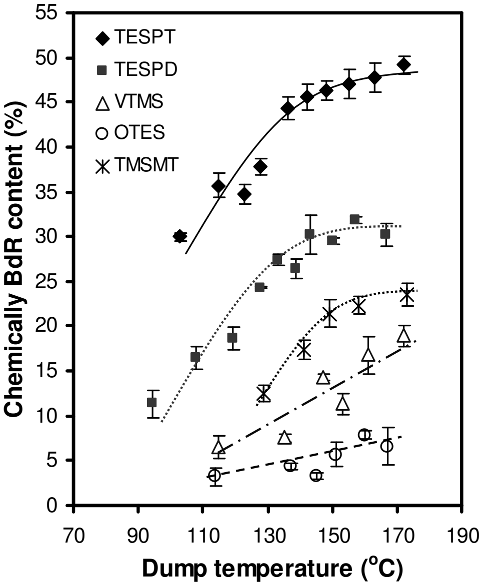

Figure 5.6 *Chemically bound rubber (BdR) content of silica-filled NR compounds prepared with different silane agents as a function of dump temperature.*

5.3.4 Mechanical properties of vulcanizates

In Figure 5.7, the highest tensile strength of vulcanizates is observed when TESPT is applied as a surface modifying agent. This is followed by TESPD, VTMS, OTES and TMSMT, respectively. For the coupling agents, TESPT, TESPD and VTMS, a decrease of tensile strength is seen when the dump temperature exceeds 150°C, indicating some sort of reversion and inevitable NR degradation under high temperature and shearing forces, as discussed in 3.3.5. The compounds with OTES, which acts as a silica hydrophobizing agent, only show an increase of tensile strength with dump temperature indicating a better silanization, but without the coupling reaction the ultimate strength is lower. Regarding TMSMT, it cannot hydrophobize the silica surface and results in the poorest silica dispersion: Figures 5.5 and 5.6, and consequently the lowest mechanical properties are obtained.

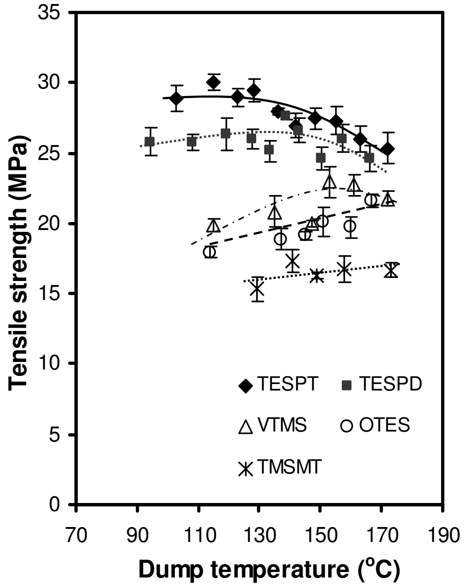

Figure 5.7 *Tensile strength of silica-filled NR vulcanizates prepared with different silane agents as a function of dump temperature.*

The reinforcement index (i.e. the ratio of modulus at 300 % strain to modulus at 100 % strain), shown in Figure 5.8, depicts a good agreement with the tensile strength: Figure 5.7. TESPT gives the highest reinforcement efficiency, followed by TESPD. Furthermore, it can be seen that the vulcanizates containing TESPT and TESPD show more or less the same maximum region of reinforcement index with regard to the dump temperature in the range of 140-150°C. The alkoxy-silanes without sulfur moiety, i.e. VTMS and OTES, show a considerably lower reinforcement efficiency, while the non-alkoxy silane, TMSMT, provides the lowest values. However, it should be noted that with increasing dump temperatures, the improvement in degree of dispersion: Figure 5.5, in the VTMS-, OTES- and TMSMT-containing compounds also improves the mechanical properties of the vulcanizates as reflected in the increase of tensile strength and reinforcement index.

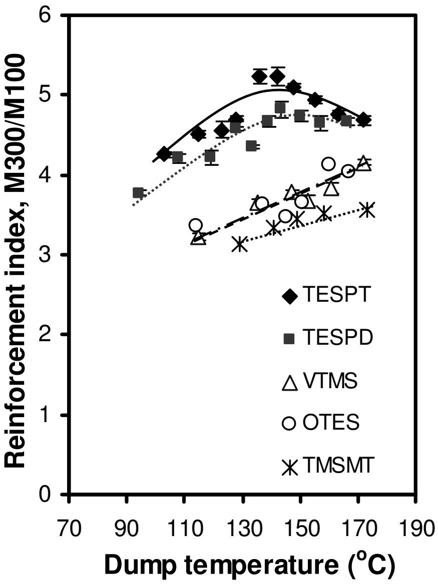

Figure 5.8 *Reinforcement index of silica-filled NR vulcanizates prepared with different silane agents as a function of dump temperature.*

Based on the results in this investigation, it can be concluded that sulfide-alkoxy-based silane coupling agents give the most practical and technical benefit for silica-reinforced natural rubber compounds. These chemicals can effectively reduce compound viscosity, filler-filler interaction, while providing relatively high filler-rubber interaction, and so lead to much better improvement in mechanical properties when compared to the only alkoxy- or sulfide-based silanes. The properties, i.e. reinforcement parameters, Payne effects, tensile strengths and reinforcement indices, of the silica-reinforced NR compounds are clearly separated into three groups. TESPT and TESPD are the most efficient coupling agents. VTMS and OTES can hydrophobize the silica surface leading to improved dispersion and so provide an intermediate level of properties. The worst case is found for TMSMT which has no alkoxy groups, and so provides no hydrophobation effect. The poor silica dispersion and strong filler-filler interactions in the TMSMT containing compounds result in the lowest mechanical properties.

5.4 CONCLUSIONS

This investigation clarifies the reinforcing mechanism of silica-filled NR compounds in the presence of silane coupling agents, in particular the most widely used ones bis-(triethoxysilylpropyl) tetra- and di-sulfide: TESPT and TESPD. When organosilanes bearing alkoxy- and sulfide functional groups only are used, there are three reaction mechanisms competitively taking place during compound mixing or in the non-productive mixing process. These mechanisms are all temperature dependent: 1) the silane-to-silica or silanization/ hydrophobation reaction; 2) silane-to-rubber or coupling reaction; and 3) rubber-rubber crosslinking originating from active sulfur released by the polysulfide-based silanes. These simultaneous reactions reach an optimum at a dump temperature of approximately 140-150°C, as determined by filler-filler and filler-rubber interaction, and mechanical properties. The network structures between silica-silane-rubber and rubber-rubber primarily account for an increase of the Mooney viscosity and chemically bound rubber content, as well as improved silica dispersion with less filler-filler interaction. The silane bearing only alkoxy groups show that it can improve the processing properties: lower Mooney viscosity, silica dispersion, Payne effect and mechanical properties compared to the one without. However, the best possible overall properties are only obtained when bifunctional coupling agents are used.

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CHAPTER 6

USE OF A DISULFIDE-BASED SILANE COUPLING AGENT WITH COMPENSATION OF SULFUR FOR SILICA-FILLED NATURAL RUBBER COMPOUNDS

Free sulfur released from bis-(triethoxysilylpropyl) tetrasulfide (TESPT) under high thermo-mechanical mixing conditions turns out to be an important factor influencing the reinforcement efficiency of silica in natural rubber (NR) compounds. In this chapter, the influences of variable quantities and different addition sequences of extra sulfur into silica-filled NR compounds, with bis-(triethoxysilylpropyl) disulfide (TESPD) as coupling agent, on the properties are investigated in comparison with the compound with bis-triethoxysilylpropyl tetrasulfide (TESPT) as reference. The results indicate that addition of extra sulfur during mixing of TESPD-silica-NR in the internal mixer significantly changes the overall properties of compounds and vulcanizates. On the other hand, compounds with extra sulfur added on a cold two-roll mill show no significant changes compared to the one without sulfur compensation. Mooney viscosity and cure characteristic of the compounds indicate that free sulfur introduced in the internal mixer causes premature crosslinking of the rubber phase as indicated by an increase of the chemically bound rubber content. The rubber-rubber crosslinking originating from free sulfur available during mixing has a strong influence on improved silica dispersibility. With increasing extra sulfur content, a lower flocculation rate constant, a lower reinforcement parameter and Payne effect are obseved. Based on this investigation, extra sulfur at approximately 0.15 – 0.20 phr, or 3.4 – 5.1 wt% relative to the TESPD content, added during mixing of TESPD-silica-NR in an internal mixer is an optimal amount to achieve better scorch safety of the compounds, and comparable mechanical properties of the vulcanizates, compared with those based on TESPT as coupling agent without extra sulfur.

6.1 INTRODUCTION

A bifunctional organosilane is one of the most essential ingredients in silica-filled rubber compounds to boost the overall properties of the rubber both before and after vulcanization.[1-4] High polar silica and non-polar commodity rubbers can be compatibilized by using the bifunctional organosilane.[3-7] As a consequence, several negative features of the mixes can be improved, e.g. the cure characteristics, compound viscosity, degree of dispersion, energy input for the compounding process, as well as processing cycle time. It also produces a remarkably strong filler-to-rubber interaction leading to a pronounced enhancement in end-use properties of rubber products, particularly tires.[7] In 1992 Michelin[8] introduced a low rolling resistant tire which combined highly dispersible silica with bis-(triethoxysilylpropyl) tetrasulfide (TESPT) as bifunctional silane coupling agent in a solution-SBR/BR based tread-compound. Since then the field of silica technology applied in the tire industry has grown tremendously in order to implement energy saving low rolling resistance tires, to comply with new legislation and to produce “Greener” products.[7,8]

As reviewed in previous chapters, TESPT today is the most commonly used silane coupling agent in the rubber industry. Apart from several benefits derived from TESPT as mentioned earlier, there remain some drawbacks. Based on previous studies,[4,6,9,10] and the investigation reported in Chapter 3, the complete silanization reaction between silane and silica during compound mixing requires an appropriate dump temperature, i.e. in the range of 140 – 150°C for SBR/BR compounds, and 135 – 150°C for NR. A high mixing temperature leads to disproportionation of TESPT, simultaneous with the liberation of free sulfur into the compound system, resulting in an undesired high compound viscosity caused by premature scorch. So, both time and temperature during mixing have to be closely controlled.[5,11] However, the results from Chapters 3 – 5 indicate that the premature scorch does not have an adverse effect on the overall properties of silica-filled NR compounds. On the other hand, the lightly crosslinked network generated by free sulfur released from TESPT during mixing provides an essential benefit towards an improved reinforcement efficiency of silica in NR. In addition to hydrophobation/silanization, these partial rubber-rubber and silica-silane-rubber networks improve the silica dispersibility in the compounds, e.g. an enhanced degree of dispersion, less re-agglomeration or flocculation, and a lower Payne effect. The improvement in terms of silica dispersion correlates well with the superior overall properties of NR vulcanizates.[12,13]

With respect to the poor scorch safety of TESPT-based compounds,[6,9,10,14] an alternative silane: bis-(triethoxysilylpropyl) disulfide (TESPD) has been made available. As illustrated in Table 5.6, the average sulfur chain length of the two silanes is different. TESPT contains approximately four atoms of sulfur in its structure, while TESPD has two sulfur atoms. According to the study in Chapter 4, TESPT shows a significantly shorter induction period or scorch time than TESPD, due to the effect of sulfur liberated by TESPT. However, the TESPT-based compounds show superior overall properties compared to those containing TESPD, and this positive effect is mainly attributed to the influence of extra free sulfur liberated from TESPT during mixing in the internal mixer.[13]

The experiments presented in this chapter aim to study the effect of free sulfur introduction under high thermo-mechanical mixing of silica/TESPD-based NR compounds. Variable quantities of extra sulfur are added into the compounds at two different mixing stages: 1) during the non-productive mixing step in the internal mixer; and 2) together with the normal curatives on the two-roll mill. The compound with presence of TESPT at 9.0 wt% relative to the silica amount is considered as reference. Mooney viscosity, cure characteristics, filler-rubber and filler-filler interactions, the flocculation process, and mechanical properties of the compounds are evaluated.

6.2 EXPERIMENTAL

6.2.1 Materials

The materials used for this investigation were the same as those described in Chapter 4. Table 6.1 shows the compound formulations.

Table 6.1 *Compound formulations.*

Ingredients	Amount (phr)	
	TESPT	TESPD + extra sulfur
NR (RSS3)	100.0	100.0
Silica (Ultrasil 7005)	55.0	55.0
TESPT	5.0	-
TESPD	-	4.4[a]
Process oil (TDAE)	8.0	8.0
Zinc oxide	3.0	3.0
Stearic acid	1.0	1.0
TMQ	1.0	1.0
DPG	1.1	1.1
CBS	1.5	1.5
Sulfur	1.5	1.5
Extra sulfur	-	Variable[b]

[a] *equivalent moles in ethoxy functionality, compared to 5.0 phr TESPT.*

[b] *the quantity of extra sulfur was varied, as detailed in Table 6.2.*

The amount of extra sulfur was varied from 0 – 0.6 phr or 0 – 13.6 wt% relative to the TESPD content. Table 6.2 shows the amounts of extra sulfur added into the compounds.

Table 6.2 *Variable quantities of extra sulfur used in this study.*

Dose of extra sulfur	Compounds								
	1	2	3[a]	4	5[a]	6	7[a]	8	9[a]
phr	0	0.02	0.05	0.10	0.15	0.20	0.30	0.45	0.60
wt% relative to TESPD content	0	0.45	1.14	2.27	3.41	5.07	6.82	10.23	13.64

[a] *Extra sulfur was added using two different procedures, either during mixing in the internal mixer or on the two-roll mill. The others are by adding extra sulfur in the internal mixer only.*

6.2.2 Compound preparation

All rubber compounds were prepared using the equipments and procedures as adopted in the experimental part of Chapter 4. The dump temperatures of the series of experiments were controlled at approximately 140-145°C. As given in Table 6.2, nine compounds were prepared by adding extra sulfur during the non-productive mixing step of TESPD-silica-NR in the internal mixer. Four additional compounds, with extra sulfur added on the two-roll mill, were also separately prepared.

6.2.3 Property analysis and testing

The properties of the compounds and vulcanizates were determined following the methods described in Chapter 3. Mooney viscosity and cure characteristics, reinforcement parameter, flocculation kinetics, Payne effect, bound rubber content and tensile properties were investigated.

6.3 RESULTS AND DISCUSSION

6.3.1 Mooney viscosity of the compounds

A first indication, which shows the effect of extra sulfur added into the compounds during mixing TESPD-silica-NR in the internal mixer, compared to adding on the two-roll mill, is the Mooney viscosity as depicted in Figure 6.1.

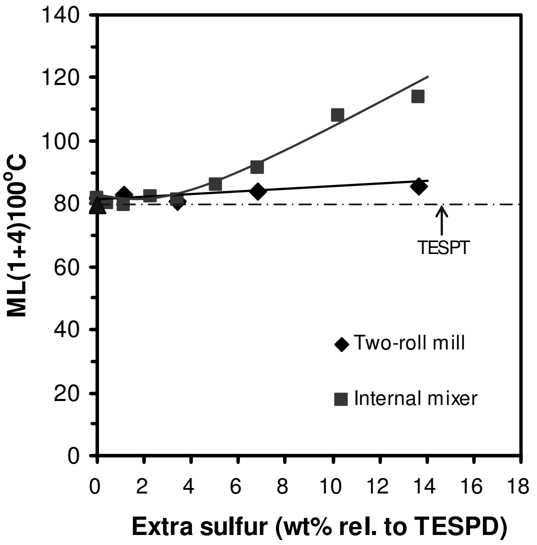

Figure 6.1 *Influence of sulfur compensation on Mooney viscosity of silica/TESPD-filled NR compounds prepared with different mixing procedures. Extra sulfur was added either on a two-roll mill or in the internal mixer, with the TESPT-containing compound included as reference.*

The introduction of extra sulfur by additional mixing on a two-roll mill causes no significant change in compound viscosity throughout the whole range of extra sulfur loadings. On the other hand, the addition of extra sulfur in the internal mixer strongly influences the viscosity of the mixes. The compounds with extra sulfur from 0 – 5.1 wt% relative to TESPD, or 0 – 0.25 phr, prepared by both mixing procedures show constant and the same Mooney viscosities. However, if the extra sulfur added into the internal mixer exceeds this range of sulfur dose, the Mooney viscosity rapidly increases. The compounds cannot be further processed when the extra sulfur loading exceeds 0.6 phr or 13.6 wt% relative to the amount of TESPD, due to an undesired high compound viscosity. Since the dump temperature of the compounds prepared in this series of experiments was controlled at approximately 140 – 145°C to ensure a complete silanization reaction, these temperatures are already sufficient to activate a crosslinking reactions between the sulfur and natural rubber.[12] High extra sulfur introduced into the compounds leads to a higher crosslink density, and consequently higher matrix viscosity. This aspect cannot be observed in the case of adding extra sulfur on the two-roll mill because of the low compounding temperature, i.e. 60-80°C.

6.3.2 Bound rubber contents in the compounds

The technique used to determine filler-rubber interaction in this work was bound rubber extraction. Ammonia treatment was applied to differentiate between the chemical and physical interactions in the compounds, as ammonia can effectively cleave physically bound rubber.[18]

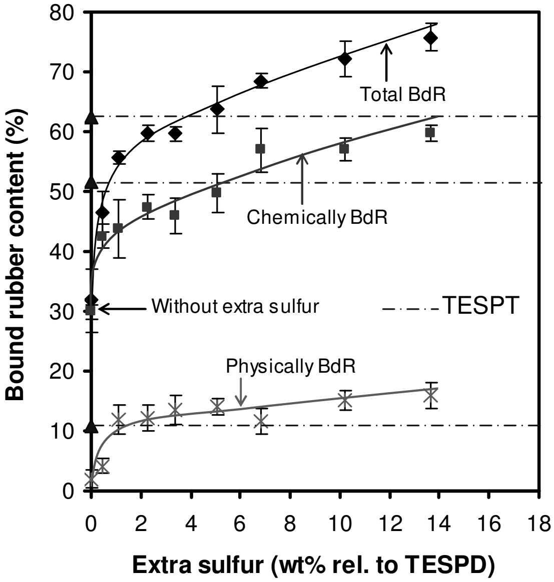

Figure 6.2 Influence of sulfur compensation on bound rubber (BdR) content of silica/TESPD-based NR compounds. Extra sulfur was added in the internal mixer. The TESPT-containing compound is included as reference.

The results in Figure 6.2 show that the TESPT-containing compound has a much higher chemically bound rubber content than the TESPD-based compound without compensation of elemental sulfur. As evidenced in Chapters 3 and 5, TESPT that possesses approximately four atoms of sulfur in its molecule can donate free sulfur into the compounds during non-productive mixing. This is an important factor for a greater extent of network contributions in TESPT compounds, when compared to TESPD-containing ones. The network structures in the compounds with TESPT mainly include filler-rubber interactions and lightly cross-linked rubber-rubber, originating from the silane-coupling and sulfur cross-linking reactions, respectively. On the other hand, TESPD provides only filler-rubber interaction since it does not liberate free sulfur into the system. The present result is in good agreement with the bound rubber data presented in Chapter 4, where variable amounts of TESPT and TESPD were investigated.[14]

Once extra sulfur is added into the compounds during mixing TESPD-silica-NR in the internal mixer, the chemically bound rubber remarkably increases. It again demonstrates that free sulfur available in the mixtures can partially cross-link the rubber phase under the high thermo-mechanical input inside the internal mixer. The slight increase of physically bound rubber with increasing extra sulfur content can be due to the chemical network structures in the rubber phase that trap additional polymer chains, inducing a higher extent of physical rubber linkages in the mixtures. The bound rubber contents of the compounds prepared by adding extra sulfur on the two-roll mill should be more or less the same level as that of the one without extra sulfur, because this measurement was carried out with the masterbatch without curatives. The results correspond well with the Mooney viscosities as depicted in Figure 6.1.

6.3.3 Cure characteristics of the compounds

6.3.3.1 Scorch behaviors. — With regard to the rather poor scorch safety of silica-filled rubber compounds with TESPT as a coupling agent, TESPD or the disulfide-based silane coupling agent has been introduced as an alternative. The rubber-rubber cross-linking caused by free sulfur released from TESPT during the intensive mixing process results in an undesired high compound viscosity, simultaneous with a shortened induction period, i.e. scorch time t_{10}, of the compounds.[6,9,10,13,14] These features cause difficulties in further processing steps, i.e. extrusion, calendering and shaping processes.

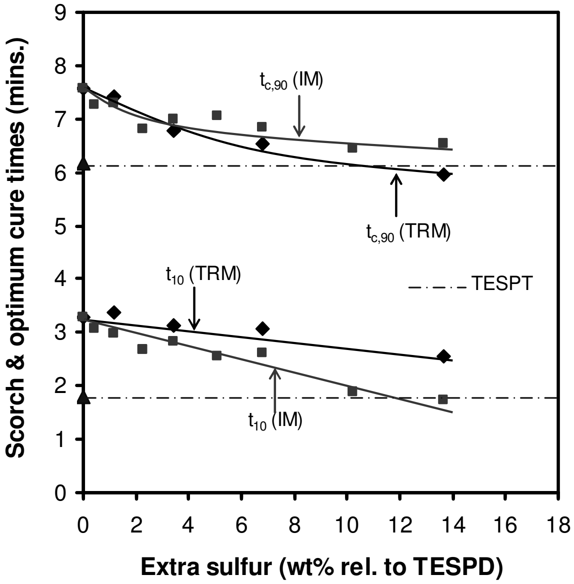

Figure 6.3 *Effect of sulfur compensation on scorch time (t_{c10}) and optimum cure time ($t_{c,90}$) of silica/TESPD-based compounds. Extra sulfur was added either on the two-roll mill (TRM) or in the internal mixer (IM), with the TESPT-containing compound included as reference.*

From the cure characteristics as shown in Figure 6.3, the TESPT-based compound has a shorter induction period or scorch time t_{10} than the one with TESPD, i.e. TESPD provides clearly better scorch safety than TESPT. With extra sulfur added into the TESPD-compounds, the scorch time remains more or less the same, except when the amount of compensated sulfur added while mixing in the internal mixer reaches 10.2 wt% relative to the TESPD content or 0.45 phr, where the scorch times of both TESPT and TESPD+sulfur compounds are similar. The lower reactivity of sulfur moieties in TESPD and the need of insertion of elemental sulfur into the disulfide to result in the reactive polysulfide, account for the longer scorch time compared to that of TESPT, as previously described by Luginsland[6] and already discussed in Chapter 4.[13] This result confirms that the sulfur released from TESPT plays a major role in the scorch time of silica-filled NR compounds.

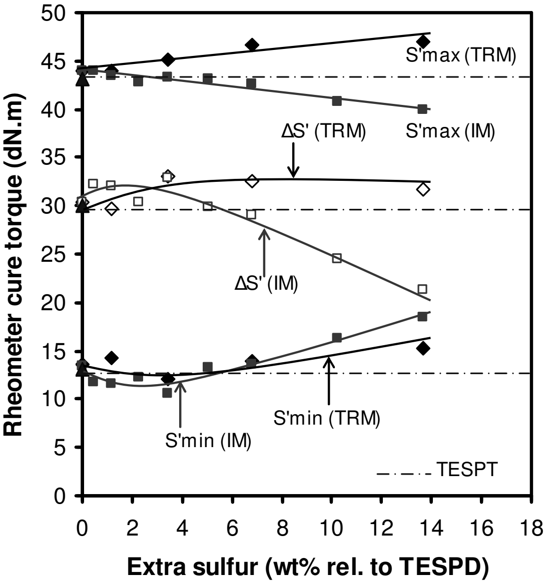

Figure 6.4 *Effect of sulfur compensation on rheometer maximum (S'_{max}), and minimum (S'_{min}) cure torques and torque difference ($\Delta S'$) of silica/TESPD-based compounds. Extra sulfur was added either on a two-roll mill (TRM) or in the internal mixer (IM); the TESPT-containing compound is included as reference.*

6.3.3.2 Rheometer cure torques. — The rheometer cure torques of the compounds are demonstrated in Figure 6.4. The minimum cure torque (S'_{min}) displays a similar trend as the Mooney viscosity as shown in Figure 6.1, as it also indicates the compound viscosity. The maximum cure torque (S'_{max}) and torque difference ($\Delta S'$) of the compounds with the elemental sulfur compensated on the two-roll mill show slightly increasing trends. Whereas the addition of extra sulfur in the internal mixer shows the opposite behavior, that is a gradual decrease in S'_{max}, as well as a sharp reduction in $\Delta S'$ when the extra sulfur exceeds 0.3 phr. This can be the result of the increase in Mooney viscosity resulting in an excessively high shear force during mixing and hence a breakdown of the rubber molecules.

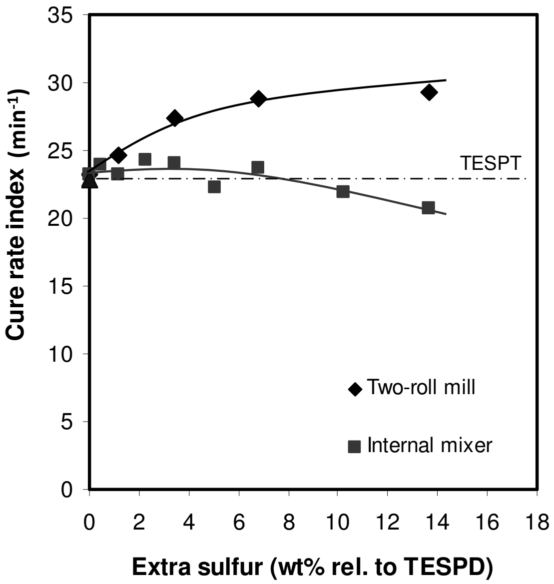

Figure 6.5 *Effect of sulfur compensation on cure rate index of silica/TESPD-based compounds. Extra sulfur was added either on a two-roll mill (TRM) or in the internal mixer (IM); the TESPT-containing compound is included as reference.*

6.3.3.3 Vulcanization kinetics. — The cure rate indices of the compounds as depicted in Figure 6.5 indicate that compensating sulfur already reacts in the internal mixer with rubber molecules as the cure rate index of the final compounds show a rather constant value with a slight decrease when the extra sulfur content exceeds 10 wt% relative to the TESPD content. This result indicates that during compound mixing in the internal mixer the rubber matrix can be partly cross-linked by compensated sulfur. At high loading of extra sulfur, the active sites on the natural rubber backbone may be reduced and consequently the rate of cross-linking reaction is lowered. The opposite is observed when extra sulfur was added into the compounds on the two-roll mill. For this mixing procedure, the cure rate index increases with increasing extra sulfur content since such extra sulfur added on the two-roll mill could not react during mixing, and thereby the total amount of sulfur available for the vulcanization reaction is increased. In addition, the active sites available for vulcanization in NR molecules remain more or less unchanged, causing in a faster cross-linking rate of the compounds. The results support the earlier explanation given for the Mooney viscosity, that the extra sulfur can prematurely cross-link the rubber matrix during the intensive thermo-mechanical mixing of TESPD-silica-NR in the internal mixer.

6.3.4 Silica dispersion and filler-filler interaction

6.3.4.1 Flocculation kinetics related to rheometer cure torques. — The flocculation parameter indicates the dispersion stability of the silica aggregates in the rubber matrix, as it determines how fast re-agglomeration of silica can develop in the compounds.[15-17]

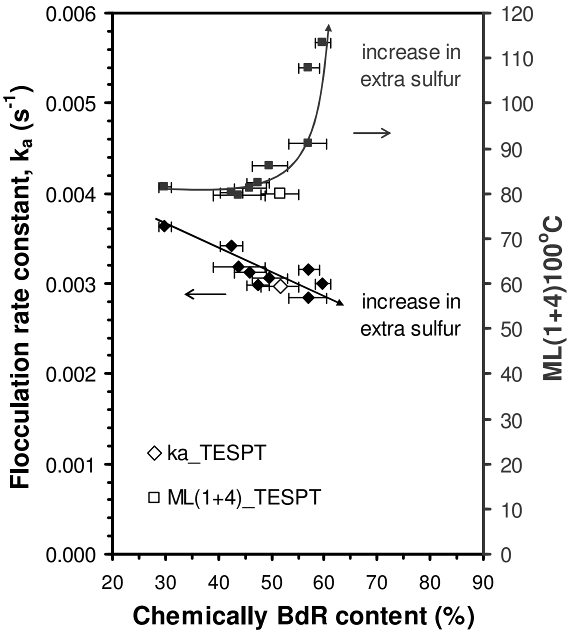

Figure 6.6 *Correlations between flocculation rate constant, Mooney viscosity and chemically bound rubber (BdR) content of silica/TESPD-based NR compounds prepared by adding extra sulfur in the internal mixer. The TESPT-containing compound is included as reference.*

Figure 6.6 displays the relationships of chemically bound rubber content, flocculation rate constant and Mooney viscosity. An increase of chemically bound rubber leads to a decrease in flocculation rate constant, indicating a better dispersion stability of the silica aggregates. This is attributed to the strong interaction between filler and rubber that potentially restricts the mobility of silica aggregates. Additionally, light rubber-rubber crosslinking coming from the networking reaction of the free sulfur available in the compounds, that results in the increased Mooney viscosity, is also one of the factors that can suppress silica migration in the rubber matrix.[12,17] However, in the latter case a clear discontinuity in the curve of flocculation rate constant would have been expected, like in the compound Mooney curve: which apparently is not the case. Consequently, it is an indication that the first explanation is the most likely.

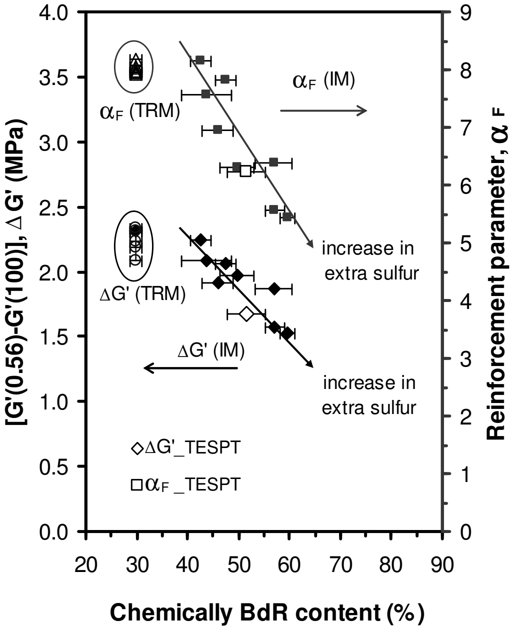

Figure 6.7 *Correlations between Payne effect, reinforcement parameter, and chemically bound rubber (BdR) content of silica/TESPD-based NR compounds. Extra sulfur was added either on the two-roll mill (TRM) or in the internal mixer (IM).*

6.3.4.2 Filler-filler interaction and degree of dispersion. — The Payne effect and reinforcement parameter were measured in order to obtain evidence of filler-filler interaction and degree of dispersion of the compounds with compensated sulfur, respectively. For this series of experiments, the properties of the vulcanized compounds were tested. The results in Figure 6.7 illustrate that the Payne effect and reinforcement parameter correlate well with the chemically bound rubber. The Lower Payne effect or less filler-filler interaction, and lower reinforcement parameter or better silica dispersion are associated with a greater extent of filler-rubber interaction or network contributions. The TESPT-based compound shows much lower filler-filler interaction and better silica dispersion than those of the TESPD compounds without sulfur compensation, due to the greater extent of bound rubber formation which results in stronger suppression of the flocculation process. Moreover, the higher matrix viscosity caused by the networking reduces the mobility of the silica aggregates as well as generates a higher shearing force in the system. The latter leads to better breakdown of silica agglomerates during mixing, providing a better degree of dispersion of the compounds. This aspect has been discussed earlier in Chapter 4. Extra sulfur of 0.3 phr or 6.8 wt% relative to TESPD content is an optimal amount which provides more or less equal levels of Payne effect and reinforcement parameter compared to the TESPT-compound. It should be noted that the extra sulfur compensation on the two-roll mill does not give any significant impact on filler-filler interaction and degree of dispersion of the compounds, as seen in the cluster of data points obtained for the compounds containing different total sulfur contents, shown on the left hand side of Figure 6.7. Again, these results demonstrate a significant dependence of the Payne effect and degree of dispersion on network contributions in the compounds.

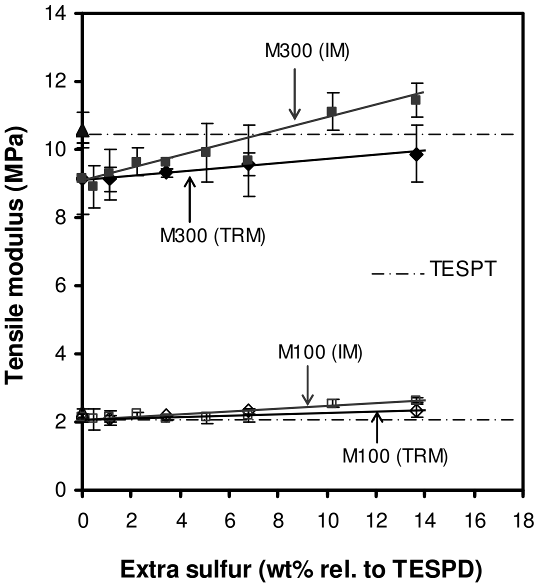

Figure 6.8 *Effect of sulfur compensation on the tensile moduli of silica/TESPD-based NR compounds. Extra sulfur was added either on the two-roll mill (TRM) or in the internal mixer (IM). The TESPT-containing compound is included as reference.*

6.3.5 Mechanical properties of vulcanizates

To determine the end use properties of the compounds, the mechanical properties of vulcanizates were evaluated. Figure 6.8 displays the tensile moduli at 100 % and 300 % elongation as a function of extra sulfur content. The effect of extra sulfur on the tensile 100% modulus is very small. TESPT provides a higher tensile 300%

modulus than TESPD without sulfur compensation. However, the addition of extra elemental sulfur at approximately 6 – 8 wt% relative to the TESPD amount during mixing TESPD-silica-NR in the internal mixer raises the tensile 300% modulus to the same level as that of TESPT. On the other hand, the addition of extra sulfur on the two-roll mill does not significantly affect the tensile modulus. The slight increase in tensile modulus of the vulcanizates with extra sulfur added on two-roll mill can solely be attributed to a higher crosslink density originating from the higher total concentration of sulfur content. So, it is clear that free sulfur available in the internal mixer during mixing plays an important role and significantly changes the vulcanizate properties.

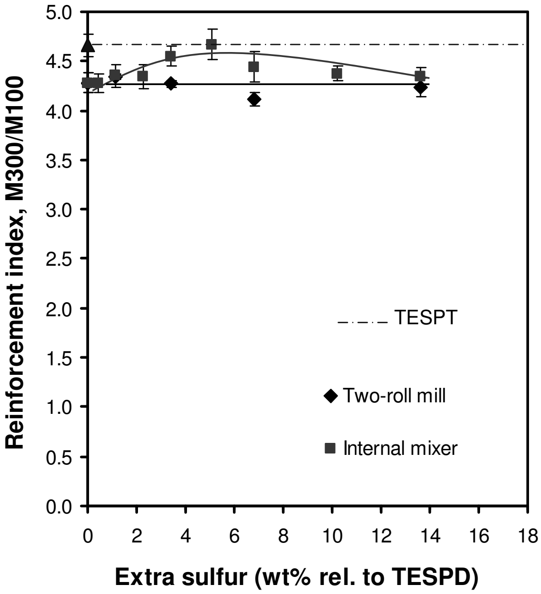

Figure 6.9 *Effect of sulfur compensation on the reinforcement index of silica/TESPD-based NR compounds. Extra sulfur was added either on the two-roll mill (TRM) or in the internal mixer (IM). The TESPT-containing compound is included as reference.*

The ratio of the modulus at 300 % strain to the modulus at 100 % strain indicates the reinforcement index of the vulcanizates, as shown in Figure 6.9. The compounds prepared by adding the corrected amount of sulfur in the internal mixer display an initial increase of reinforcement index, but reach a maximum at the same level as that of the TESPT-based compound, when the extra sulfur is equal to 5.1 wt% relative to the TESPD amount or 0.3 phr; thereafter the reinforcement index starts to decrease again. This property deterioration is possibly due to the negative effect of the very high Mooney viscosity together with rather short induction period of the compounds, leading to an inefficient processibility during vulcanization. The excessively high viscosity of the rubber compound also leads to molecular chain breakdown during mixing and hence lowers the molecular weight and mechanical properties. The addition of extra sulfur on the two-roll mill shows no influence on reinforcement index. The tensile strength shows a similar trend as the reinforcement index, as illustrated in Figure 6.10. A gradual decrease in elongation at break is observed for the case of adding sulfur in the internal mixer, as commonly observed as the result of a higher crosslink density.

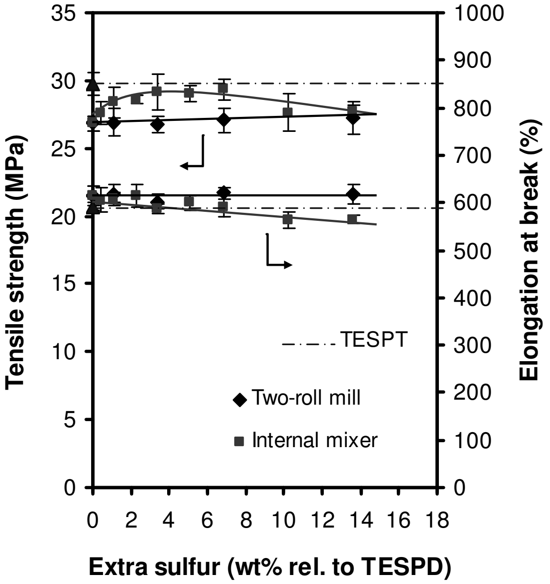

Figure 6.10 *Influence of sulfur compensation on tensile strength and elongation at break of TESPD-based NR compounds. Extra sulfur was added either on the two-roll mill (TRM) or in the internal mixer (IM). The TESPT-containing compound is included as reference.*

Based on the results obtained in this investigation, the role of free sulfur available during mixing the silica-filled compounds in the internal mixer can be well understood. Addition of extra sulfur during the dispersion of silica into NR matrix in the presence of TESPD, as well as during the silanization reaction, significantly improves the overall properties of the compounds. The extra free sulfur available during mixing at elevated temperature in the internal mixer leads to:

1) An increase in matrix viscosity during compounding, that creates higher shear forces and consequently greater breakdown of agglomerates, as well as easier dispersion of the particulate silica into the rubber matrix, and so better silica dispersion;

2) Formation of light pre-crosslinking in the rubber phase that can suppress the flocculation tendency of silica aggregates, leading to lower filler-filler interaction;

3) An increase in chemically bound rubber, as free sulfur can insert into the disulfide to create an active polysulfide, so that chemical bonds between silica-silane-NR can be formed as in the case of TESPT, according to the study of Luginsland (2002).[6]

With the addition of compensating amounts of sulfur later on, together with the curatives on the two-roll mill, all these effects are by-passed and the sulfur can merely act as an extra crosslinking agent in a compound which is basically less well-dispersed. The effects are then negligibly small.

6.4 CONCLUSIONS

Extra sulfur added into the silica/TESPD-filled compounds during the non-productive mixing step in the internal mixer, to compensate for the sulfur deficiency compared to the TESPT-based system, plays a significant role in the overall properties of compounds and vulcanizates. With increasing extra sulfur content the Mooney viscosity remained constant if the extra sulfur was added on two-roll mill, but started to increase rapidly when the extra sulfur was added in the internal mixer non-productive step at a sulfur loading exceeding 0.51 wt% relative to the TESPD amount or 0.20 phr. This is due to the effect of some premature cross-linking occurring during mixing, as confirmed by the result of the cure rate index. The scorch time of TESPD-based compounds is longer than that of TESPT, but is shortened with increasing extra sulfur content, to reach the same level as that of TESPT when the compensated sulfur is about 10 wt% relative to the amount of TESPD or 0.45 phr. The results demonstrate overall that the addition of extra sulfur in the internal mixer non-productive step gives a positive contribution towards improved silica dispersion, which can be attributed to some network formation that can suppress the mobility of silica aggregates, leading to better degree of dispersion, as demonstrated by the Payne effect, a higher amount of chemically bound rubber content and lower reinforcement parameter. The tensile properties of silica/TESPD vulcanizates are only slightly enhanced by adding free sulfur in the internal mixer relative to TESPD alone. Adding compensating sulfur during the productive step on the two-roll mill has practically no effect, as all benefits in the non-productive internal mixer step are by-passed; it then merely acts as some extra curative in an overall poorer dispersed compound, with minimal overall effects.

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CHAPTER 7

ALTERNATIVE SECONDARY ACCELERATOR FOR SILICA-FILLED NATURAL RUBBER FORMULATIONS

Dithiophosphate (DTP) displays a good efficiency towards improved overall properties of silica-reinforced natural rubber (NR) compounds, when it is used as secondary accelerator in a sulfenamide primary accelerated sulfur vulcanization system. When comparing DTP with diphenylguanidine (DPG) in the role of synergistic secondary accelerator with sulfenamide, (i.e. n-cyclohexyl-2-benzothiazole-sulfenamide or CBS), DTP is more reactive and gives better reversion resistance, a faster vulcanization rate and lower reversion, respectively. This leads to a lower amount of secondary accelerator required for vulcanization, and better aging properties of the DTP-based compounds. An increase of chemically bound rubber content accompanied with a lowered Payne effect is obtained when the amount of secondary accelerator is increased. A potential coupling ability of DTP, in particular of zinc dithiophosphate, can be postulated. Based on the mechanical and dynamic properties of vulcanizates, the minimal amounts of DTP and DPG required to optimize the overall properties of compounds and vulcanizates are approximately 0.8, and 1.1 phr, i.e. 1.4 and 2.0 wt% relative to silica content, respectively.

7.1 INTRODUCTION

The chemical adsorption of curatives on silica surfaces is one of the concerns for silica-reinforced rubber compounds, since the polar silanol groups of silica can provide strong adsorptive interactions with polar chemicals through hydrogen bonding or Van der Waals forces. This negatively affects the performance of some key ingredients present in the compounds, particularly accelerators, and results in a decrease of crosslink density and a consequent deterioration of end-use properties.[1-3] To minimize the accelerator adsorption onto silica and thus improve the cure characteristics, either glycols or amines are normally added into the rubber compounds.[1,2] For silica-reinforced compounds, diphenylguanidine (DPG) is commonly used as it acts not only as a synergistic secondary accelerator for sulfenamide accelerated sulfur vulcanization, but also as a catalyst for the silanization reaction between silica and the silane coupling agent.[4-6]

However, DPG has become suspect for its toxicity since it contains an aromatic amine which can liberate highly toxic free aniline during mixing and vulcanization.[7-9] As documented by the Environmental Protection Agency (EPA), the main effect of aniline by any route of exposure is a blood disorder in which oxygen delivery to the tissues is impaired.[10] Recently, dithiophosphate (DTP) accelerator has been proposed as an alternative for DPG. It was claimed that DTP functions as a synergist for sulfenamide primary accelerators with considerably less hazardous potential.[4,7,8]

This chapter presents the role of dithiophosphate on overall properties of silica-filled NR compounds when used in combination with a sulfenamide primary accelerator. The compound with diphenylguanidine and sulfenamide combination is taken as reference. Variable quantities of dithiophosphate and diphenylguanidine are investigated. Cure characteristics, Mooney viscosity, filler-rubber and filler-filler interactions of the compounds as well as mechanical, dynamic and heat aging properties of the vulcanizates are evaluated.

7.2 EXPERIMENTAL

7.2.1 Materials

The materials used for this experiment, i.e. natural rubber, silica, TESPT silane coupling agent, TDAE oil, zinc oxide, stearic acid, TMQ, CBS, sulfur, and diphenylguanidine (DPG) were the same as those described in the experimental paragraph of Chapter 3. Two grades of dithiophosphate (DTP) supplied by RheinChemie (Germany) were employed, i.e. bis-(ethylhexylthiophosphoryl) polysulfide (SDT) in a form of 70 wt% phosphoryl polysulfide bound to 30 wt% highly active silica with 22 wt% of sulfur content active in the SDT (Rhenocure® SDT/S), and dibutyldithiophosphate zinc salt (TP) supplied as silica-bound solid with 67 wt% zinc dibutyldithiophosphate and 14 wt% of sulfur content active in TP (Rhenocure® TP/S).

7.2.2 Compound formulations

The formulations for filled and gum compounds are shown in Table 7.1. The quantities of DPG and DTP were varied as detailed in Table 7.2. The chemical structures of these secondary accelerators are also given in this table.

Table 7.1 *Formulations for gum and filled compounds.*

Ingredient	Dosage (phr)	
	Gum	Filled
Natural rubber	100.0	100.0
ZnO	3.0	3.0
Stearic acid	1.0	1.0
TMQ	1.0	1.0
Ultrasil 7005	-	55.0
TESPT	-	5.0
TDAE oil	-	8.0
DPG, SDT or TP	0.55[a]	Variable[b]
CBS	1.0	1.5
Sulfur	1.5	1.5

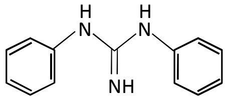
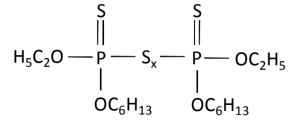
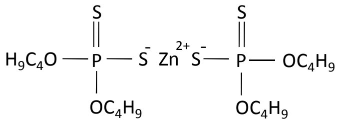
[a] *Bulk secondary accelerator content of 0.55 phr as shown in Table 7.2.*

[b] *The variable amounts of DPG and DTP are shown in Table 7.2.*

7.2.3 Compound preparation

Silica-filled NR compounds were prepared following the same methods as described in Chapter 4. Gum or unfilled compounds with different secondary accelerators were prepared by using two-roll mill. The gum compound with CBS 1.0 phr, without secondary accelerator was additionally prepared and considered as a control.

Table 7.2 *The chemical structures and variable quantities of DPG and DTP (i.e. SDT and TP) used in the compounds.*

Type of secondary accelerator	Chemical structure	Bulk (phr)	Active content	
			(phr)	(wt% rel. to silica conc.)
Without		0	0	0
DPG, diphenylguanidine		0.55	0.55	1.00
		1.13	1.13	2.05
		1.94	1.94	3.52
SDT, bis-ethylhexyl-phosphorylpolysulfide (70 wt%)		0.55	0.39	0.70
		1.13	0.79	1.44
		1.94	1.36	2.46
TP, dibutyldithio-phosphate zinc salt (67 wt%)		0.55	0.37	0.70
		1.13	0.76	1.37
		1.94	1.30	2.36

7.2.4 Properties analysis and testing

Cure characteristics, Mooney viscosity, bound rubber content, Payne effect, tensile and dynamic mechanical properties of the compounds were measured according to the methods and instruments as described in Chapter 3.

The degree of cure reversion of the compounds was calculated by using the data from the cure characteristics as expressed in Equation (7.1):

$$\textit{Degree of reversion (\%)} = \frac{S'_{\max} - S'_{f}}{S'_{\max}}\, x\, 100 \qquad (7.1)$$

where S'_{max} = Rheometer maximum torque
S'_{f} = Rheometer cure torque at final (measurement) time

The heat aging resistance of the vulcanizates was evaluated using dumbbell-shaped specimens that were exposed to hot air at 100°C for 72 h. The aged samples were tested for their tensile properties and the percentage change in properties was calculated with reference to the unaged specimens, according to ISO 188.

7.3 RESULTS

7.3.1 Mooney viscosity of the compounds

Figure 7.1 shows rising trends of Mooney viscosity with increasing secondary accelerator content, to a certain optimum loading where after the Mooney viscosities tend to level off. The increase of Mooney viscosity can be attributed to an enhancement of filler-rubber interactions/network contribution, to be verified and discussed in the bound rubber results in paragraph 7.3.3. The TP and SDT secondary accelerators show a constant viscosity at lower loadings compared to DPG. The leveling off of Mooney viscosity is observed at approximately 0.4 phr, and 1.1 phr of dithiophosphate and DPG loading, respectively.

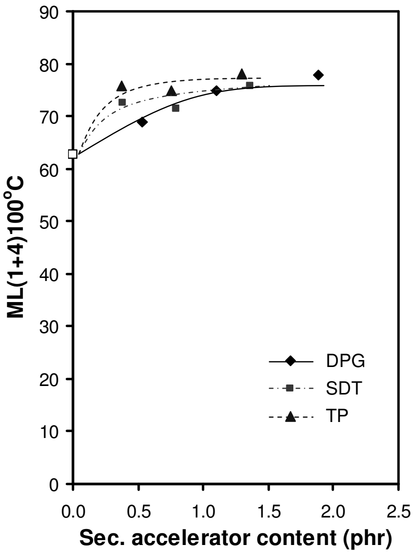


Figure 7.1 *Mooney viscosity of silica-filled NR compounds with different types and dosages of secondary accelerators combined in a sulfenamide primary accelerated sulfur vulcanization system.*

7.3.2 Cure characteristics of gum and filled compounds

7.3.2.1 Gum compounds. — Unfilled NR compounds with various accelerator systems show different cure behaviors as can be seen in Figure 7.2. Rheometer maximum torque and slope of the cure curves increase when either DPG, TP or SDT is combined with CBS, indicating a higher crosslink density and faster cure rate, respectively. The results clearly show the synergistic effect of diphenylguanidine and dithiophosphate with the sulfenamide type primary accelerator. The compound with the CBS/DPG combination shows the highest rheometer maximum torque, but a strong reversion is observed after the optimum cure time (i.e. at about 5 mins.), indicating a degradation of polysulfidic crosslinks under the high thermal cure condition. DTP (i.e. TP and SDT) assisted CBS accelerator systems give better stability towards reversion as observed in the more plateau-like rheometer cure torques.

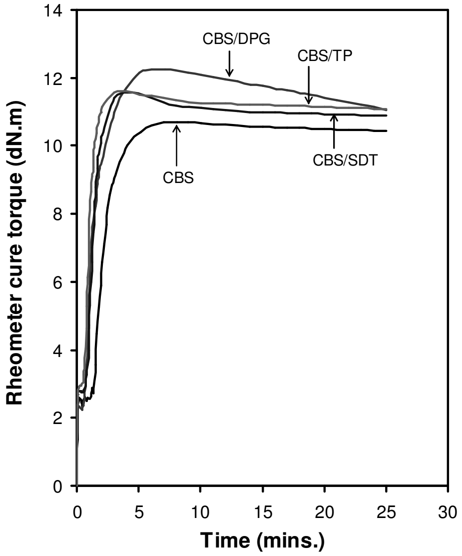


Figure 7.2 *Cure curves at 150°C of gum NR compounds with different accelerator systems. CBS primary accelerator was used without and with either DPG, SDT or TP as a secondary accelerators.*

These results correspond well with the work of Issel *et al.*,[4] in which the reason for the different reversion stabilities was quoted to be a difference in types of crosslinking bonds. The use of CBS and the combination of CBS/DPG generates a greater amount of polysulfidic crosslinks which have a rather low bond energy: 170 kJ/mol, compared to mono- and di-sulfidic crosslinks: 270 and 220 kJ/mol, respectively.[11] The addition of DTP as secondary accelerators in the CBS system provides a larger proportion of mono- and di-sulfidic linkages compared to polysulfidic ones, and thereby the reversion resistance is improved.[4,12]

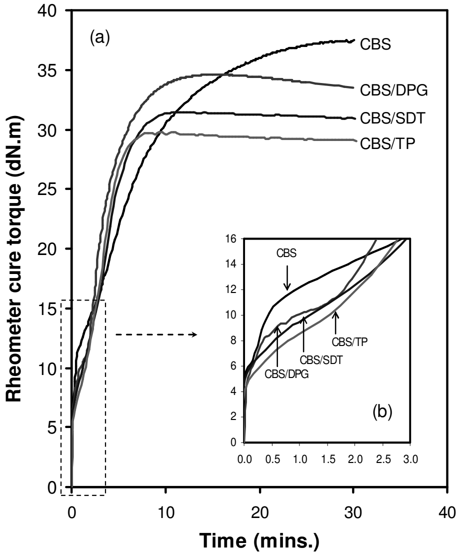


Figure 7.3 *Effect of different secondary accelerators on cure behaviors of silica-filled NR compounds with the CBS primary accelerated sulfur vulcanization system. The quantities of active DPG, SDT and TP used were 1.13, 0.79 and 0.76 phr, respectively.*

7.3.2.2 Filled compounds. — In Figure 7.3 the compound without secondary accelerators (with only CBS) shows the highest rheometer maximum torque and the slowest cure rate. The combination of CBS with secondary accelerators, particularly dithiophosphate, decreases the rheometer maximum torques of the compounds, which can be due to a change in degree of filler-filler interaction in the silica-filled rubber compounds. As documented in previous studies,[13,14] besides the network structures, i.e. filler-rubber and rubber-rubber linkages, filler-filler interaction also contributes to the rheometer torque level. The use of a secondary accelerator as a synergist to sulfenamide should enhance the crosslinking efficiency, so the opposite effect: the reduction of the maximum torque may be ascribed to reduced filled-filler interactions by the secondary accelerators. The results indicate that dithiophosphate can effectively reduce filler-filler interaction to a greater extent than diphenylguanidine. Another evidence which supports the reduced degree of filler-filler interaction in the compounds is the silica re-agglomeration or flocculation development during the induction period of vulcanization. The flocculation of silica can develop under thermal conditions, and leads to an appearance of a hump in the curve at the onset of curing as shown in Figure 7.3(b).[13,14] A larger hump indicates a higher degree of flocculation of silica particles/aggregates, and thus higher filler-filler interaction as a consequence. With the lower content of secondary accelerator but greater overall sulfur content, the TP- and SDT-based compounds show a smaller hump compared to DPG-curve, indicating a lower flocculation degree, and thus lead to a lower rheometer maximum torque as a result of lower filler-filler interactions in the compounds.

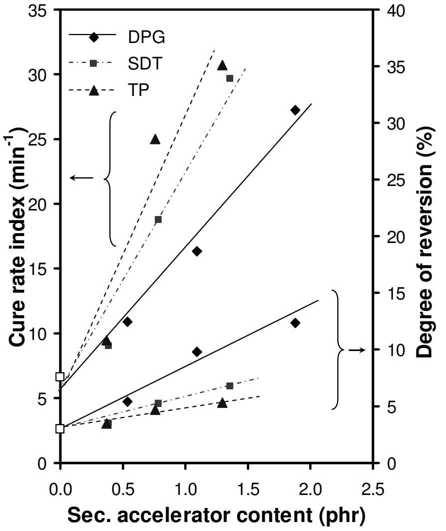


Figure 7.4 *Influence of various amounts of secondary accelerators on cure rate index and degree of reversion of silica-filled NR compounds with CBS used as primary accelerator.*

From the cure characteristics of the filled compounds, the cure rate indices and percents of reversion are obtained as displayed in Figure 7.4. The rate of vulcanization linearly increases with increasing the amounts of secondary accelerators. Dithiophosphate, in particular zinc dithiophosphate (i.e. TP), give a faster cure rate with lower degree of reversion than diphenylguanidine. The DPG-containing compounds show a stronger reversion than the TP- and STD-based compounds, even though the reversion tendency is more pronounced with increasing amount of secondary accelerators. The results observed in the filled compounds are in good agreement with those reported for the unfilled compounds: Figure 7.2.

7.3.3 Filler-rubber and filler-filler interactions

The chemically bound rubber contents and Payne effects of the compounds with various accelerator systems are demonstrated in Figure 7.5. By increasing the amount of secondary accelerators, the chemically bound rubber content significantly increases, whilst the Payne effect decreases, indicating a higher extent of filler-rubber linkages, and lower filler-filler interaction, respectively. The increase of bound rubber content tends to level off after 1.1 phr of DPG. The use of a secondary accelerator to combine with the CBS primary accelerator clearly enhances filler-rubber interaction, and both dithiophosphate and diphenylguanidine show similar chemically bound rubber contents.

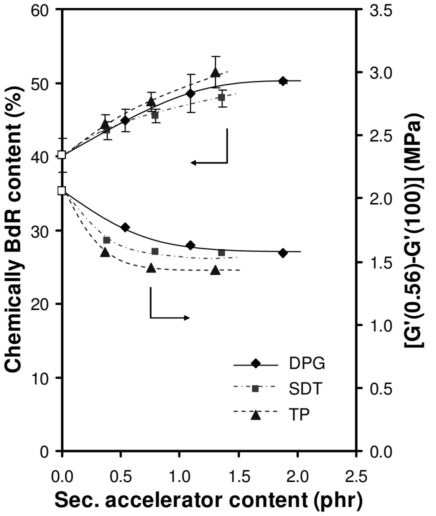


Figure 7.5 *Chemically bound rubber (BdR) content and Payne effect as a function of secondary accelerator loading of silica-filled NR compounds with sulfenamide as primary accelerator.*

Regarding the Payne effect signaling filler-filler interaction, TP provides the lowest filler-filler interaction among the different types of compounds studied. SDT and DPG give more or less a similar minimum level of filler-filler interaction. The amount of TP and SDT at about 0.8 phr is sufficient to minimize the filler-filler interaction, compared to a higher DPG amount of 1.1 phr to reach the minimal degree of Payne effect. The reduction of filler-filler interaction is in accordance with the increase of bound rubber content, i.e. filler-rubber interaction. The overall results indeed indicate a higher efficiency of the dithiophosphates to reduce filler-filler interaction and enhance filler-rubber bonding than DPG.

7.3.4 Mechanical and dynamic properties of vulcanizates

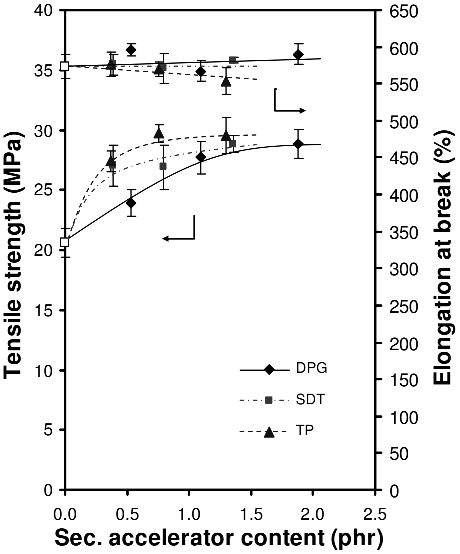


Figure 7.6 *Tensile strength and elongation at break as a function of secondary accelerator loading of silica-filled NR vulcanizates with sulfenamide as primary accelerator.*

Ultimate tensile properties, i.e. tensile strength and elongation at break of the vulcanizates as a function of secondary accelerator content are shown in Figure 7.6. DPG and DTP provide comparable tensile strength to the vulcanizates, but the optimal amounts of these secondary accelerators are different. Tensile strength shows maximum values when the amounts of DPG and DTP (i.e. TP and SDT) are about 1.1 phr, and 0.8 phr, respectively. Elongation at break of the TP-based vulcanizates slightly drops with increasing amount of secondary accelerators, but for DPG and SDT it shows no significant change.

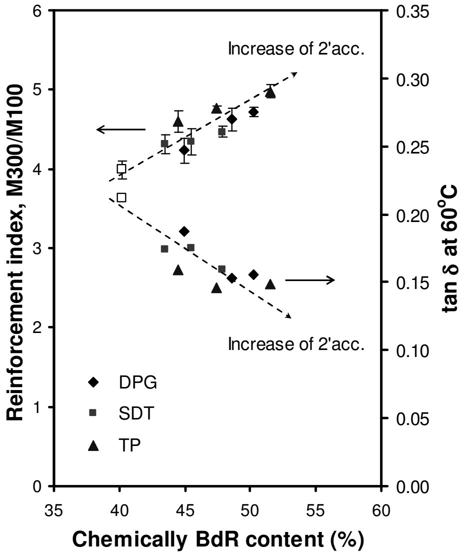


Figure 7.7 *Correlations between reinforcement index, tan δ at 60°C and chemically bound rubber (BdR) content of silica-filled NR vulcanizates prepared with different accelerator systems. Open symbols are for the compound with CBS without secondary accelerator.*

The reinforcement index and tan δ at 60°C show good correlations with the chemically bound rubber content, as shown in Figure 7.7. Increase of the secondary accelerator leads to improvement in mechanical and dynamic properties of the vulcanizates as the reinforcement index gradually increases and tan δ at 60°C decreases. DPG and the TP grade dithiophosphate offer the comparable reinforcement indices and loss tangents at 60°C, which indicates a comparable rolling resistance of vulcanizates for tire tread applications made thereof.

7.3.5 Aging properties of vulcanizates

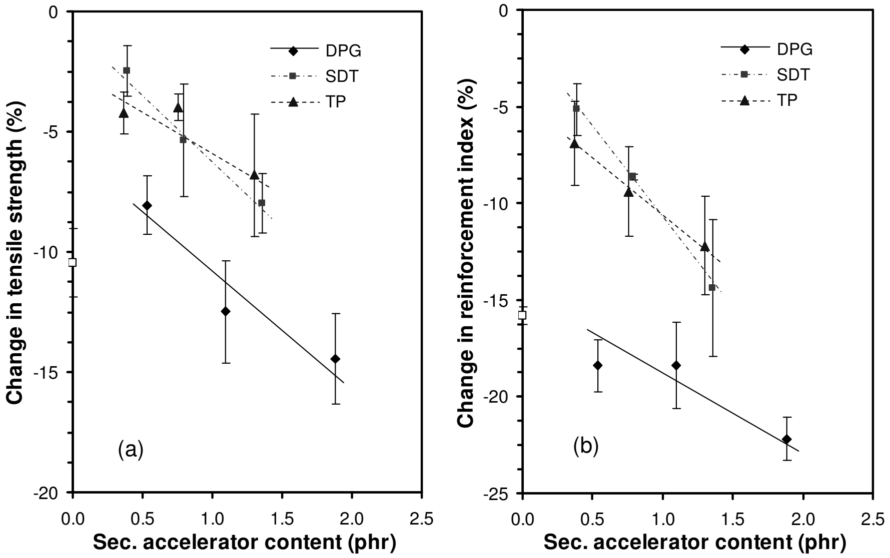


Figure 7.8 *Percent change of (a) tensile strength and (b) reinforcement index after aging at 100ºC, 72 hrs of silica-filled NR vulcanizates prepared with different accelerator types.*

The changes in properties of the vulcanizates after aging under hot air conditions of 72 hrs at 100°C are displayed in Figure 7.8. The results show different heat aging resistances between the vulcanizates prepared with dithiophosphate and diphenylguanidine as secondary accelerator. The compounds with dithiophosphate, i.e. TP and SDT, show a lower percentage change of the properties indicating a better heat aging resistance compared to the ones with diphenylguanidine. This can be due to their different proportions of mono- plus di-sulfidic crosslinks, vs. polysulfidic crosslinks, as reported by Issel *et al.*[4] These results are also in good correspondence with the degree of reversion as observed in the cure characteristics, as shown in Figure 7.4.

7.4 DISCUSSION

Reversion stability of the compounds is one of the benefits obtained when dithiophosphate is used as a secondary accelerator in a sulfenamide primary accelerated sulfur vulcanization system, as can be seen in Figures 7.2 – 7.4. Based on a previous study in polydiene compounds,[12] it was concluded that use of only a sulfenamide type accelerator generates a relatively low crosslink density, with a majority of polysulfidic crosslink structures compared to mono- and di-sulfidic crosslinks. The combination of sulfenamide and dithiophosphate raises the crosslink density and lowers the polysulfidic proportion in the compounds, i.e. an increase of the mono- and di-sulfidic crosslink structures. In general, polysulfidic crosslinks have lower bond energies compared to mono- and di-sulfidic crosslinks,[11] leading to a lower stability towards reversion and aging under high thermal conditions. Therefore, dithiophosphate gives advantages in terms of reversion resistance and aging properties as demonstrated in Figures 7.4 and 7.8, respectively. The results in Figure 7.8 clearly show that dithiophosphate, both TP and SDT grades, provides a better heat aging resistance of vulcanizates when compared to diphenylguanidine.

In addition to the improvement in reversion resistance, dithiophosphate, and particularly zinc-dithiophosphate TP can effectively reduce filler-filler interactions in the compounds as discussed earlier for the results of rheometer cure torque and Payne effect: Figures 7.3 and 7.5, respectively. As demonstrated in Chapters 3 – 6, the filler-filler interaction can be reduced by network contributions which include filler-rubber interactions and rubber-rubber linkages. The created network can restrict the mobility of silica aggregates, leading to a better silica dispersion stability: lower flocculation rate, and an improved degree of silica dispersion. The chemically bound rubber content as shown in Figure 7.5 initially increases with increasing amount of secondary accelerators. In the case of DPG, it is well understood that DPG can additionally boost the silanization reaction and consequently improve filler-rubber interaction. For DTP, there is so far no in-depth study on the precise mechanism of DTP towards the silanization reaction. However, it has been proposed by Issel *et al.*[4] that dithiophosphate, especially zinc dithiophosphate, enhances the coupling efficiency, i.e. increases the filler-rubber crosslinks in silica-filled rubber systems. Herein, possible reaction mechanisms among silica, zinc dithiophosphate and NR are proposed as given in Figures 7.9 and 7.10. Considering the chemical structure of TP-dithiophosphate, it was postulated[4] that the dipolar zinc soap of TP would easily partially attach to the polar silica surface, and then the alkoxy groups of dithiophosphate would react with silanol groups of the silica contributing to the silanization reaction: Figure 7.9. The sulfur atom on the other side of the dithiophosphate molecule then potentially reacts with rubber molecules, leading to a silica-rubber bridge formation: Figure 7.10. In the case of SDT, bearing a polysulfidic structure and so acting as a sulfur donor, SDT can liberate free sulfur to the system under the high thermal mixing conditions and produce a higher extent of network contributions, and as a consequence a higher chemically bound rubber content. The incorporation of SDT during mixing silica-TESPT-NR in the internal mixer so results in a greater extent of network contributions, and hence less filler-filler interactions of the compounds. Therefore, apart from rising the crosslink density by the synergistic effect of the secondary accelerators, the improved properties of the compounds can also be related to the chemically bound rubber increased by those secondary accelerators.

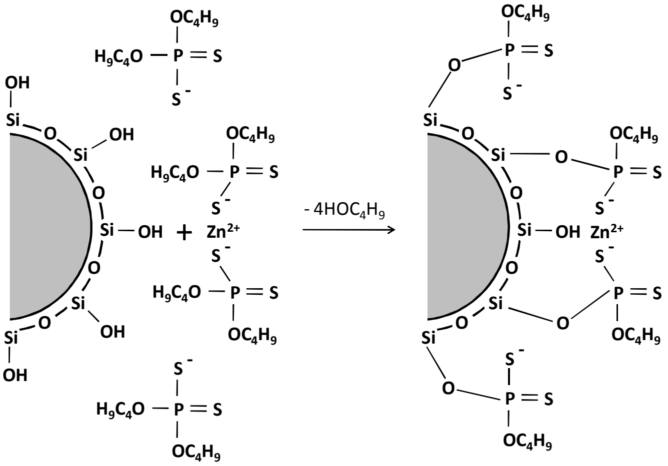


Figure 7.9 *Postulated reactions between silica and zinc dithiophosphate.*

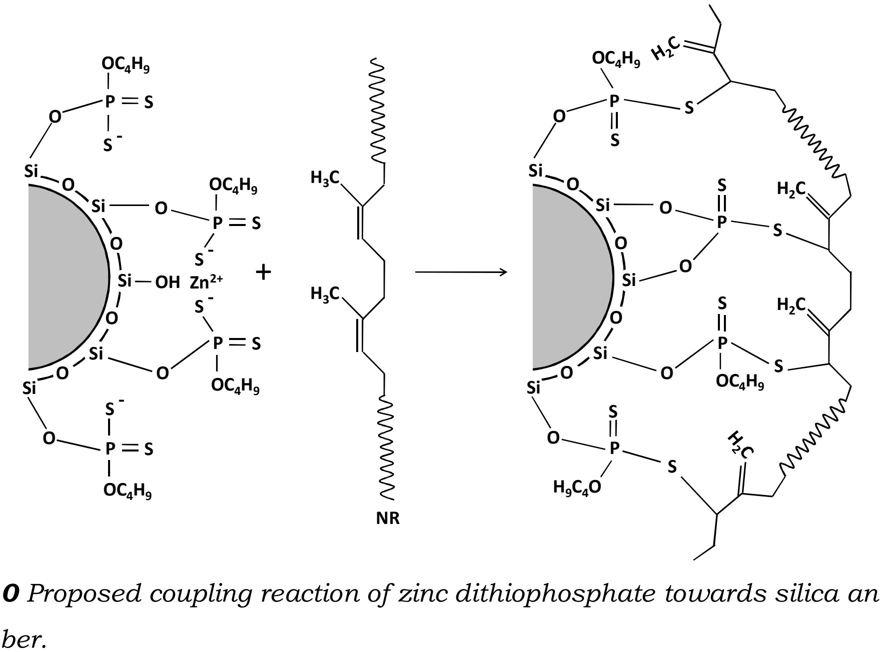


Figure 7.10 *Proposed coupling reaction of zinc dithiophosphate towards silica and natural rubber.*

Based on the mechanical and dynamic properties as shown in Figures 7.6 and 7.7, dithiophosphate and diphenylguanidine provide comparable overall properties. However, the required quantities to reach the optimum levels of compound and vulcanizate properties for these two secondary accelerators are different. Due to the higher reactivity of the dithiophosphates in the sulfenamide accelerated sulfur vulcanization in natural rubber, as indicated by a faster cure rate index compared to diphenylguanidine: Figure 7.4, the system needs a smaller amount of DTP. It was shown that 0.8 phr DTP and 1.1 phr DPG (or 1.4 and 2.0 wt% relative to the silica content, respectively) are the minimal amounts for optimized formulations.

7.5 CONCLUSIONS

In this investigation, the efficiency of DTP as an alternative for DPG on the reinforcement of silica in NR compounds has been verified. DTP acts as a synergist for the sulfenamide primary accelerator and is more reactive compared to DPG, leading to a smaller required dosage of DTP to reach optimum properties. DTP gives better reversion stability under high thermal annealing, and superior heat aging resistance of the vulcanizates. Addition of secondary accelerators can raise the extent of chemically bound rubber, accompanied with lower filler-filler interactions. Based on the mechanical and dynamic properties of the vulcanizates, optimum overall properties are obtained when DTP and DPG are used at 0.8 and 1.1 phr, i.e. 1.4 and 2.0 wt% relative to silica content, respectively.

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CHAPTER 8

SYNERGISTIC EFFECTS OF EPOXIDE FUNCTIONAL GROUPS ON NATURAL RUBBER AND SILANE COUPLING AGENTS ON REINFORCING EFFICIENCY OF SILICA

Polar functionality attached onto natural rubber has a significant impact on the reinforcing efficiency of silica. Parallel studies involving various levels of epoxidation on natural rubber (ENR) in the absence of TESPT coupling agent, as well as a combination of ENRs with different loadings of TESPT, provide a better understanding of the various factors which influence the properties of silica-filled ENR compounds. Based on the overall properties, the best possible combination to optimize processibility, to reduce filler-filler interaction, and improve vulcanization rate as well as vulcanizate properties, is to utilize ENR with an epoxide content in the range of 20 – 30 mol%, together with a small portion of TESPT, i.e. 2 – 4 wt% relative to the silica content. This leads to a reduction of approximately 60 – 80 % of TESPT when compared to the conventional NR compounds, where the optimal loading of TESPT was 9.0 wt% relative to the silica content.

8.1 INTRODUCTION

In addition to the use of silica surface modifying agents and/or silane coupling agents, compatibilization between silica and hydrocarbon rubbers can be promoted by the use of polar polymers. As reviewed in Chapter 2, the silanol groups on the silica surface have potential to form physical interactions or even chemical bonds with functionalized rubbers such as chlorosulfonated polyethylene (CSM),[1] carboxylated nitrile rubber (XNBR),[2] and epoxidized natural rubber (ENR).[3-5] The polar-modified rubbers can be used either as raw material[6,7] or as compatibilizer.[8,9]

In this chapter, the influences of epoxide content in ENRs in the absence of a silane coupling agent, resp. a combination of ENRs with TESPT at varying loadings are evaluated on the overall properties of silica-filled ENR compounds. Filler-filler interaction, network contributions, Mooney viscosity, cure characteristics, dynamic and mechanical properties of the compounds and vulcanizates are investigated.

8.2 EXPERIMENTAL

8.2.1 Materials

The ENRs with various epoxide levels were prepared in-house and are used as raw material. The chemicals employed for the synthesis of ENRs were high ammonia (HA) NR latex (Yala Latex, Thailand), formic acid (Fluka Chemie, Switzerland), hydrogen peroxide (Riedel-De Haën, Germany), alkylphenol ethoxylate or Teric N30 (Huntsman Corp. Australia Pty., Australia), and commercial grade methanol (J.T. Baker, USA).

The ingredients used for the rubber formulations, i.e. silica, TESPT silane coupling agent, TDAE oil, zinc oxide, stearic acid, TMQ, CBS, sulfur, and DPG were the same as those described in Chapter 3.

8.2.2 Preparation and characterization of epoxidized natural rubber

8.2.2.1 Modification procedure. — The ENRs were prepared using HA latex with a dry rubber content (DRC) of approximately 60 wt% via an *in-situ* performic epoxidation reaction in which the performic acid was generated by a reaction between formic acid and hydrogen peroxide (H_2O_2) inside the reactor. The recipe used for this synthesis is given in Table 8.1.

Table 8.1 *Recipe for ENR synthesis.*

Ingredients	Quantity	
	mole	g
HA latex (60 wt% DRC)	2.0	226.7
Hydrogen peroxide (50% w/w)	4.0	272.0
Formic acid (94% w/w)	1.0	48.9
Teric N30 (10% w/w)	-	15.0[a]

[a] *approximately 1.0 phr*

The epoxidation reaction as shown in Figure 8.1 was carried out in a continuously stirred reactor, at a temperature of 40°C. The latex was first diluted to have a DRC of approximately 20 wt% and then stabilized against coagulation by adding a non-ionic surfactant, i.e. Teric N30, and held for 15 minutes. After that, formic acid was added dropwise, followed by the hydrogen peroxide. The entire quantity of each reagent was charged into the reactor over a time period of 1.5 hours. Because the degree of epoxidation depends significantly on the reaction time,[10] the modification times were varied at 2.5, 4.5, 6.0, 9.5 and 14.5 hours, in order to obtain different concentrations of epoxide functionality in a variety of ENRs.

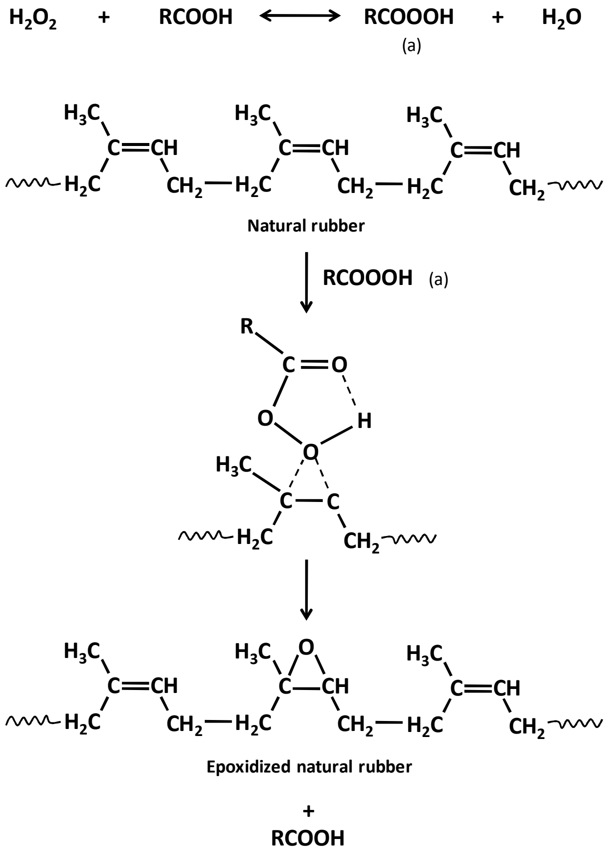


Figure 8.1 *Mechanism of epoxidation reaction in the preparation of the ENRs.*[11]

After the modification reaction was finished, the ENR latex was coagulated with methanol, thoroughly washed with water and then dried in a vacuum oven at 40°C for approximately 72 hours.

8.2.2.2 Characterization of the ENR structure. — The ^{1}H-NMR technique as previously described in Chapter 5 was performed to analyze the molecular structure and to determine the exact level of epoxide content in the ENRs. Deuterated chloroform ($CDCl_3$) was used to dissolve the ENR samples. The ^{1}H-NMR spectra of the ENRs are shown in Figure 8.2.

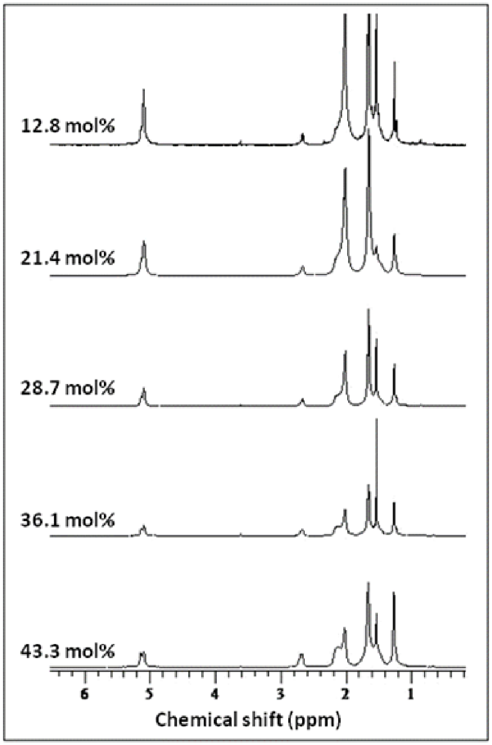


Figure 8.2 *^{1}H-NMR spectra of the ENRs with various levels of epoxide functionality.*

The absorption peaks at chemical shifts of 2.7 and 5.1 ppm indicate the resonances of a proton in an oxirane ring and isoprene unit, respectively (see Figure 8.1). The integral values under these peaks at 2.7 and 5.1 ppm are taken to calculate the epoxide content in ENR according to Equation 8.1[12]:

$$\text{Epoxide content (mol\%)} = \frac{I_{2.7}}{I_{2.7} + I_{5.1}} \times 100 \qquad (8.1)$$

where $I_{2.7}$ and $I_{5.1}$ are the integrals of the absorption peaks at the chemical shifts of 2.7 and 5.1 ppm, respectively.

In the present work, five levels of epoxide content in the ENRs were prepared. The different mol% epoxide contents in the ENRs prepared by using different reaction times are given in Table 8.2 and Figure 8.3.

Table 8.2 *Degree of epoxidation of ENRs at varying reaction times.*

Reaction time (h)	Mol% epoxide (by ^{1}H-NMR)	Notation
2.5	12.8	ENR-13
4.5	21.4	ENR-21
6.0	28.7	ENR-29
9.5	36.1	ENR-36
14.5	43.3	ENR-43

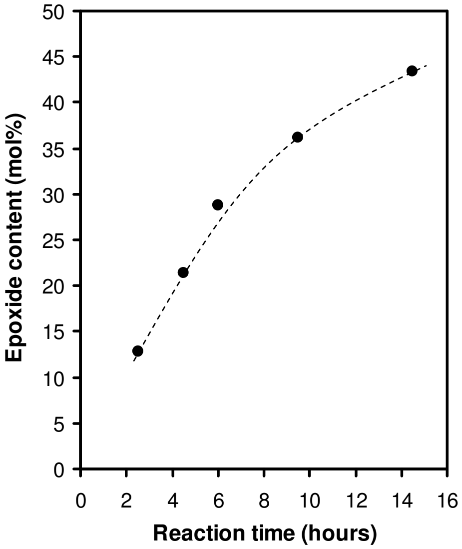


Figure 8.3 *Epoxide content in ENRs as a function of epoxidation reaction time.*

8.2.3 Compound preparation

The effect of the degree of epoxidation in the ENRs was investigated in parallel with variation of the TESPT concentrations. Table 8.3 shows the compound formulation used in this study.

Table 8.3 *Compound formulation.*

Ingredient	Dosage (phr)
Rubber (ENRs[a] or NR)	100.0
ZnO	3.0
Stearic acid	1.0
TMQ	1.0
Ultrasil 7005	55.0
TESPT	Variable[b]
TDAE oil	8.0
DPG	1.1
CBS	1.5
Sulfur	1.5

[a] *ENRs with 12.8, 21.4, 28.7, 36.1, and 43.3 mol% epoxide were studied.*

[b] *The quantity of TESPT used for each ENR compound was varied from 0 – 12 wt% relative to the silica content.*

All silica-filled ENR compounds were prepared following the same methods as described in Chapter 4. The unmodified NR (i.e. Ribbed Smoked Sheet 3, RSS 3) compounds with and without TESPT were prepared and treated as a reference.

8.2.4 Property analysis and testing

Mooney viscosity, Payne effect, cure characteristics, tensile and dynamic mechanical properties of the compounds were investigated according to the methods and instruments as described in Chapter 3.

8.3 RESULTS

8.3.1 Mixing torque and mixing temperature

The processibility of silica-filled ENR compounds can initially be determined by monitoring the mixing torque during mixing in the internal mixer.

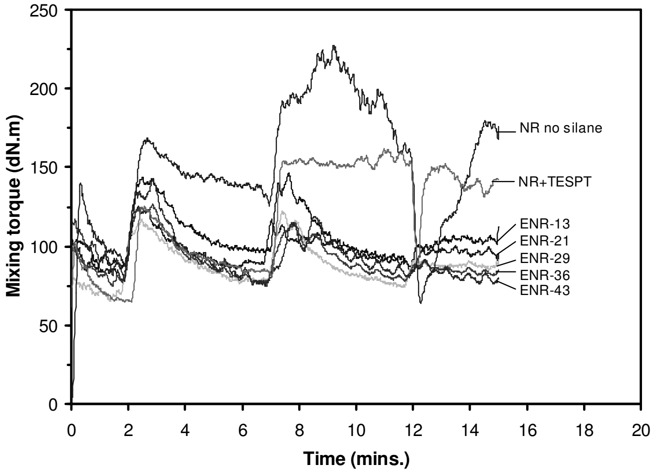


Figure 8.4 *Mixing torques of silica-filled ENR compounds with various epoxide contents, as indicated for each line. Silica-filled unmodified NR compounds without and with TESPT at 9 wt% relative to silica content are considered as references.*

All ENR compounds show lower mixing torques compared to normal NR either with or without TESPT used, as observed in Figure 8.4. The reduced mixing torque is more pronounced when the epoxide content in ENRs increases. The mixing torques in the mastication step, i.e. the first 2 mins., show similar values, but after the addition of silica, the mixing torques of the ENR and unmodified NR compounds are clearly separated. This indicates an effect of filler dispersion. The epoxide functionality on NR molecules increases their polarity,[13] and then enhances the compatibility with the polar active silica, leading to lower shear forces during compound mixing and so decreased mixing torque. The effect of epoxide groups on ENR and TESPT in unmodified NR results in similar mixing torques in the first interval of silica mixing. However, in the second half-addition of silica, NR with TESPT shows higher mixing torques compared to ENRs compounds which may be attributed to premature crosslinks by sulfur in the TESPT, as discussed in Chapter 3.

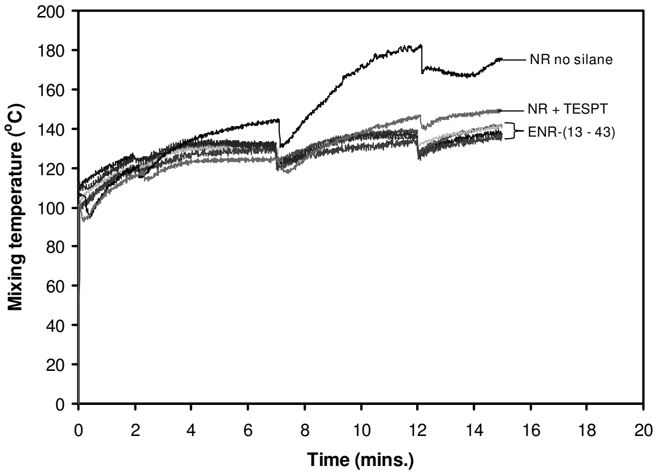


Figure 8.5 *Mixing temperatures developed during compound mixing in the internal mixer of silica-filled ENR compounds with various epoxide contents. Silica-filled unmodified NR compounds without and with TESPT at 9 wt% relative to silica content are considered as references.*

The mixing torques correspond well with the heat generation during compound mixing in the internal mixer as seen in the temperature profiles given in Figure 8.5. The ENR compounds show lower mixing temperatures than those of the compounds prepared with unmodified NR both with and without TESPT.

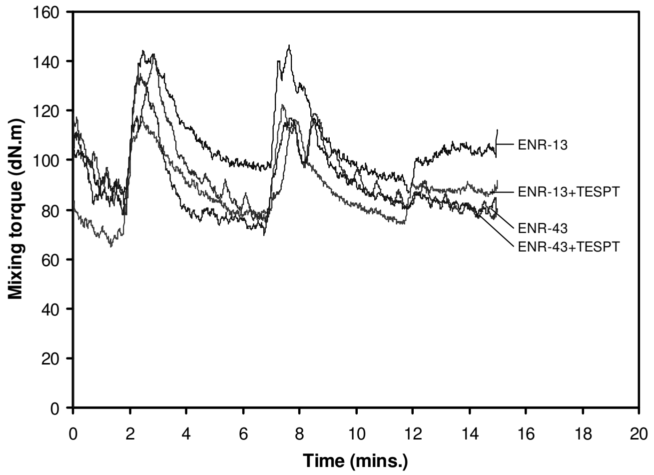


Figure 8.6 *Mixing torques of silica-filled ENR compounds with 13 and 43 mol% epoxide contents, compared between the ones with and without TESPT at 9 wt% relative to the silica content, as indicated for each line.*

The epoxide groups in the ENRs are expected to react with the silanol groups of the silica and compatibilize the two phases. However, the possibility of a synergistic effect between the epoxide groups and the silane coupling agent is also studied in this work. Figure 8.6 shows the mixing torques of the silica-filled ENR compounds with and without TESPT as silane coupling agent. The addition of TESPT into the ENR-13 based compounds clearly reduces mixing torque, whilst the ENR with 43 mol% epoxide content exhibits no significant difference in mixing torques between the compounds with and without TESPT. These results indicate that the ENR with low mol% epoxide content has not enough polar functional groups to hydrophobize the silica surface and the addition of TESPT helps to improve hydrophobation and silica dispersion. The ENR with high concentration of epoxide groups: ENR-43, can improve the silica dispersion due to a better polarity matching without the need for silica surface modifying agents.

8.3.2 Filler-filler interaction and network contributions

8.3.2.1 Payne effect. — In order to determine filler-filler interaction in the compounds, the storage moduli at 0.56 and 100% strain were measured as the difference in moduli at small and large deformation indicates the level of filler-filler interactions in the compounds.[14] The Payne effect of the silica-filled ENR compounds with and without TESPT is shown in Figure 8.7. Figure 8.7(a) shows that ENR-13, and ENR-21 incur a strong decrease in Payne effect with increasing TESPT content up to 6.0 and 3.7 wt% relative to the silica content, respectively, and thereafter level off. The ENR-29 compounds show only a slight decrease in Payne effect when TESPT at 1.8 wt% relative to silica is added and thereafter a more or less constant value. Therefore, the minimal levels of TESPT content required to optimize the Payne effect for each compound are different, depending on the availability of functional groups in the rubber matrix, as seen in Figure 8.7(b). The combination of epoxide groups in ENR-13 and ENR-21 with TESPT results in the lowest Payne effects. The higher levels of the storage modulus difference in ENR-29, ENR-36, and ENR-43, in the presence of TESPT may be attributed to the presence of the large amounts of epoxide groups which can create additional interactions and/or linkages between themselves. The epoxide groups can be ring-opened and form crosslinks between adjacent molecules, as reported by NG and Gan.[15] For ENR-36 and ENR-43, the Payne effect slightly decreases with increasing TESPT loading, as a result of a dilution effect.

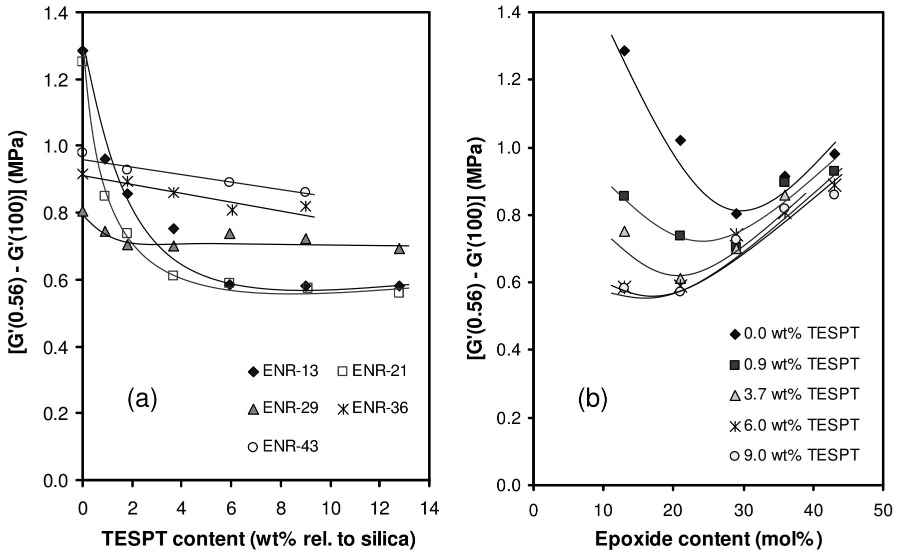


Figure 8.7 *Payne effect as functions of (a): TESPT content; and (b): epoxide content in the ENR compounds.*

With respect to the influence of epoxide content, the compounds without TESPT show a decrease in Payne effect when the epoxide functionality is increased from 13 – 29 mol%, and then Payne effect increases again with a further rise in epoxide content, as shown in Figure 8.7(b). This observation suggests that only a specific level of epoxide groups is required to interact with the silanol groups on silica surface. The presence of a too high concentration of epoxide groups has an adverse effect. The addition of TESPT can still clearly lower the Payne effect or filler-filler interaction in the ENR-13 and ENR-21 based compounds, but it shows only a small influence on the Payne effect of the compounds based on ENR-29, ENR-36 and ENR-43. Based on the minimum Payne effect observed for each set of compounds, a shift of the minimum points is noticeable in the sense that: the higher the epoxide content, the lower the TESPT loading required. Furthermore, it can be seen that after the optimum level, all the compounds show a rise in Payne effect.

To demonstrate the intrinsic properties of the different types of rubbers used as raw materials, the storage moduli of these matrices were additionally tested under strain variation. The results are given in Figure 8.8.

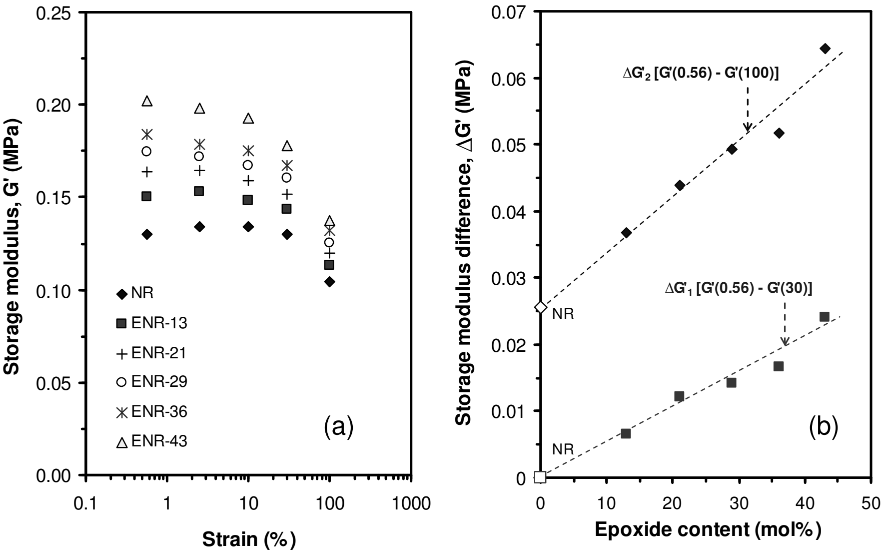


Figure 8.8 *(a) Storage modulus at varying deformations, and (b) storage modulus differences at 0.56 and either 30% (ΔG'1) or 100% (ΔG'2) strain of neat unmodified NR, and ENRs with various levels of epoxide functionality.*

Figure 8.8 shows the storage moduli from small to large deformations of unmodified NR and the ENRs. The ENRs with a greater degree of polarity have significantly higher storage moduli at small deformation, i.e. below 10% strain, as seen in Figure 8.8(a), as a result of interactions between their epoxide functional groups. In order to determine the degree of intrinsic interaction forces in each rubber, the storage modulus difference was calculated and plotted against epoxide content, as shown in Figure 8.8(b). The results reveal that a higher epoxide content leads to higher interaction forces as the storage modulus differences at 0.56 and 30 or 100% strain linearly increase. Till 30 % strain the pure NR keeps a constant modulus, to decrease for higher shrains due to non-linearity. On the other hand, for the ENRs these non-linear effects already start to be visible at lower strain. Therefore, the increase of Payne effect after the optimum level of about 25 mol% epoxide on the NR: Figure 8.7, is mainly because of a dominant effect of interaction forces associated with the polar nature of ENR itself. At low epoxide levels in the case of ENR-13 and ENR-21, the interactions between the epoxide moieties and silanol groups on the silica are still playing the main role, causing the reduction of filler-filler interactions.

8.3.2.2 Network contributions. — The network contributions can be further evaluated by the storage moduli at 100% strain, since the entire physical filler-filler linkages are assumed to be destructed,[14] as depicted in Figure 8.9.

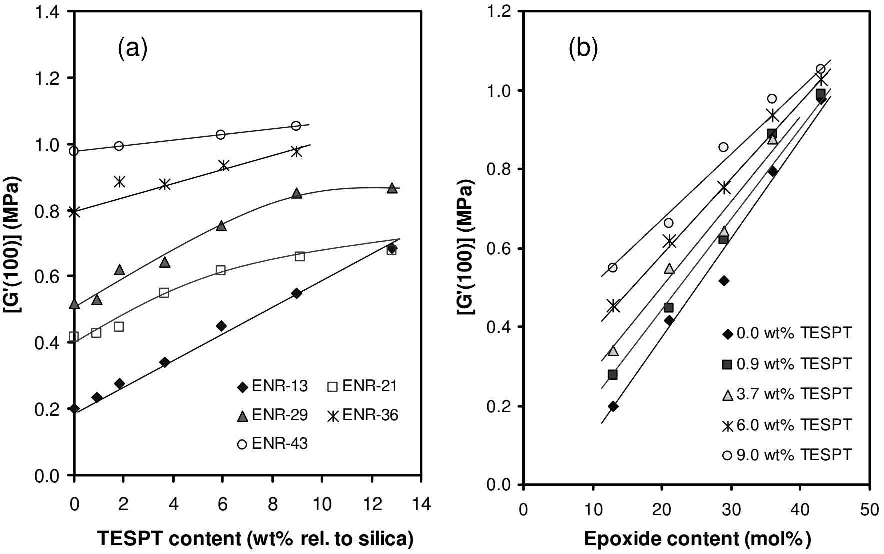


Figure 8.9 *Storage modulus at 100% strain as functions of (a): TESPT amount; and (b): epoxide content in ENRs for the silica-filled ENR compounds.*

It can be seen that higher amounts of TESPT and stronger polarity of the ENRs: Figures 8.9(a) and 8.9(b), respectively, result in higher network contributions in the compounds. These network structures can originate from several factors: 1) filler-to-rubber interactions; 2) self-association of polar materials; and 3) rubber-rubber bonding by free sulfur released from TESPT. When TESPT is excluded, the ENR-36 and ENR-43 clearly show higher storage moduli, mainly attributed to self-association of epoxide groups. These two ENRs show the least dependence on TESPT loading.

8.3.3 Compound viscosity and cure characteristics

8.3.3.1 Mooney viscosity. — Mooney viscosities of the compounds prepared with the various ENRs containing different levels of epoxide functionality are shown in Figure 8.10.

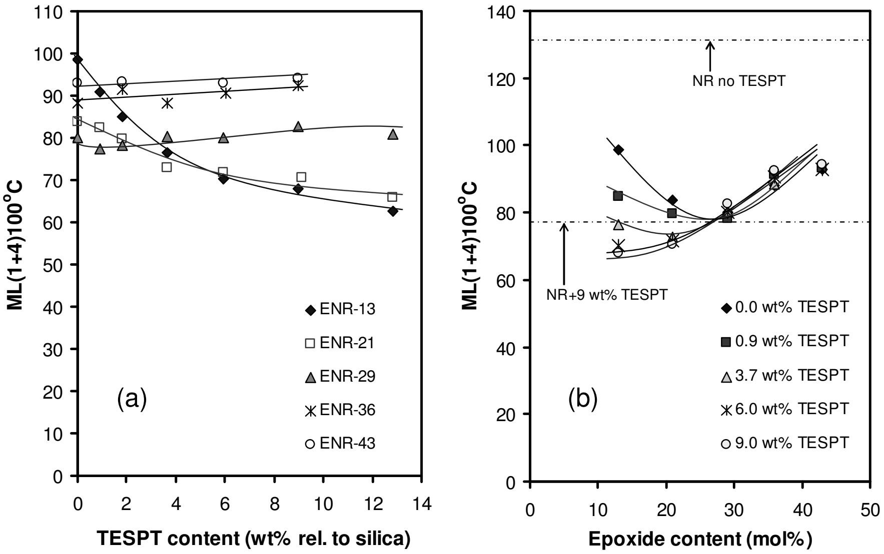


Figure 8.10 *Mooney viscosities as functions of (a): TESPT content; and (b): epoxide content in ENRs. Silica-filled normal NR compounds without and with TESPT at 9 wt% relative to the silica content are shown as references by dashed lines.*

The influence of silane loading at a given epoxide content can be seen in Figure 8.10(a). The ENR-13 and ENR-21 compounds show a sharp decrease in compound viscosity when the TESPT amounts are increased from 0 – 6.0 phr or 0 – 3.7 wt% relative to the silica content, respectively. After those ranges of TESPT concentration, the Mooney viscosities do not change much anymore. ENR-29 shows a marginal drop in Mooney viscosity when TESPT is added from 0 – 1.8 wt% relative to the amount of silica, and after that it slightly increases. For ENR-36 and ENR-43, the Mooney viscosities of the compounds tend to increase slightly with increasing TESPT content.

The effect of epoxide groups available on the ENRs on Mooney viscosity at a given amount of TESPT is shown in Figure 8.10(b). Considering the compounds without TESPT, an increase of epoxide content from 13 – 29 mol% results in a sharp decrease in Mooney viscosity, after that the Mooney viscosity increases again. TESPT at 6.0 and 3.7 wt% relative to the silica content is the optimal quantity which can minimize the viscosities of ENR-13 and ENR-21 based compounds, respectively. The addition of TESPT into ENR-29, ENR-36 and ENR-43 based compounds does not affect the Mooney viscosities much, as seen in the overlapping data points in Figure 8.10(b).

The change of Mooney viscosities with regard to epoxide group contents and TESPT loading as shown in Figure 8.10 resembles very much the various Payne effects as displayed in Figure 8.7. As previously discussed for the Payne effects, the ENRs with low content of epoxide groups can not completely hydrophobize the silica surface and the addition of TESPT still has a positive effect for hydrophobization and compatibilization. The compounds therefore have a lower Mooney viscosity as well as Payne effect. When the ENRs contain a high concentration of epoxide groups, in addition to interaction with the silanol groups of silica these polar groups tend to associate among themselves causing an increase in Mooney viscosity.

8.3.3.2 Cure characteristics of the compounds. — Figure 8.11 shows that the changes of cure rheometer minimum torques with regard to TESPT and epoxide contents exhibit again the same trend as with the Mooney viscosities (Figure 8.10), since the rheometer minimum torque is also an indication for compound viscosity.

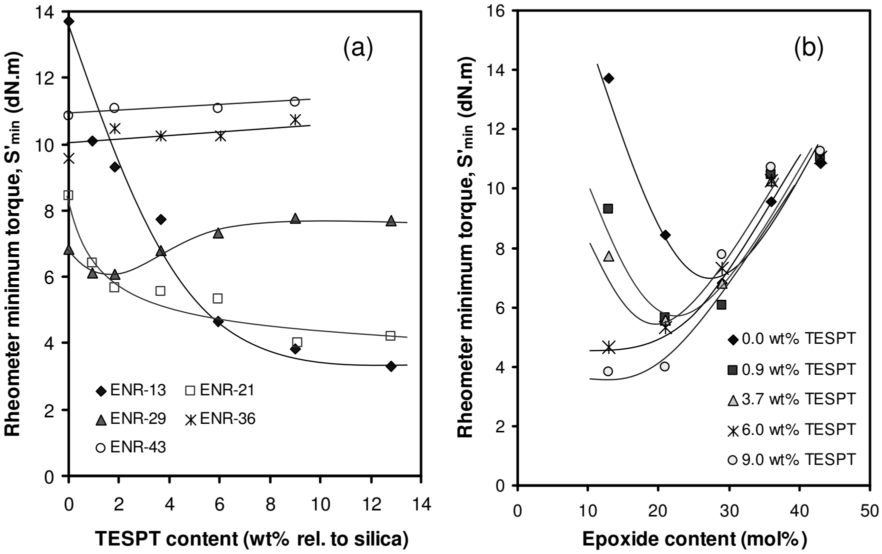


Figure 8.11 *Rheometer minimum torques as functions of (a): TESPT loading; and (b): epoxide content in the ENRs.*

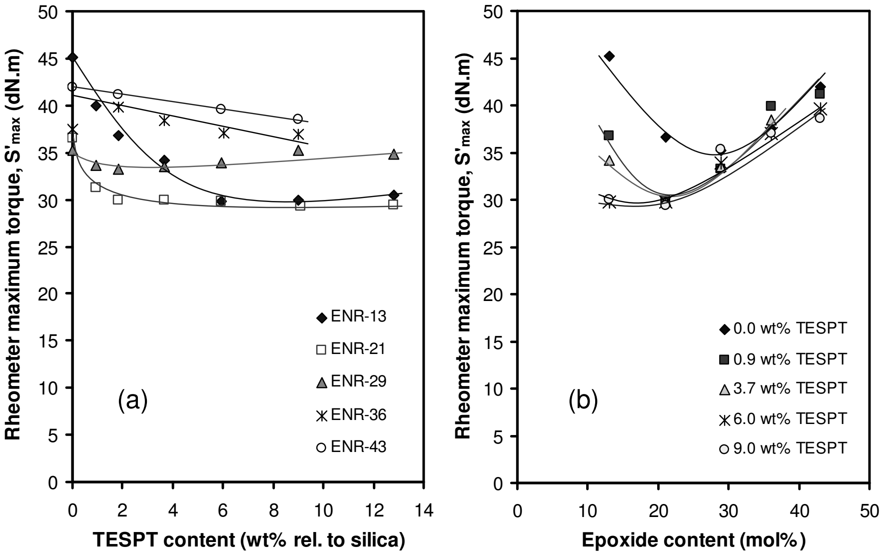


Figure 8.12 *Rheometer maximum torques as functions of (a): TESPT loading; and (b): epoxide content in the ENRs.*

Rheometer maximum torques of the compounds are shown in Figure 8.12. This parameter reflects the entire extent of network contributions in the reinforcing filler-based compounds, including both chemical and physical entities: i.e. rubber crosslinks; filler-rubber interactions; as well as the filler-filler network. These results demonstrate similar trends to the Payne effects and compound viscosities as shown in Figures 8.7, 8.10 and 8.11, because these complex network contributions also simultaneously dertermine the rheometer maximum torques of the compounds.

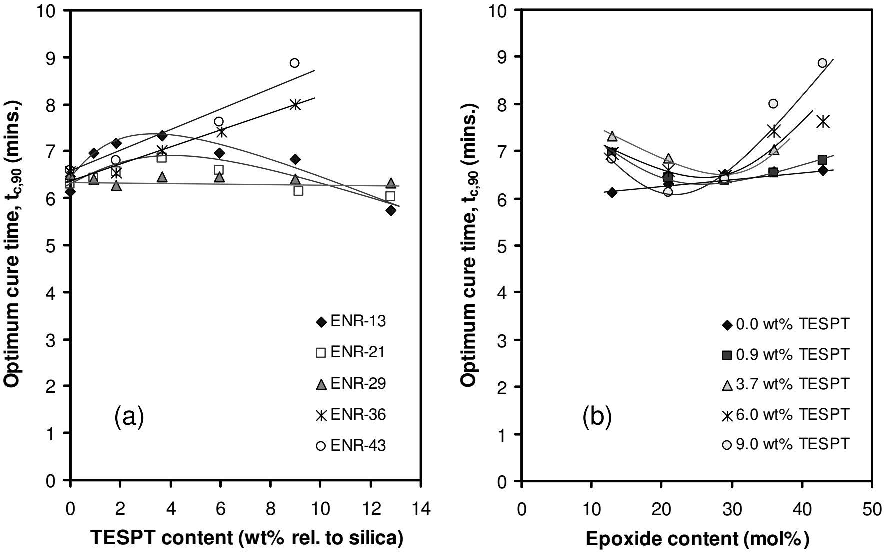


Figure 8.13 *Optimum cure times $t_{c,90}$ as functions of (a): TESPT loading; and (b): epoxide content in the ENRs.*

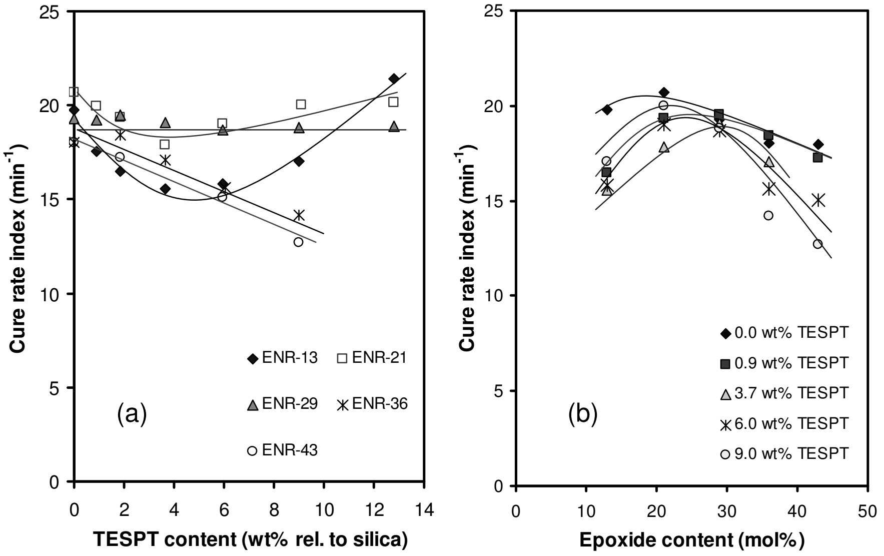


Figure 8.14 *Cure rate index as functions of (a): TESPT loading; and (b): epoxide content in the ENRs.*

Optimum cure times of the compounds are shown in Figure 8.13 and are reworked in terms of cure rate index as illustrated in Figure 8.14. The ENR compounds with different levels of epoxide groups show different responses towards TESPT addition with regard to cure rate index. The cure rate index of the ENR-13 and ENR-21 compounds initially decreases with increasing TESPT amount, but then tends to increase after the TESPT exceeds 3.7 wt% relative to the silica amount. The ENR with 29 mol% epoxide content exhibits a rather constant cure rate index with TESPT loading. ENR-36 and ENR-43 show decreasing trends when TESPT is increased. These different cure behaviors are also observed in Figure 8.14(b) in which the cure rate index increases when the epoxide contents are in the range of 13 – 21 mol%, but tends to decrease after the epoxide content exceeds 29 mol%. For the silica-filled ENR compounds in which two polar functional groups, i.e. epoxide and silanol groups play a role, the cure properties can be affected by chemical adsorption of highly polar basic accelerators. The silanol group on silica itself is acidic in nature and retards the curing reaction. Further, the greater extent of double bond transformation into epoxide rings reduces the number of active available double bonds for sulfur curing, and therefore reduces the cure reactivity. With these various factors involved, the cure behavior of this silica-filled ENR system is complicated. Considering the compounds based on ENRs with 13 – 29 mol% epoxide but without TESPT, see Figure 8.12, polar interactions between silanol and epoxide groups provide better polarity matching, reduce filler-filler interaction and so improve the cure rate index. This is because chemical adsorption on the silica surface can be minimized. A further increase of epoxide content, i.e. 36 – 43 mol%, significantly reduces the cure rate index. This can be either because of self-association of epoxide groups leaving the silanol groups free to adsorb curatives, or interference of excess epoxide groups with the vulcanization reaction. The addition of TESPT in the system with excess epoxide further decreases the cure rate index as the excess polar TESPT will also interfere with the curatives and hence slow down the curing reaction.

8.3.4 End-use properties of the compounds

8.3.4.1 Dynamic mechanical properties. — Tan δ at 60°C is well-known as an indication for rolling resistance of tires made from the compounds. The use of ENR as matrix for silica-filled compounds in the presence and absence of TESPT results in changes of tan δ at 60°C as shown in Figure 8.15.

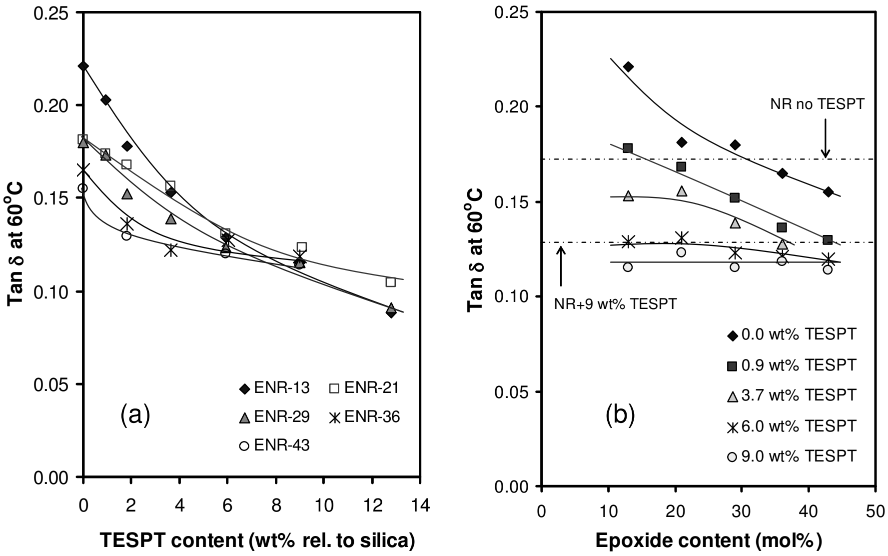


Figure 8.15 *Tan δ at 60 °C as functions of (a): TESPT amount; and (b): epoxide content in ENRs.*

The influence of silane content on tan δ at 60°C at a given epoxide level can be seen in Figure 8.15(a). Increase of the TESPT loading results in a sharp decrease in tan δ at 60°C of the compounds based on ENRs with 13, 21 and 29 mol% epoxide content, and a slight decrease for ENR-36 and ENR-43. Basically, tan δ relates strongly to network contributions in the compounds. The dynamic mechanical test was performed at 3.5 % strain and a frequency of 10 Hz, where the filler network begins to break. The results are therefore strongly influenced by network contributions originating from filler-rubber interactions and physical/chemical crosslinks. These results are in good correspondence with the storage modulus at 100% strain (Figure 8.9). Without TESPT, the increase of epoxide contents leads to a strong decrease in tan δ at 60°C as visualized in Figure 8.15(b). This can be linked to the greater filler-rubber interaction/network formation as reflected by the higher storage modulus at high strain in Figure 8.9. The combination of epoxide functionality with TESPT silane coupling agent jointly improve the tan δ at 60°C or rolling resistance of tires. Therefore, there is a possibility to reduce the amount of TESPT needed in silica-filled ENR formulations.

8.3.4.2 Mechanical properties. — Tensile properties of the vulcanizates are shown in Figure 8.16.

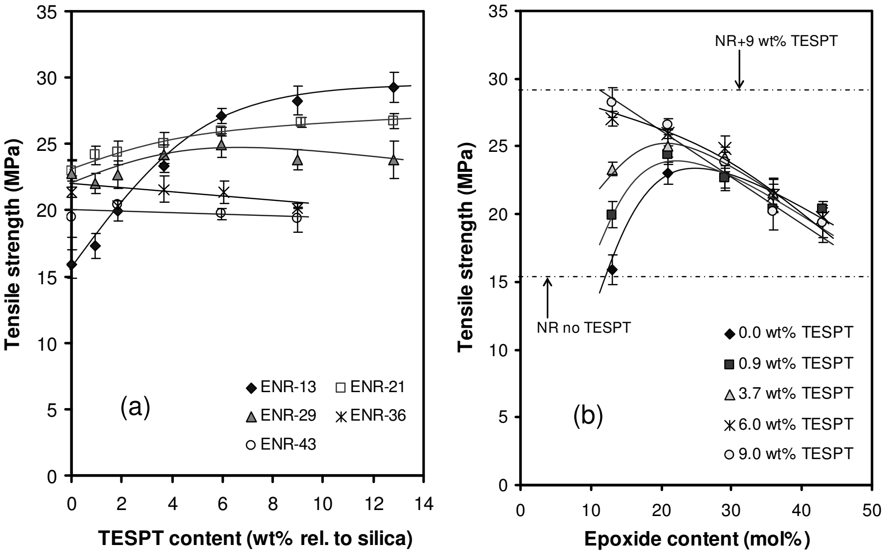


Figure 8.16 *Tensile strength as functions of (a): TESPT amount; and (b): epoxide content in ENRs. Silica-filled unmodified NR compounds without and with TESPT at 9 wt% relative to the silica content are included as references.*

The tensile strength clearly shows effects of TESPT loading and epoxide content, as depicted in Figures 8.16(a) and 8.16(b), respectively. Without TESPT, the ENR-21 and ENR-29 compounds show the best possible tensile strength obtained by the utilization of the epoxide functional groups only for the silica-filled system. As seen in Figure 8.16(b), the tensile strength of ENR-21 and ENR-29 compounds without the use of TESPT lies almost in the middle between the tensile strength of NR compounds with and without TESPT. A further increase in degree of polarity by more epoxide functionality shows an adverse effect towards tensile properties. The use of ENR-13 clearly requires TESPT to enhance its tensile strength, as seen in a substantial increase of this property with TESPT loading. The optimum tensile strength for ENR-13 is observed when it is used in combination with 6.0 wt% TESPT relative to silica content. Under this condition, the property reaches more or less the same level as that of unmodified NR with optimal TESPT loading. The tensile strength of the ENRs with higher degree of epoxidation shows less dependence on silica coupling agent addition, and this property is decreasing especially when the epoxide content exceeds 29 mol%. The self-association[13,15] of epoxide groups that creates another type of crosslink and contributes to a higher degree of crosslinking, as observed by the high storage modulus at 100 % strain (Figure 8.9) and Mooney viscosity (Figure 8.10 and Table 8.3), subsequently has an adverse effect on the ultimate tensile properties.

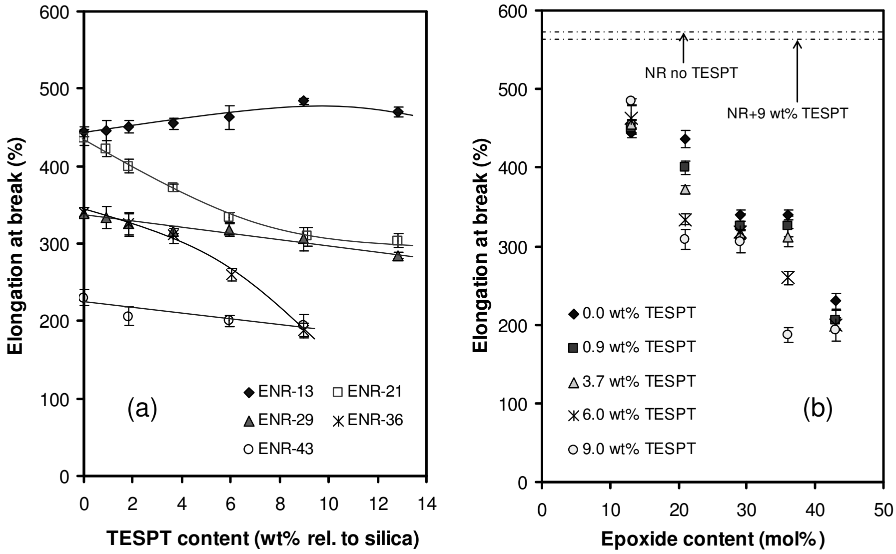


Figure 8.17 *Elongation at break as functions of (a): TESPT amount; and (b): epoxide content in ENRs. Silica-filled unmodified NR compounds without and with TESPT at 9 wt% relative to silica content are included as references.*

Figure 8.17(a) shows that all ENR compounds, except ENR-13, have a decrease in elongation at break with increasing TESPT loading, whilst the ENR-13 compounds show a slight increase of elongation at break when the TESPT content is increased up to 9.0 wt% relative to the silica content. Considering the effect of epoxide content as shown in Figure 8.17(b), the increase of epoxide content leads to a sharp decrease in elongation at break, and all ENR compounds have lower elongation at break than NR both with and without TESPT. These results correspond with the tensile modulus at 100 % elongation as shown in Figure 8.18. Again, the network contribution as described for the dynamic modulus (Figure 8.9) can significantly affect the extensibility and flexibility of the vulcanizates.

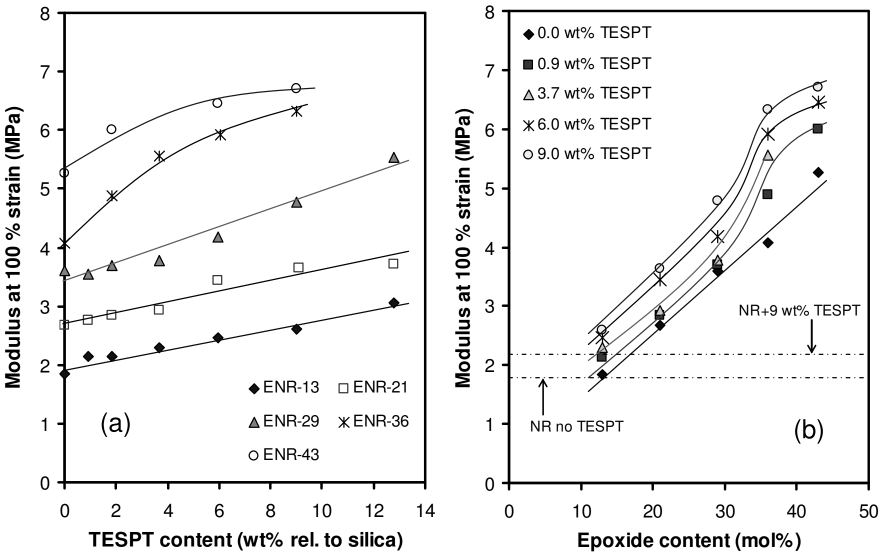


Figure 8.18 *Tensile modulus at 100 % strain as function of (a): TESPT amount; and (b): epoxide content in ENRs. Silica-filled unmodified NR compounds without and with TESPT at 9 wt% relative to silica content are included as references.*

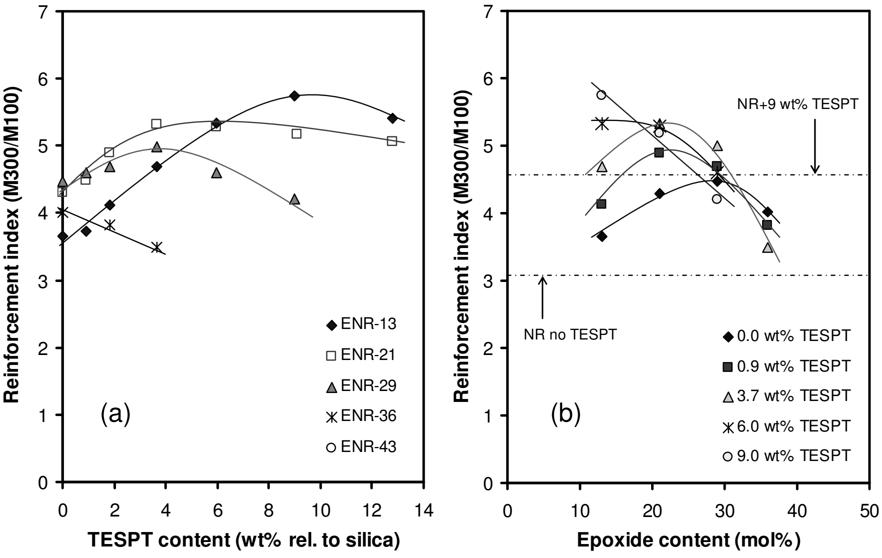
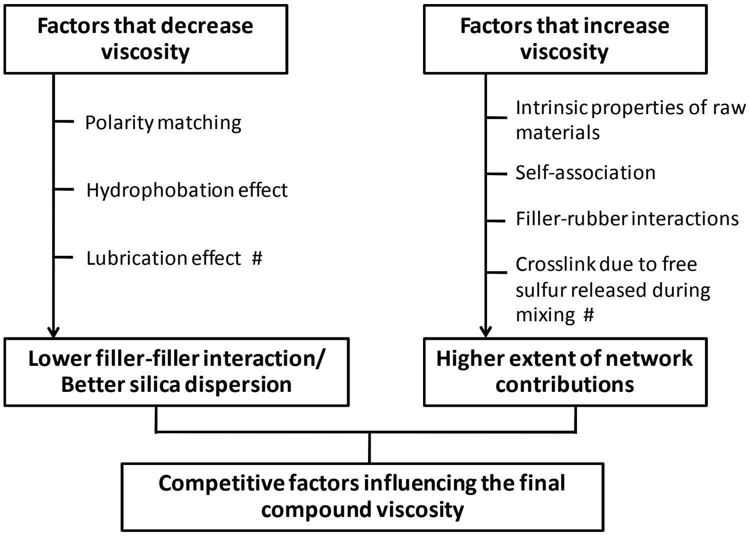


Figure 8.19 *Reinforcement index as functions of (a): TESPT amount; and (b): epoxide content in ENRs. Silica-filled unmodified NR compounds without and with TESPT at 9 wt% relative to silica content are included as references.*

The compounds based on ENR-13, ENR-21 and ENR-29 show their optimum reinforcement indices when TESPT amounts at 9.0, 3.7, and 3.7 wt% relative to the silica content are combined, respectively, as shown in Figure 8.19(a). A further increase of TESPT loading results in a decrease in reinforcement index. In Figure 8.19(b), the ENR compounds without TESPT show an increase of reinforcement index with increasing epoxidation degree up to 29 mol% to match more or less the same level as that of an unmodified NR compound in the presence of TESPT. However, a further increase of epoxide content leads to a decrease again in reinforcement index. With the presence of TESPT, the results show the same trends as the tensile strength: Figure 8.16. The compounds based on ENR-13, ENR-21 and ENR-29 in combination with suitable TESPT contents, show higher reinforcement index compared to that of silica/TESPT filled NR compound. This reflects a good synergistic effect between epoxide groups and TESPT towards enhanced reinforcing efficiency of silica in ENR compounds.

8.4 DISCUSSION

With regard to the changes in Payne effect and compound viscosity, the phenomena apparently relate well to the overall properties of silica-filled ENR compounds and vulcanizates. There are several factors competitively influencing the compound viscosities of silica-filled polar-modified NR systems as can be summarized in Scheme 8.1.



these factors can only take place in the system with the presence of silane coupling agent.

Scheme 8.1 *Competitive factors influencing compound viscosities of silica-filled ENR compounds with and without TESPT silane coupling agent.*

The change in compound viscosities as indicated by Mooney viscosity and rheometer minimum torque, Figures 8.10 and 8.11, respectively, can be discussed by considering several factors which are simultaneously and competitively taking place in the compounds. "A better silica dispersion" resulting from a lower filler-filler interaction or Payne effect is a key factor that strongly reduces the viscosity of the compounds. Considering the ENRs with epoxide contents in the range of 13 – 29 mol% in Figures 8.10(b) and 8.11(b), the compounds without TESPT show a decrease in compound viscosities, due to a dominant effect of silica dispersibility. Epoxide groups can result in polar-polar interactions with silanol functionalities on the silica, and then lead to better compatibility of the mixes resulting in a lower filler-filler interaction and hence a reduction of compound viscosity as corresponding to Payne effect: see Figure 8.7. Apart from the polarity matching between silica and ENR, when TESPT is additionally applied in the compounds, the enhanced hydrophobation and additional lubrication effects in the ENR-13 and ENR-21 compounds also lead to a strong reduction in compound viscosity. The only slight change of compound viscosity in ENR-29 with varying TESPT contents points to the fact that this level of epoxide content is just enough to hydrophobize the silica surface and the addition of TESPT has only a minor additional effect on the properties.

Table 8.4 *ML(1+4)100°C of normal NR and ENRs with various levels of epoxide functionality.*

Rubber type	ML(1+4)100°C
Normal NR (i.e. RSS 3)	72.9
ENR-13*	85.4
ENR-21*	89.0
ENR-29*	90.8
ENR-36*	93.4
ENR-43*	96.0

** mol% epoxide content*

After the compounds show their optimum low compound viscosities due to the presence of appropriate combinations of either epoxide functionality or TESPT, other factors play a dominant role towards increased compound viscosities. The rise of compound viscosity can be mainly attributed to "the increment of network contributions": Scheme 8.1. The ENRs with different levels of epoxide functionality have variable basic properties which certainly affect their compound viscosities. As shown in Table 8.4, the Mooney viscosities of the ENRs increase with increasing epoxide content, as the ENRs themselves possess a relatively high polarity in their structures, and so tend to form self-association *via* hydrogen bonding or polar interactions between either the same or neighboring molecules, and even self-crosslink due to the opening of the oxirane rings.[15] Figure 8.20 shows the possible self-crosslinking of epoxidized natural rubber. This network generation contributes to the increase of compound viscosity.

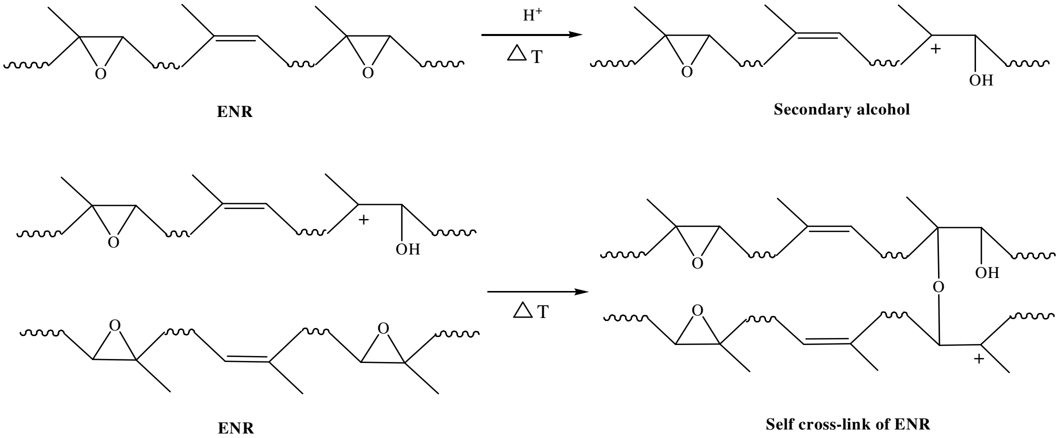


Figure 8.20 *Self-crosslinking of epoxidized natural rubber under acidic and high thermal conditions.*[15]

In addition to the possibility of physical interactions generated between ENR and silica *via* polar-polar interactions, chemical silica-to-ENR coupling has been proposed, as reviewed in Chapter 2.[4,5] For the compounds with TESPT coupling agent, strong chemical filler-rubber interaction can be formed through silane chemistry contributing to network structures. Moreover, TESPT can additionally release free sulfur into the system, and then cause light rubber-rubber crosslinking during the high thermo-mechanical mixing conditions as indicated earlier in Chapters 3 and 5. The combination of these factors which involve network formation leads to the increase in compound viscosities of silica-filled ENR systems.

8.5 CONCLUSIONS

The epoxide functionality on natural rubber molecules has a significant influence on both processing and end-use properties of silica-filled ENR compounds. The mixing torque, Payne effect, and compound viscosity remarkably decrease with the presence of epoxide functional groups up to 29 mol% on ENR compared to silica-filled normal NR compounds. A high content of epoxide groups, e.g. ENR-36 and ENR-43, adversely affects the processibility and most of the properties. Addition of TESPT into silica-filled ENRs with epoxide contents of 13 and 21 mol% further enhances compound processibility and vulcanizate properties, whilst the use of TESPT has the least effect on the ENR-29 compound. Based on the overall properties, epoxide groups on ENR alone can not provide the properties to match with those of silica-TESPT filled unmodified NR. But, the right combination of epoxide groups and TESPT as silane coupling agent leads to similar level of properties compared to the TESPT-normal NR system. With the synergistic effect of polar epoxide groups, the silane coupling agent loading needed can be reduced down to half or even lower compared to conventional silica-filled NR compounds.

8.6 REFERENCES

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APPENDIX

VERIFICATION OF INTERACTIONS BETWEEN SILICA AND EPOXIDIZED SQUALENE AS A MODEL FOR EPOXIDIZED NATURAL RUBBER

Unmodified squalene (Sq) and epoxidized squalene (ESq), as models for natural rubber and epoxidized natural rubber, were mixed with silica in a reactor at 140 – 145 °C, which corresponds to the optimal mixing dump temperature of silica-filled NR or ENR compounds. The mixtures were prepared with and without TESPT silane coupling agent. The bound silica in the mixtures was extracted and checked for its composition by using Fourier-transform infrared (FT-IR) spectroscopy. The results indicate that Sq and ESq with the help of TESPT can chemically link to the silica surface, as the FT-IR spectra of purified bound silicas show absorption peaks of hydrocarbon structures. The epoxidized squalene also produces chemical interaction with silica in the absence of TESPT, but to a lesser extent compared to the one with TESPT, as indicated by the absorption intensity. On the other side, the silica in the Sq mixture without TESPT shows no traces of hydrocarbon, indicating that there is no noticeable chemical interaction involved.

INTRODUCTION

The main interactions between silica and polar rubbers come from hydrogen bonding or other interaction forces, e.g. polar-polar and Van der Waals forces.[1-3] It has been reported in literature that polar rubbers can form strong chemical interaction or chemically link to silica particles at vulcanization temperatures, thus function as a coupling agent.[4-8]

Manna *et al.*,[7] and George *et al.*,[8] have proposed a mechanism of reaction between epoxidized natural rubber (ENR) and silica, showing that at high temperature chemical linkages between the rubber and silica could be formed. In Chapter 8, the results showed that ENR with 20 – 30 mol% epoxidation as matrix requires less TESPT silane coupling agent compared to TESPT needed for conventional NR compounds. The improvement in reinforcing efficiency of silica by using ENR can be mainly attributed to better silica dispersion as well as greater and stronger filler-rubber interaction enhanced by the polar epoxide groups. However, the evidence for filler-rubber interactions in polar rubber systems has not been clearly demonstrated.

The present experiments are executed to confirm the linkage type of filler-to-rubber interactions in silica-filled NR and ENR compounds in the presence and absence of TESPT silane coupling agent. Unmodified squalene (Sq) and epoxidized squalene (ESq) are used as model compounds for NR and ENR, respectively. The reactions between silica and model squalenes are carried out at high temperature to resemble the optimum rubber compound dump temperature. The bound silicas in the mixtures are extracted and analyzed for their compositions by using the FT-IR technique.

EXPERIMENTAL

Materials

Squalene, 98.0% (Alfa-Aesar, USA) was used as a model compound for NR. It contains 6 double bonds in a molecule as illustrated in Figure 1. Epoxidized squalene (ESq) was prepared in-house. The chemicals, i.e. formic acid, hydrogen peroxide, and Teric N30 used for ESq synthesis were the same as those applied for the preparation of ENR, as detailed in Chapter 8. Silica and bis-triethoxysilylpropyl tetrasulfide (TESPT) were the same as described in Chapter 3. Acetone (Lab-Scan, Ireland) and distilled water were also employed.

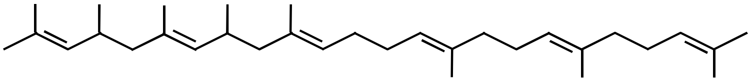


Figure 1 *Molecular structure of squalene.*

Preparation and characterization of epoxidized squalene, ESq

Preparation of performic acid. — For this reaction, the performic acid was separately prepared through the reaction between formic acid and hydrogen peroxide in a continuously stirred reactor at ambient temperature. 1 mol of formic acid was added into the reactor which contains distilled water in a sufficient amount to dilute the obtained performic acid to 35 % w/w. 1 mol of hydrogen peroxide was subsequently added dropwise. The entire amount of hydrogen peroxide was charged in a time period of about 3 h. The reaction was continued for 24 h.

Epoxidation procedure. — The epoxidation reaction of squalene was carried out in a stirred reactor at ambient temperature. 1 mol of squalene was charged into the reactor, followed by addition of 6 mol performic acid. The reaction mixture was continuously stirred over a time period of 24 h. After completion of the reaction, the resulting epoxidized squalene was neutralized by washing several times with water.

Characterization of the ESq structure. — The chemical structure and actual mol% epoxide of the product were characterized by means of the proton nuclear magnetic resonance (^{1}H-NMR) spectroscopic technique, as described in the experimental part of Chapter 8. The ^{1}H-NMR spectra of unmodified squalene and epoxidized squalene are shown in Figure 2.

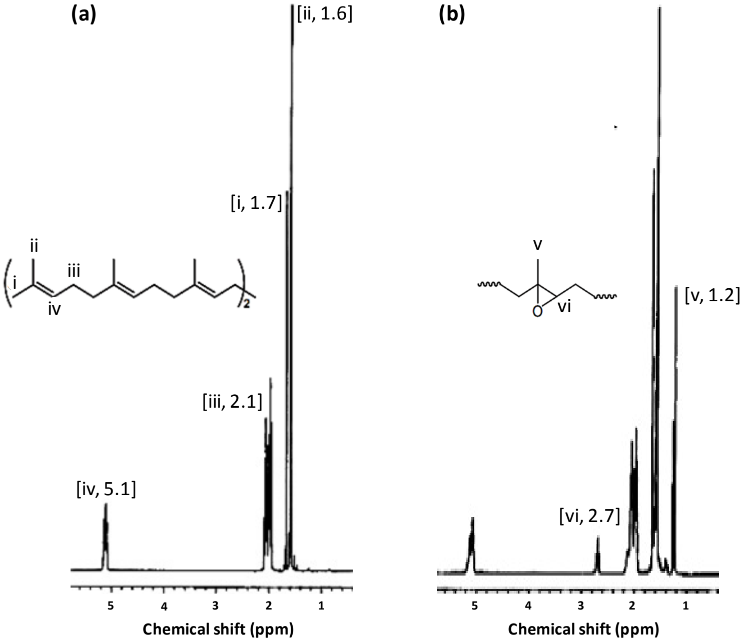


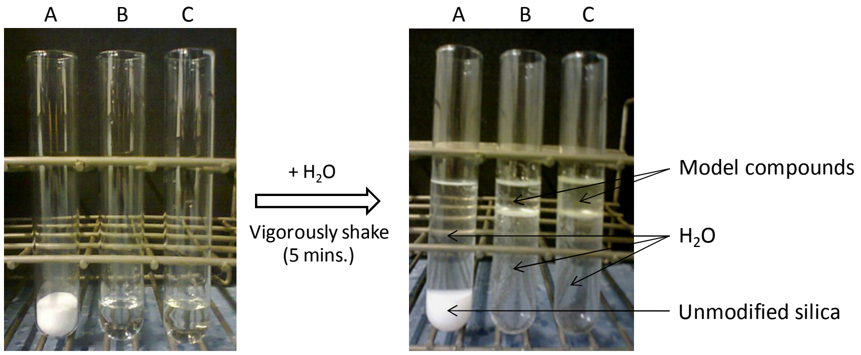
Figure 2 *^{1}H-NMR spectra of (a) unmodified squalene and (b) epoxidized squalene.*

For the spectrum of pure squalene as shown in Figure 2(a), signal characteristics of the trans-1,4-isoprene unit appear at 1.6, 1.7, 2.1 and 5.1 ppm, which are assigned, respectively, to methyl-, methylene-, and alkene protons as indicated in the figure, according to Saito *et al.*[9] After epoxidation of squalene two new peaks at 1.2 and 2.7 ppm are observed , which are assigned to protons associated with the epoxide ring as indicated in Figure 2(b). The epoxide content in ESq was calculated from the integral of absorption peaks at 2.7 and 5.1 ppm assigned to protons on the epoxide ring and on the double bonds, respectively, according to Equation 8.1. In this experiment, the integrals at chemical shifts of 2.7 and 5.1 ppm were 0.29 and 1.00, respectively. As a consequence, epoxidized squalene with 22.5 mol% epoxide content was achieved.

Reactions between squalene, epoxidized squalene and silica in the presence and absence of TESPT silica coupling agent

Reaction procedure. — Squalene and epoxidized squalene were used as the model compounds for NR and ENR, respectively. The reaction was performed at high temperature to mimic the mixing dump temperature that is required for silica-filled NR compounds, as reported in Chapter 3. The model compound was first introduced into a continuously stirred reactor which was positioned in an oil bath with the medium temperature of 145 ^{o}C. Subsequently, silica at 20 wt% relative to the amount of model compound was added and the reaction was continued for 1 h. In case of the compound with TESPT silane coupling agent, the silane was charged at 10 wt% relative to the silica content at the same adding moment as the silica.

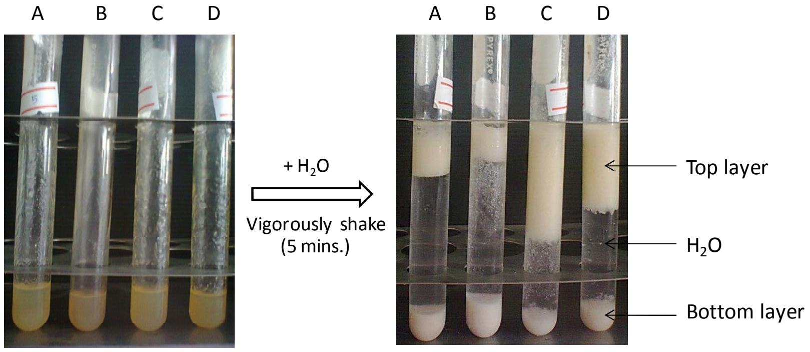
Component separation. — After the reaction of the silica-model compound was completed, distilled water was added to separate the components in the mixture, since squalenes and silica are basically different in terms of specific gravity and degree of polarity. Squalene is a hydrocarbon molecule with a density of 0.86 g/cm^3, so it is phase separated floating on water. Unmodified silica is hydrophilic, so silica will soon sink in water after water adsorption on its surface, as shown in Figure 3.



(a) (b)

Figure 3 *Pure forms of A: silica; B: Sq; and C: ESq; (a) before and (b) after addition of water.*

The separated layers in water of different compounds after heating at 145°C for 1 h are shown in Figure 4. The silica with its surface modified by squalene hydrocarbon moieties by chemical interaction or bonding is expected to be more hydrophobic and to be partly associated in the squalene or epoxidized squalene phase.



(a) (b)

Figure 4 *Mixtures of silica and model compounds after heating 1 h at 145°C and with and without TESPT; before (a) and after (b) component separations with water. A: ESq+silica; B: Sq+silica; C: ESq+silica+TESPT; and D: Sq+silica+TESPT.*

The components in the silica-filled model compounds are clearly separated with water located in the middle as displayed in Figure 4. As previously demonstrated in Figure 3, the model squalene is separated as a top layer due to its lower specific gravity, while unmodified silica sinks into water due to its high hydrophilicity. However, after the reaction, silica is visible in both the top and bottom layers in different proportions. The silica in the top layer, i.e. the squalene layer, indicates that the silica surface of these particles has been chemically modified by means of silica-to-model squalene interactions. A higher proportion of silica in the top layer implies that there is a greater extent of interaction/reaction in such a system.

Investigation of components present in the separate layers. — The divided layers of silica-filled model compounds in water as shown in Figure 4, were separately taken out of the reactor. Since squalene can well dissolve in acetone, the separated mixtures were washed 10 times by using 20 ml of acetone each time on filter paper with a fine particle retention of approximately 3 µm (grade no. 6). The residual solid on filter paper was dried in a vacuum oven at 100°C for 24 h. To make sure that the unbound squalene had been totally removed, the residual silica was further extracted with acetone using a Soxhlet extraction method for 24 h. After that the silicas obtained from both layers were again dried in a vacuum oven at 100°C for 24 h, and finally weighed.

The bound silicas obtained from the top layers under each condition were further analyzed by Fourier-transform infrared (FT-IR) spectroscopy in order to verify a trace of model squalenes, i.e. unmodified and epoxidized squalenes, chemically reacted onto the silica surface. The virgin forms of squalene, and modified squalene were also characterized. To characterize the original pure silica and purified bound silica obtained from the reactions, the potassium bromide or KBr disc sample preparation technique was used and the weight ratio between KBr powder and silica sample was kept constant to ensure an equal concentration in each sample analysis.

RESULTS AND DISCUSSION

Residual silica content in each separate layer

After purification of the residual silicas present in each layer of the mixtures, the quantities of silicas were determined, as illustrated in Figure 5.

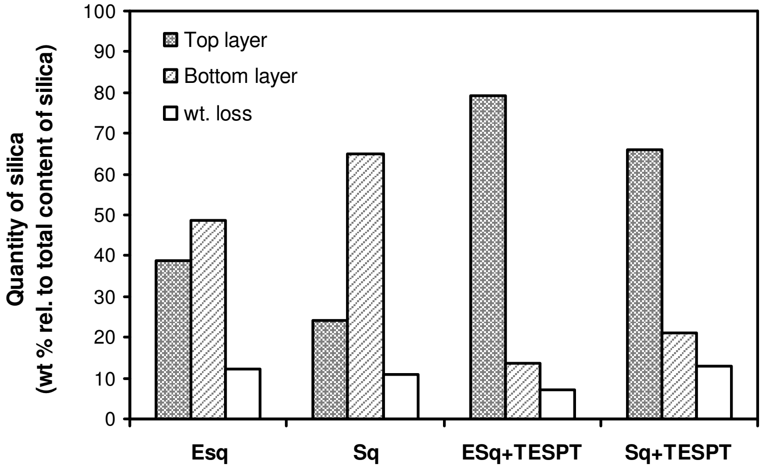


Figure 5 *Quantity of residual silicas consisting in each separated layer of the mixtures.*

Figure 5 shows the percent weight of silicas residing in each separated layer of mixtures. As discussed for Figure 4, the ability to float on water of silica particles/aggregates comes from the model compounds which are potentially either physically or chemically reacted onto the silica surface, and then assist the bound silica to move to the top layer, while unbound silica sinks to the bottom layer. In the absence of TESPT, the amount of silica in the top layer of epoxidized squalene is clearly higher compared to unmodified squalene. The results indicate that the epoxidized squalene has a greater or stronger interaction with silica than the unmodified squalene. The incorporation of TESPT significantly raises the bound silica in both unmodified and modified squalene, which can be seen in Figure 4, as well as reflected in the higher percentage of silica contained in the top layer compared to the mixtures without TESPT in Figure 5.

FT-IR spectra of unmodified, epoxidized squalenes and silica

The virgin forms of squalene, epoxidized squalene and silica as received were characterized for their molecular structures by the FT-IR technique.

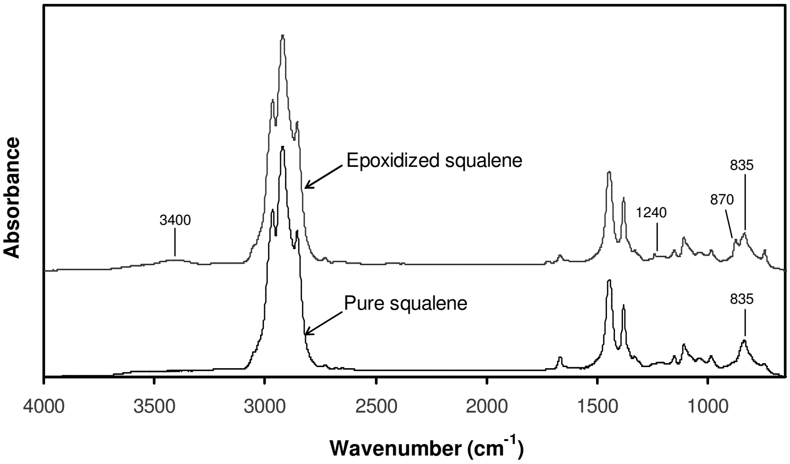
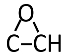


Figure 6 *Absorbance spectra of virgin squalene and epoxidized squalene.*

Comparing the FT-IR spectra of unmodified and epoxidized squalenes as depicted in Figure 6, epoxidized squalene shows additional peaks at 1240 and 870 cm^{-1} which are respectively assigned to C–O and  vibrations on the oxirane rings in its structure. The absorption peak at 835 cm^{-1} is a characteristic peak of =C–H bending in the isoprene unit and the broad peak at 3400 cm^{-1} of epoxidized squalene is due to O–H stretching vibrations.

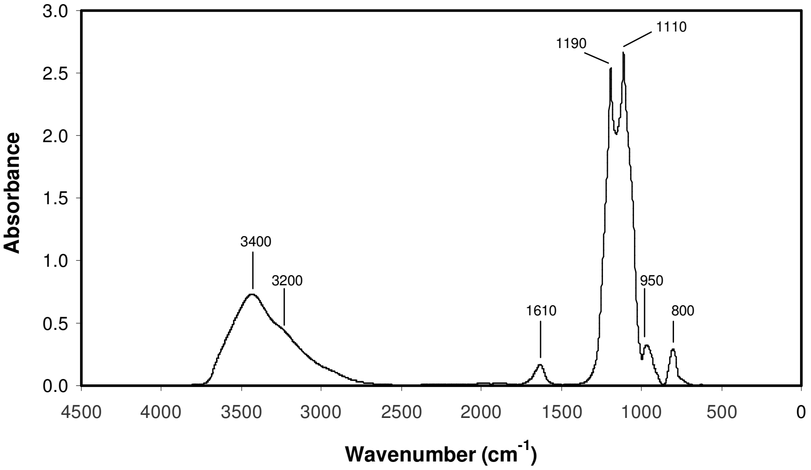


Figure 7 *FT-IR spectrum of pure silica.*

The signals appearing in the spectrum of pure silica as shown in Figure 7 are listed in Table 1.[10] The spectrum shows peaks at 800, 1110 and 1190 cm^{-1}, which are assigned to Si–O stretching vibrations. The signals of silanol groups (Si–OH) appear at 950 and 3400 cm^{-1}. In addition, absorption bands at 3200 and 1610 cm^{-1} are observed as a result of stretching and deformation vibrations of adsorbed water molecules, respectively.

Table 1 *Infrared absorbance signals of silica and their assignments.*[10]

Wavenumber (cm^{-1})	Assignment
800	Si–O
950	Si–OH
1110, 1190	Si–O–Si
1610	O–H (water)
3200	O–H (water)
3400	Si–OH (hydrogen bonded)

Characterization of bound silica

The purified silicas obtained from the top layers were analyzed for their chemical structures by FT-IR; the infrared spectra are shown in Figure 8.

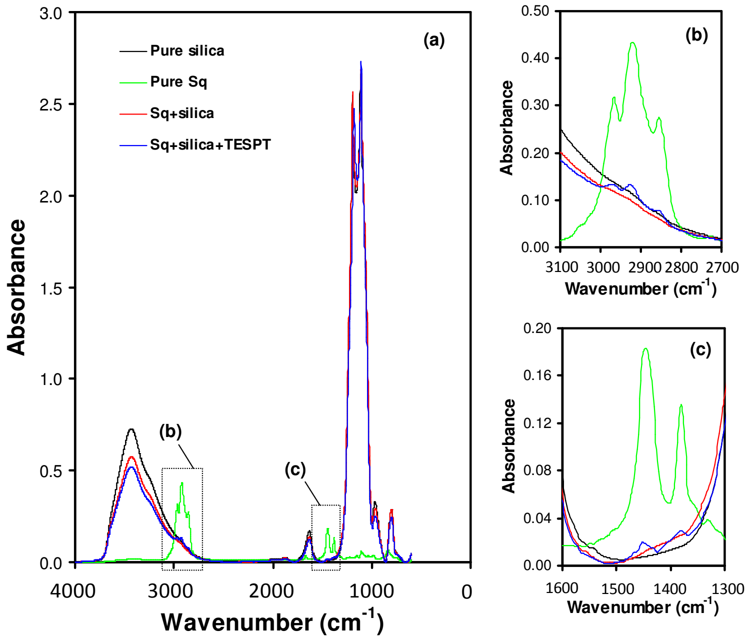


Figure 8 *Infrared spectra of silica, squalene, and purified bound silicas obtained from the top layer of silica and squalene mixtures, with and without TESPT.*

All FT-IR analysis was carried out using an equal concentration of sample in the KBr powder to ensure that the intensity of the peaks is not affected by concentration according to the Beer-Lambert Law, but only influenced by the presence of different functional groups. In addition to the characteristic peaks of silica as summarized in Table 1, the modified silica from the mixture with TESPT shows weak absorption peaks at the wavenumbers of 1380, 1440, 2850, 2910 and 2960 cm^{-1} which correspond to the vibrations of C–H in the squalene structure. This indicates the presence of squalene bound to the silica surface. On the other side, squalene without TESPT does not react with silica as none of the characteristic peaks of C–H stretching and bending vibrations are observed. Based on this squalene model compound study, we can refer to the natural rubber that needs silane coupling agent to produce chemical filler-to-rubber bonds in the silica-filled system.

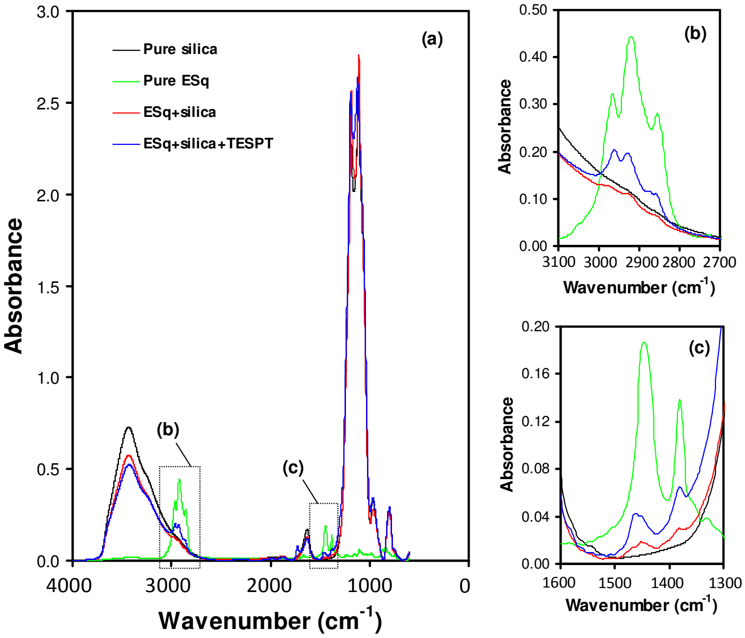


Figure 9 *Infrared spectra of silica, squalene, and purified bound silicas separated from the top layer of silica and epoxidized squalene mixtures with and without TESPT.*

The FT-IR spectra of modified silicas that were separated from the mixtures of epoxidized squalene with and without TESPT are shown in Figure 9. The spectra of modified silicas from both mixtures display the signals of hydrocarbon bonds, i.e. at 1380, 1440, 2850, 2910, and 2960 cm^{-1} resembling the adsorption bands of squalene, so indicating the chemical nature of the bond of model epoxidized squalene to silica. However, the intensities of the absorption bands are different from the virgin squalene case, reflecting a difference in concentration of epoxidized squalene bonds to the silica surface. The incorporation of TESPT into the ESq/silica mixture clearly enhances the content of hydrocarbon that is chemically attached to the silica surface. This implies that chemical interactions/bonding between silica and epoxidized natural rubber are increased by using TESPT in the practical rubber compounds.

Absorbance ratio between the signals of hydrocarbon bonds and Si-O in modified silicas

To compare the absorption intensity of hydrocarbon on silica, the absorbance ratio is calculated versus the peak at 800 cm^{-1}, which is assigned to Si-O of silica, as expressed in Equation 1:

$$\text{Absorbance ratio} = \frac{A_x}{A_x + A_r} \qquad (1)$$

where A_x is the absorbance peak height at x cm^{-1}.

A_r is the absorbance peak height of a reference peak at 800 cm^{-1}.

An example of the measurement of absorbance peak height can be seen in Figure 10. The results of peak height ratios are shown in Figure 11.

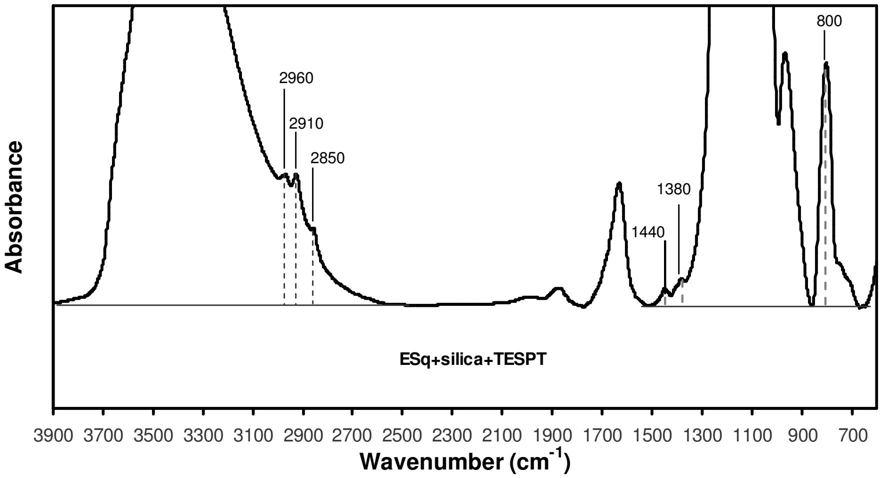


Figure 10 *Example of measurement of absorbance peak height at 800, 1380, 1440, 2850, 2910 and 2960 cm^{-1}.*

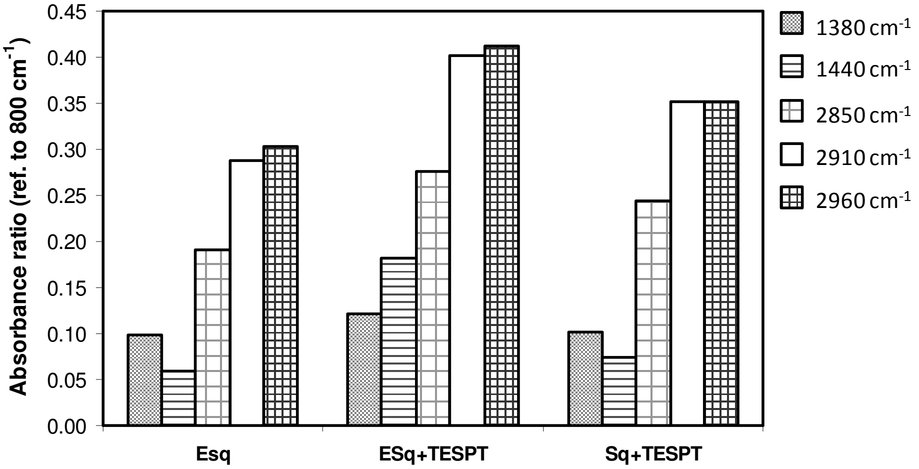


Figure 11 *Absorbance ratios at different peaks associated with vibrations of hydrocarbon bonds referred to Si-O bonds at 800 cm^{-1} in modified silicas.*

The peaks at 1380 and 1440 cm^{-1} are assigned to C–H bending, while the ones at 2850, 2910, and 2960 cm^{-1} are due to C–H stretching vibrations. Figure 11 clearly shows that the systems with TESPT coupling agent provide a higher absorbance ratio indicating a higher extent of filler-rubber interaction, compared to the system which contains epoxide functional groups only, i.e. ESq. In the presence of TESPT, the absorbance ratios are larger when epoxidized squalene is used instead of unmodified squalene. The results support the conclusion drawn in Chapter 8 based on practical silica-filled epoxidized natural rubber compounds that the epoxide functional group and TESPT silane coupling agent provide synergistic effects on chemical filler-rubber interactions.

Proposed interactions of silica, model compounds, TESPT and water

With regard to the component separation of the mixtures as depicted in Figure 4, the characteristic features of silica aggregates/agglomerates dispersed in each layer can be proposed as shown in Figure 12.

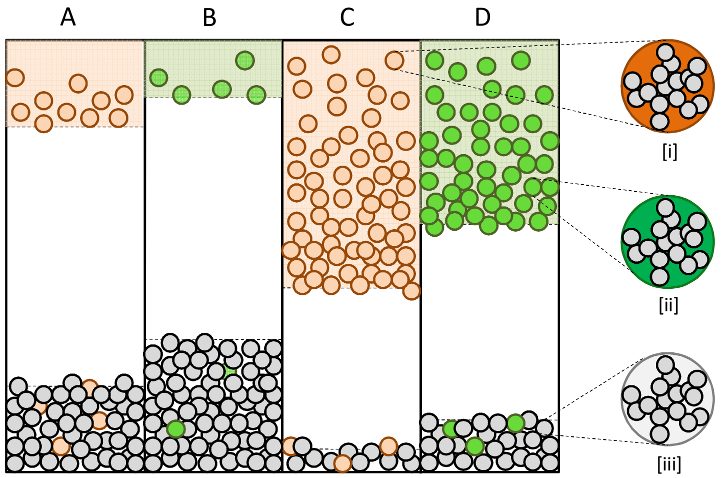


Figure 12 *Possible silica aggregates/agglomerates in each layer of the mixtures after component separation as experimentally observed in figure 4. A: ESq+silica; B: Sq+silica; C: ESq+silica+TESPT; and D: Sq+silica+TESPT.*

Figure 12 shows different levels of silica in each layer of the mixtures as shown earlier in Figures 4 and 5. A spherical shape of silica aggregates/ agglomerates is assumed as illustrated in Figures 12[i], 12[ii] and 12[iii]. With the evidence obtained from FT-IR analysis as shown in Figures 8 and 9, the interactions between silica-epoxidized squalene: Figure 12[i] and silica-squalene: Figure 12[ii] in the presence of TESPT silane coupling agent can be proposed as shown in Figure 13 and 14, respectively. In addition, hydrogen bonding between silica and water: Figure 12[iii] is also postulated in Figure 15.

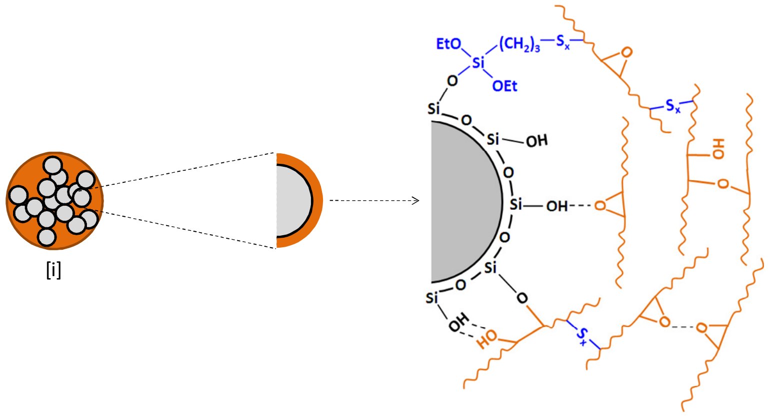


Figure 13 *Postulated interactions between silica and epoxidized squalene in the presence of TESPT as silane coupling agent.*

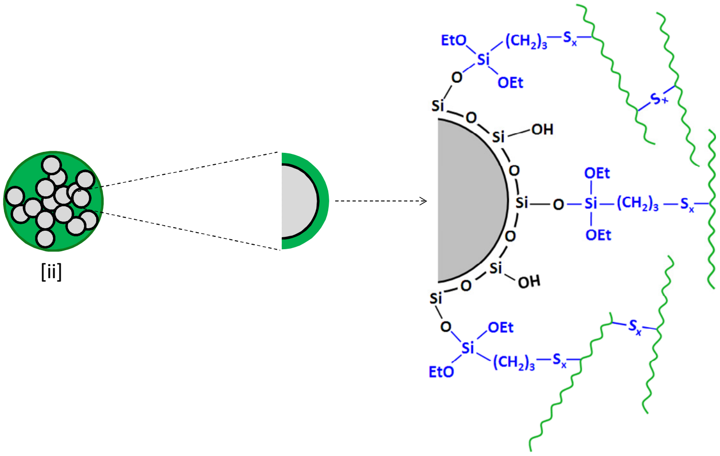


Figure 14 *Postulated interactions of silica and squalene in the presence of TESPT as silane coupling agent.*

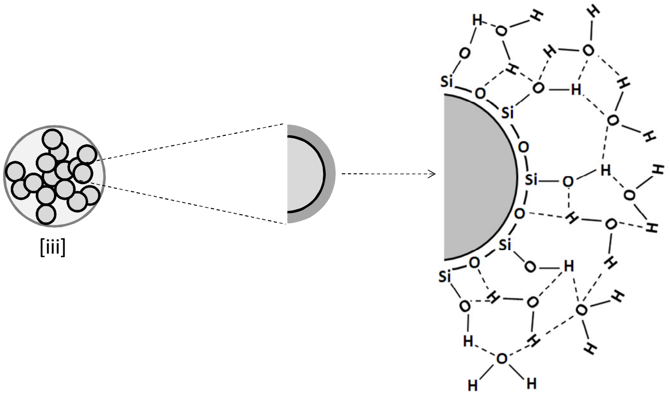


Figure 15 *Interaction between silica and water.*

CONCLUSIONS

Epoxidized squalene (ESq) with 22.5 mol% epoxidation was synthesized and used as a model compound for epoxidized natural rubber (ENR). Reactions between model squalenes, i.e. unmodified squalene (Sq) and ESq, and silica with and without TESPT silane coupling agent were carried out at 145^{o}C according to the optimal mixing dump temperature for silica-filled NR or ENR compounds. Part of silica was surface modified by the model compounds and separated from the original silica which sank in water. The modified silica in the top layer was extracted with acetone to remove unbound hydrocarbons prior to characterization by the FT-IR technique. The FT-IR spectra of the purified modified silicas separated from the mixture of Sq with TESPT, and ESq with and without TESPT display the characteristic absorption peaks of C–H in the structure of model squalenes, indicating the presence of chemical silica-to-model compound interactions or bonding, more so than when ummodified squalene is used. This reflects the ability to create more strong/chemical filler-rubber interactions in silica-filled ENR compounds under high thermal conditions during mixing and vulcanization than in compounds based on unmodified NR, in either the presence or absence of TESPT.

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SUMMARY

Natural rubber (NR) is a renewable material, which combines excellent mechanical and dynamic properties. It has been and still is in use in a variety of applications, mostly in the form of filled vulcanizates. Silica filler technology used for rubber is relatively new, since silica can reinforce rubber and gives high performance of articles, particularly in tires. The major problem of this combination is that silica has a relatively high polarity by nature and can not easily be mixed with NR which is a non-polar material. In addition, NR is rather susceptible to degradation under excessive mixing conditions, compared to its synthetic counterparts.

Bifunctional organosilane coupling agents effectively solve the incompatibility drawback as they are able to hydrophobize silica to become more compatible with hydrocarbon rubber and to additionally strengthen the interaction between silica and rubber. Bis-(triethoxysilylpropyl) tetrasulfide (TESPT) is the most commonly used silane coupling agent in the rubber industry nowadays. However, silane chemistry is rather complicated because of the necessary *in-situ* reactions during rubber processing. The mixing temperature necessary for silica/silane filled rubber requires a high energy input. In the present project, the mixing conditions and formulation for the silica/silane/NR system are optimized and subsequently a search for alternative routes for improving processability and utility of silica-rubber mixes is carried out. Polar-modified natural rubber is of interest in this context because it may lead to a reduction or a possible replacement of conventional silane coupling agents.

After an introducing **Chapter 1**, **Chapter 2** covers an overview of the state-of-the-art of silica-technology for Natural Rubber and modified Natural Rubber.

In the present thesis, the experiments first focus on optimization of the mixing conditions, which are key parameters for silica reinforcement and have not yet been fully explored for NR compounds. The aim is to gain better understanding of the influence of mixing conditions on the properties of silica-filled NR compounds. The results are presented in **Chapter 3** in which the properties of both unvulcanized compounds and vulcanizates show a strong dependence on mixing dump temperature, since the silanization reaction and silica dispersion are strongly dependent on this parameter. The optimal mixing conditions for silica-filled NR compounds with TESPT as coupling agent are a dump temperature in the range of 135-150°C, and 10 mins mixing interval of silica-silane-rubber prior to addition of the other ingredients: zinc oxide (ZnO), stearic acid, stabilizer (polymerized 2,2,4-trimethyl-1,2-dihydroquinoline: TMQ) and secondary accelerator diphenylguanidine (DPG). Mixing performed till dump temperatures above 150°C leads to a decrease in vulcanizate properties as a result of NR degradation. During mixing of silica-filled NR compounds with TESPT as coupling agent, it is seen that, in addition to the silanization reaction, premature crosslinking reactions take place since NR starts to react with sulfur releasing from TESPT beginning at a temperature as low as 120°C. However, this phenomenon does not have an adverse effect on the eventual vulcanizate properties.

Besides the production process, in particular the mixing procedure, the properties of rubber goods also depend on the choice of rubber type and compound composition: fillers, curing agents and other additives, as well as the shape and design of the articles. In order to obtain products with superior properties and more effective processing, **Chapter 4** discusses the rubber recipe which plays a significant role in silica-reinforced NR properties. Type and amount of silica and silane coupling agent, as well as the amount of diphenylguanidine are optimized. The results demonstrate that compound viscosity, curing behavior and vulcanizate properties of the silica-filled NR are much improved by incorporating silane coupling agents. TESPT clearly gives better overall properties than the disulfide-based silane: TESPD, except for scorch safety. The use of TESPT provides a greater extent of filler-rubber interactions and dispersion stability, therefore better tensile strength and tear resistance, when compared to the use of TESPD. Both types of silane show optimal loadings at approximately 9.0 wt% relative to the amount of silica.

DPG acts as a synergist to sulfenamide primary accelerators, as well as activator for the silanization reaction, because more DPG added decreases the Payne effect and increases the bound rubber content as indicative for filler-rubber interactions. Tensile strength and reinforcement index M300/M100 increase with the addition of DPG up to its optimal amount of 2 wt% relative to the silica content. The optimal quantities of both silane coupling agent and DPG required in the formulation are correlated to the cetyl trimethylammonium bromide (CTAB) specific surface area of the silicas.

Highly dispersible (HD) silicas provide higher bound rubber contents than conventional silicas and these are in accordance with the DBP-values, indicating higher silica structure. The use of higher structure silicas results in a lower Payne effect, i.e. better filler-rubber interaction, but also generates a faster flocculation process (demixing) or less dispersion stability when compared with conventional silicas. A higher silica structure leads to better dispersion, smaller aggregate sizes and thus faster flocculation. The HD-silica reinforced-NR vulcanizates show better reinforcement index and lower tan δ at 60^{o}C, indicative for lower rolling resistance if used in tire treads, compared to those based on conventional silica filled compounds. The vulcanizate properties linearly correlate with the chemically bound rubber contents before vulcanization.

To gain better insight in the chemical mechanisms of bifunctional organosilanes, especially TESPT in reaction with silica and NR, different types of modifying agents are employed to investigate the role of key functionalities contained in the modifying chemicals. The properties of silica-filled NR compounds and vulcanizates prepared with different silane agents are correlated with the phenomena of reinforcement. The mechanisms of the reactions that take place during processing of the silica-based NR compounds are defined in **Chapter 5**. The investigation clarifies that when organosilanes bearing alkoxy- and sulfide-functional groups are used, there are three reaction mechanisms competitively taking place during primary compound mixing or in the non-productive mixing process. These mechanisms are all temperature dependent: 1) the silane-to-silica or silanization/hydrophobation reaction; 2) silane-to-rubber or coupling reaction; and 3) rubber-rubber crosslinking originating from active sulfur released by the polysulfide-based silanes. These simultaneous reactions reach an optimum at a dump temperature of approximately $140\text{-}150^{o}$C, as determined by filler-filler and filler-rubber interactions, and mechanical properties corresponding to the findings in Chapters 3 and 4. The network structures between silica-silane-rubber and rubber-rubber primarily account for an increase of the Mooney viscosity and chemically bound rubber content, as well as improved silica dispersion with less filler-filler interaction. The silane bearing only alkoxy groups show that it can improve the processing properties: lower Mooney viscosity, better silica dispersion, lower Payne effect and mechanical properties compared to the one without coupling agent. However, the best possible overall properties are only obtained when bifunctional coupling agents: TESPT and TESPD are used.

With regard to the scorch safety of silica-filled compounds containing different levels of sulfur moiety in the silane structures, TESPT which contains an average sulfur chain length of four atoms is studied in comparison with the two atoms of sulfur-based one: TESPD. The difference in sulfur moiety may cause inferior properties for TESPD-silica-filled compounds when compared to TESPT, as found in Chapter 4. **Chapter 6** includes an investigation of sulfur compensation for the TESPD-added compounds in comparison with the compound plus TESPT as reference. The overall results demonstrate that the addition of extra sulfur in the internal mixer during the primary non-productive step gives a positive contribution towards improved silica dispersion, which can be attributed to some network formation that can suppress the mobility of silica aggregates, leading to better degree of dispersion, as demonstrated by the lower Payne effect, higher amount of chemically bound rubber and lower reinforcement parameter. The tensile properties of silica/TESPD vulcanizates are only slightly enhanced by adding free sulfur in the internal mixer relative to TESPD alone. Addition of compensating sulfur during the productive step on the two-roll mill has practically no effect, as all benefits gained in the non-productive internal mixer step are by-passed; it then merely acts as some extra curative in an overall poorer dispersed compound, with minimal overall effects. Based on this investigation, extra sulfur at approximately 0.15 – 0.20 phr, or 3.4 – 5.1 wt% relative to the TESPD content, added during mixing of TESPD-silica-NR in an internal mixer is an optimal amount to achieve better scorch safety of the compounds, and comparable mechanical properties of the vulcanizates, compared to those based on TESPT as coupling agent without extra sulfur.

Diphenylguanidine (DPG) as a secondary curing accelerator for silica compounds is suspect for its toxicity, therefore alternative substances such as dithiophosphates (DTP) have been identified to replace DPG. In **Chapter 7**, a comparative study between DPG and DTP's used in a silica-filled NR compounds is performed. In this investigation, the efficiency of DTP's as alternatives for DPG on the reinforcement of silica in NR compounds is confirmed. DTP's act as synergists for the sulfenamide primary accelerator and are more reactive compared to DPG, leading to a lower required dosage of DTP to reach optimum properties. DTP's give better reversion stability under high thermal annealing, and superior heat aging resistance of the vulcanizates. Addition of secondary accelerators can raise the extent of chemically bound rubber, accompanied with lower filler-filler interactions. Based on the mechanical and dynamic properties of the vulcanizates, optimum overall properties are obtained when DTP and DPG are used at 0.8 and 1.1 phr, i.e. 1.4 and 2.0 wt% relative to silica content, respectively.

Chapter 8 focuses on the influence of epoxide functionality in Epoxidized Natural Rubber (ENR) on the compatibility of silica-filled ENR compounds. Parallel studies with respect to various levels of epoxidation in ENR in the absence of TESPT, as well as a combination of ENRs with different loadings of TESPT are carried out. The epoxide functionality on natural rubber molecules has a significant influence on both processing and end-use properties of silica-filled ENR compounds. The mixing torque, Payne effect, and compound viscosity remarkably decrease with the presence of epoxide functional groups up to 29 mol% on ENR compared to silica-filled normal NR compounds. A high content of epoxide groups, e.g. ENR-36 and ENR-43, adversely affects the processibility and most of the properties. Addition of TESPT into silica-filled ENRs with epoxide contents of 13 and 21 mol% further improves compound processibility and vulcanizate properties, whilst the use of TESPT has only minor effect on the ENR-29 (29 mol% epoxide content) compound. Based on the overall properties, epoxide groups on ENR alone can not provide the properties to match with those of silica-TESPT filled unmodified NR. But, the right combination of epoxide groups and TESPT as silane coupling agent leads to similar levels of properties compared to the TESPT-normal NR system. With the synergistic effect of the polar epoxide groups, it can be concluded that the best possible combination to optimize processibility, to reduce filler-filler interaction, and improve vulcanization rate as well as vulcanizate properties, is to utilize ENR with an epoxide content in the range of 20 – 30 mol%, together with a small portion of TESPT, i.e. 2 – 4 wt% relative to silica content. This leads to an essential reduction of approximately 60 – 80 % of TESPT when compared to the conventional NR compounds, in which the optimal loading of TESPT was 9.0 wt% relative to silica content.

The qualitative experiments in the **Appendix** are executed to confirm the linkage type of filler-to-rubber interactions in silica-filled NR and ENR compounds in the presence and absence of TESPT silane coupling agent. Unmodified squalene (Sq) and epoxidized squalene (ESq) are used as model compounds for NR and ENR, respectively. Reactions between model squalenes and silica with and without TESPT silane coupling agent are carried out at 145°C according to the optimal mixing dump temperature for silica-filled NR or ENR compounds. Part of the silica is surface modified by the model compounds and separated from the original silica which sinks in water. The modified silica in the top layer was extracted with acetone to remove unbound hydrocarbons prior to characterization by the FT-IR technique. The FT-IR spectra of the purified modified silicas separated from the mixture of Sq with TESPT, and ESq with and without TESPT display the characteristic absorption peaks of C–H in the structure of model squalenes, indicating the presence of chemical silica-to-model compound interactions or bonding, more so than when ummodified squalene is used. This reflects the ability to create more strong/chemical filler-rubber interactions in silica-filled ENR compounds under high thermal conditions during mixing and vulcanization than in compounds based on unmodified NR, either in the presence or absence of TESPT.

Overall, the reinforcement of rubber products by silica reinforcing fillers is not entirely novel, as it has been improved significantly during recent years after the introduction of the low rolling resistant tires by Michelin in 1992, promoting more effective fuel consumption for automotive transport. Although this silica-silane technology provides numerous benefits, it is more susceptible to processing problems when compared to the use of conventional carbon black. Many different aspects of the silica technology for NR have been explored in the present thesis. Based on the results in this practical research, reinforcement of silica in NR is a versatile technology. Mixing parameters and chemical ingredients formulated in the compounds significantly govern the overall properties of silica-filled NR products. The findings presented in this thesis contribute to a much better understanding of the mechanistic aspects which provides an essential fundament as well as a better control of this technology. Furthermore, a reduction of the optimal quantity of expensive silane coupling agents applied for conventional compounds can potentially be implemented by use of polar-modified NR.

SAMENVATTING

Natuurrubber (NR) is een hernieuwbaar materiaal, dat excellente mechanische en dynamische eigenschappen bezit. Het werd en wordt gebruikt in verschillende toepassingen, meestal in de vorm van gevulde vulcanisaten. Het gebruik van silica als vulstof voor rubber is relatief nieuw, omdat silica rubber kan versterken en derhalve goede eigenschappen verleent, in het bijzonder in banden. Het grootste probleem met deze combinatie is de relatief hoge polariteit van de silica, zodat het zich moeilijk laat mengen met de a-polaire NR. Bovendien is NR nogal gevoelig voor afbraak onder invloed van zware mengcondities in vergelijking met synthetische tegenhangers.

Bifunctioneleorganosilaancouplingagents lossen het onverdraagzaamheids-probleem effectief op, daar zij silica hydrofoob kunnen maken, zodat het beter verdraagzaam wordt met de koolwaterstof-gebaseerde rubber en daarmee de interactie tussen silica en rubber vergroten. Bis-(triethoxysilylpropyl) tetrasulfide (TESPT) is de meest gebruikte silaancoupling agent in de rubber industrie. Echter, de chemie van silanenis erg gecompliceerd, omdat zij *in-situ* moeten reageren gedurende de verwerking van de rubber. In het huidige project worden de mengcondities en de rubber formulering voor het systeem silica/silaan/NR geoptimaliseerd. Vervolgens worden diverse routes onderzocht om de verwerkbaarheid en bruikbaarheid van de silica-rubber mengsels te verbeteren. Polair gemodificeerde NR is in dit verband van belang, omdat het kan leiden tot een reductie of zelfs volledige vervanging van conventionele silaancouplingagents.

Na een inleiding in **Hoofdstuk 1**, wordt in **Hoofdstuk 2** een overzicht gepresenteerd van de stand der techniek op het gebied van silica technologie voor Natuurrubber en gemodificeerde Natuurrubber.

In dit proefschrift richten de eerste experimenten zich op optimalisatie van de meng-condities, welke doorslaggevende parameters zijn voor silica versterking en welke voor NR mengsels nog niet volledig zijn onderzocht. Het doel is om een beter begrip te verwerven van de invloed van mengcondities op de eigenschappen van silica-gevulde NR mengsels. De resultaten worden in **Hoofdstuk 3** gepresenteerd. De eigenschappen van zowel ongevulcaniseerde mengsels alsvulcanisaten vertonen een sterke afhankelijkheid van de mengsel lossings-temperatuur, aangezien de silaniserings-reactie en de silica dispersie sterk afhangen van deze parameter. De optimale mengcondities voor silica-gevulde NR mengselsmet TESPT als coupling agent zijn een lossings-temperatuur in de orde van 135-150°C, en 10 minuten meng-interval van de silica-silaan-rubber vóór de toevoeging van de andere ingrediënten: zinkoxide (ZnO), stearinezuur, stabilisator (gepolymeriseerd 2,2,4-trimethyl-1,2-dihydroquinoline: TMQ) en de secundaire versneller difenylguanidine (DPG). Mengen tot lossings-temperaturen hoger dan 150°C leidt tot een afname in vulcanisaat-eigenschappen tengevolge van NR afbraak. Gedurende het mengen van silica-gevulde NR mengsels met TESPT als coupling agent wordt waargenomen, dat naast de silaniserings-reactie ook voortijdige vernettingvan de rubber plaatsvindt, daar NR begint te reageren met zwavel dat door TESPT al vanaf een temperatuur zo laag als 120°C wordt vrijgegeven. Echter, dit fenomeen heeft geen negatief effect op de uiteindelijk verkregen vulcanisaat-eigenschappen.

De eigenschappen van rubber artikelen hangen, naast het productie-proces en in het bijzonder de meng-procedure, ook af van de keuze van het rubber-type en de mengsel-samenstelling: vulstoffen, vernettings-middelen en andere toeslagstoffen, en bovendien van de vormgeving van de artikelen. Teneinde producten te verkrijgen met superieure eigenschappen en een effectievere verwerking wordt in **Hoofdstuk 4** het rubber recept besproken, dat een significante rol speelt in de silica-versterkte NR eigenschappen. Het type en de hoeveelheid silica en silaancoupling agent, evenals de hoeveelheid difenylguanidine worden geoptimaliseerd. De resultaten tonen aan, dat de mengsel viscositeit, het vulcanisatie-gedrag ende vulcanisaat-eigenschappen van de silica-versterkte NR aanzienlijk verbeteren door de inbouw van silaancouplingagents. TESPT geeft over het geheel genomen duidelijk betere eigenschappen dan het disulfide-gebaseerde silaan TESPD, behalve voor aanvulcanisatie-stabiliteit (scorchsafety). Het gebruik van TESPT leidt tot een hogere mate van vulstof-rubber interacties en stabiliteit van de dispersie, derhalve betere trek- en scheursterkte in vergelijking met TESPD. Beide silaan types vertonen optimale doseringen bij ong. 9.0 gew.% ten opzichte van de hoeveelheid silica.

DPG werkt synergistisch samen met de sulfenamide primaire vulcanisatie-versnellers, naast de rol als activator voor de silaniserings-reactie, omdat meer toegevoegd DPG het Payne-effect verlaagt en de zgn. mate van “Bound Rubber” verhoogt, beide indicaties voor vulstof-rubber interacties. Treksterkte en versterkings-index M300/M100 nemen toe bij toevoegen van DPG tot aan z’n optimale hoeveelheid

van 2 gew.% betrokken op het silica-gehalte. De optimale hoeveelheden van zowel silaancoupling agent als DPG vereist in de formulering worden gecorreleerd aan het cetyltrimethylammonium bromide (CTAB) specifieke oppervlak van de silica's.
Hoog dispergeerbare (HD) silica's geven hogere BoundRubber gehaltes dan conventionele silica'sen deze komen overeen met de DBP-waardes, welke een hogere silica-structuur aangeven. Het gebruik van hoger gestructureerde silica's resulteert in een lager Payne effect, d.w.z. betere vulstof-rubber interactie, maar veroorzaakt ook een sneller flocculatie-proces (ontmenging) of verlaagde dispersie-stabiliteit in vergelijking met conventionele silica's. Een hogere silica structuur leidt tot betere dispersie, kleinere aggregaat-groottes en dus snellere flocculatie. De HD-silica versterkte NR vulcanisaten vertonen een betere versterkings-index en lagere tan δ bij 60^{o}C, een indicatie voor lagere rolweerstand indien gebruikt in banden-loopvlakken, in vergelijking met conventionele silica-gevulde mengsels. De vulcanisaat-eigenschappen correleren lineair met de chemisch gebonden Bound Rubber gehaltes gemeten vóór vulcanisatie.

Om meer inzicht te verwerven in de chemische mechanismen van de bifunctioneleorganosilanen, in het bijzonder TESPT in reactie met silica en NR, worden verschillende typen modificatie agentia aangewend om de rol van hun belangrijkste functionaliteiten te onderzoeken. De eigenschappen van silica-gevulde NR mengsels en vulcanisaten bereid met verschillende silaancouplingagents worden gecorreleerd met de versterking. De mechanismen van de reacties die optreden gedurende verwerking van silica-gebaseerde NR mengsels worden gedefiniëerd in **Hoofdstuk 5**. Het onderzoek toont aan, dat bij gebruik van organosilanen met alkoxy- en sulfide-functionele groepen, er drie reactie-mechanismen in onderlinge competitie optreden gedurende de eerste mengsel menging, ook wel de "non-productivemixing" genoemd. Deze mechanismen zijn alle temperatuur-afhankelijk: 1) de silaan-silica of silanizerings/ hydrofoberings reactie; 2) de silaan-rubber of koppelings-reactie; en 3) rubber-rubber vernettingafkomstig van actieve zwavel vrijkomend vanuit de polysulfide-gebaseerde silanen. Deze simultane reacties bereiken een optimum bij een lossings-temperatuurvan ongeveer 140-150^{o}C, zoals bepaald door vulstof-vulstof en vulstof-rubber interacties, en de mechanische eigenschappen corresponderend met de waarnemingen in hoofdstukken 3 en 4. De netwerk structuren tussen silica-silaan-rubber en rubber-rubber geven primair een toename van de Mooney viscositeit en chemisch gebonden Bound Rubber, evenals verbeterde silica dispersie met minder

vulstof-vulstof interactie. De silaan die alleen alkoxy-groepen bezit laat zien dat het de verwerkings-eigenschappen kan verbeteren: lagere Mooney viscositeit, betere silica dispersie, lager Payne effect en mechanische eigenschappen in vergelijking met een mengsel zonder coupling agent. Echter, de beste overall eigenschappen worden alleen verkregen wanneer bifunctionelecouplingagents worden gebruikt: TESPT en TESPD.
Met betrekking tot de scorchsafety van silica-gevulde mengsels met verschillende hoeveelheden zwavel-atomen in de silaan-structuur ingebouwd, wordt TESPT met een gemiddelde zwavel-lengte van vier atomen vergeleken met TESPD met twee zwavel-atomen. Het verschil in zwavel-hoeveelheid zou inferieure eigenschappen kunnen veroorzaken bij de TESPD- vs. de TESPT-gebaseerde mengsels, zoals vastgesteld in hoofdstuk 4. **Hoofdstuk 6** omvat een onderzoek naar zwavel-compensatie bij de mengsels op TESPD-basis in vergelijking met het mengsel met TESPT als referentie. De overall resultaten tonen aan, dat de toevoeging van extra zwavel in de interne menger gedurende de primaire non-productivemengstap een positieve bijdrage levert aan een beteresilica verdeling, hetgeen kan worden toegeschreven aan een lichte mate vannetwerk-vorming die de beweeglijkheid van silica aggregaten onderdrukt. Dit leidt tot een betere dispersie-graad, zoals blijkt uit een lager Payne-effect, een grotere hoerveelheid chemisch gebonden Bound Rubber en een lagere reinforcement parameter. De trek-rek eigenschappen van silica/TESPD vulcanisaten worden slechts lichtelijk verbeterd door de toeveoging van vrije zwavel in de interne menger vergeleken met TESPD alleen. Toevoegen van compenserende zwavel gedurende de mengstap op de wals (productive step) heeft practisch geen effect, daar alle voordelen verkregen in de non-productive interne mixer stap worden omzeild; het werkt dan slechts als wat extra vulcanisatie-middel in een overall slechter gedispergeerd mengsel, met minimale overall effecten. Op basis van dit onderzoek is onveer 0.15 – 0.20 phr extra zwavel, of 3.4 – 5.1 gew.% t.o.v. de TESPD hoeveelheid, gedoseerd gedurende het mengen van TESPD-silica-NR in de interne menger, een optimale hoeveelheid om betere scorchsafety van de mengsels te bereiken, en vergelijkbare mechanische eigenschappen van de vulcanisaten vergeleken met TESPT als coupling agent zonder extra zwavel.

Difenylguanidine (DPG) als secundaire versneller voor silica mengsels is toxicologisch verdacht, om reden waarvan alternatieven als dithiofosfaten (DTP) ter vervanging van DPG zijn geïdentificeerd. In **Hoofdstuk 7** wordt een vergelijkend onderzoek verricht tussen DPG en diverse DTP's in silica-gevulde NR mengsels. In dit onderzoek wordt de efficiëntie van DTP's als alternatieven voor DPG voor versterking van silica in NR mengsels bevestigd. DTP's werken synergistisch bij de primaire sulfenamide versneller en zijn zelfs reactiever vergeleken met DPG, hetgeen leidt tot een lagere vereiste dosering van DTP om optimale eigenschappen te bereiken. DTP's geven betere reversiestabiliteit onder hoge thermische annealingconsities, en superieure thermische verouderings-weerstand van de vulcanisaten. Toevoegen van secundaire versnellers kunnen de mate van chemisch Bound Rubber verhogen, hetgeen gepaard gaat met lagere vulstof-vulstof wisselwerkingen. Gebaseerd op de mechanische en dynamische eigenschappen van de vulcanisaten, worden optimale overall eigenschappen verkregen wanneer DTP en DPG gebruikt worden in hoeveelheden van respectievelijk 0.8 en 1.1 phr, d.w.z. 1.4 en 2.0 gew.% t.o.v. het silica-gehalte.

Hoofdstuk 8 richt zich op de invloed van epoxide functionaliteit in geËpoxideerde Natuur Rubber (ENR) op de verdraagzaamheid van silica-gevulde ENR mengsels. Parallelle studies met betrekking tot verschillende niveuas van epoxidatie in ENR in afwezigheid van TESPT, evenals een combinatie van ENR's met verschillende doseringen van TESPT worden doorgevoerd. De epoxide functionaliteit op NR moleculen heeft een significante invloed op verwerking en eind-eigenschappen van silica-gevulde ENRmengsels. Meng-koppel, Payne effect en mengsel viscositeit verminderen opmerkelijk bij aanwezigheid van epoxide-functionele groepen tot 29 mol% op de ENR (ENR-29) vergeleken met silica-gevulde normale NR mengsels. Een hoger epoxide-gehalte, bijv. ENR-36 en ENR-43, heeft een negatieve invloed op de verwerkbaarheid en de meeste eigenschappen. Toevoegen van TESPT aan de silica-gevulde ENR's met epoxide-gehaltes van 13 en 21 mol% verbetert de mengsel verwerkbaarheid verder en de vulcanisaat-eigenschappen, terwijl het weinig effect heeft in het ENR-29 mengsel. Op basis van de verzamelde eigenschappen kunnen epoxide-groepen op de ENR alléén niet de eigenschappen opleveren van silica-TESPT gevulde ongemodificeerde NR. Echter, de juiste combinatie van epoxide groepen en TESPT als silaancoupling agent leidt tot vergelijkbareeigenschappen t.o.v. het TESPT normale-NR systeem. Vanwege het synergistisch effect van de polaire epoxide groepen, kan er worden geconcludeerd dat de best mogelijke combinatie om verwerkbaarheid te optimaliseren, om vulstof-vulstof interactie te reduceren, de vulcanisatie snelheid en vulcanisaat eigenschappen te verbeteren, is een ENR te gebruiken mmet een epoxide-gehalte in de orde van 20 – 30 mol%, samen met een klein deel TESPT, d.w.z. 2 – 4 gew% betrokken op het silica gehalte. Dit leidt tot een essentiële reductie van ongeveer 60 – 80% TESPT vergeleken met conventionele NR mengsels, waarvoor de optimale dosering TESPT 9.0 gew.% was t.o.v. het silica gehalte.

De kwalitatieve experimenten in de **Appendix** zijn uitgevoerd teneinde het type binding te verifiëren van vulstof-rubber interacties in silica-gevulde NR en ENR mengsels in aan- en afwezigheid van TESPT silaancoupling agent. Ongemodificeerdesqualeen (Sq) en geëpoxideerdesqualeen (Esq) worden gebruikt als modelverbindingen voor respectievelijk NR en ENR. Reacties tussen model squalenen en silica met en zonder TESPT silaancoupling agent worden uitgevoerd bij 145°C als de optimale lossingstemperatuur na mengen van silica-gevulde NR of ENR mengsels. Een gedeelte van de silica wordt op het oppervlak gemodificeerd door de model-verbindingen en scheidt zich af van de oorspronkelijke silica, dat zinkt in water. De gemodificeerde silica in de top-laag is geëxtraheerd met aceton om ongebonden koolwaterstoffen te verwijderen voorafgaand aan karakterisering met de FT-IR techniek. De FT-IR spectra van de gereinigde gemodificeerde silica's gescheiden van het mengsel van Sq met TESPT, en Esq met en zonder TESPT, vertonen de karakteristieke adsorptie-pieken van C-H in de structuur van de model squalenen. Dit duidt op de aanwezigheid van chemische silica-model verbinding interacties of binding, te meer wanneer gemodificeerde squaleen wordt gebruikt. Dit duidt op het vermogen om sterkere chemische vulstof-rubber interacties aan te gaan in silica-gevulde ENR mengsels onder hoge thermische condities gedurende mengen en vulcaniseren, dan in mengsels gebaseerd op ongemodificeerde NR, hetzij in aanwezigheid hetzij in afwezigheid van TESPT.

Over het geheel genomen is versterking van rubber producten met silica versterkende vulstoffen niet geheel nieuw, aangezien het significant verbeterd is gedurende de afgelopen jaren na de introductie van lage rolweerstand banden door Michelin in 1992 ter bevordering van lagere brandstof-verbruiken in automobiel-transport. Ofschoon deze silica-silaan technologie ontelbare voordelen biedt, is het gevoeliger voor verwerkings-problemen in vergelijking met het gebruik van conventionele roet. Vele verschillende aspecten van de silica-technologie zijn onderzocht in dit proefschrift. Gebaseerd op de resultaten van deze practische research is versterking van silica in NR een veelzijdige technologie. De meng parameters en chemische ingrediënten in de mengsels bepalen in hoge mate de overall eigenschappen van silica-gevulde NR producten. De waarnemingenweergegeven in dit proefschrift dragen bij aan een veel beter begrip van de mechanistische aspecten, hetgeen een essentieel fundament biedt voor, evenals een betere controle over deze technologie. Bovendien kan mogelijk een besparing van de optimale hoeveelheid van dure silaancouplingagents voor conventionele mengsels worden bereikt door gebruik te maken van polair-gemodificeerde NR.

SYMBOLS AND ABBREVIATIONS

SYMBOL	**DESCRIPTION**
G'	Storage moduli
G'_0	Storage moduli of unfilled compound
$\Delta G'$	Storage moduli difference or Payne effect
k_a	Flocculation rate constant
M100	Tensile modulus at 100% strain
M300	Tensile modulus at 300% strain
M300/M100	Reinforcement index
ML(1+4),100^{o}C	Mooney viscosity at 4 mins. with preheating for 1 min., measured at 100^{o}C
S'_{min}	Rheometer minimum torque
S'_{max}	Rheometer maximum torque
$-S_2-$	Disulfide
$-S_4-$	Tetrasulfide
T_{10}	Rheomerter cure time at 10% cure
T_{95}	Rheomerter cure time at 95% cure
$T_{c,90}$	Rheomerter optimum cure time at 90% cure
Tan δ	Loss angle
T_g	Glass transition temperature
α_F	Reinforcement parameter

ABBREVIATION	**DESCRIPTION**
ASTM	American society of testing materials
BdR	Bound rubber
BET	Brunauer-Emmett-Teller nitrogen-adsorption
BR	Butadiene rubber
CBS	N-cyclohexyl-2-benzothiazolesulfenamide
CHNS-O	CHNS-O elemental analyzer
CR	Chloroprene rubber

CRI	Cure rate index
CSM	Chlorosulfonated polyethylene rubber
CTAB	Cetyl-trimethyl-ammoniumbromide
CV-silica	Conventional silica
DBP	Dibutylphthalate
DEG	Diethyleneguanidine
DPG	Diphenylguanidine
DRC	Dried rubber content
DTP	Dithiophosphate
E.B.	Elongation at break
ENR	Epoxidized natural rubber
ENR-xx	Epoxidized natural rubber with xx mol% epoxide content
EPA	Environmental protection agency
EPDM	Ethylene-propylene-diene-monomer rubber
ESq	Epoxidized squalene
FT-IR	Furrier transformed infrared spectroscopy
HA NR Latex	High ammonia natural rubber latex
HD-silica	Highly dispersible silica
^{1}H-NMR	Proton-nuclear magnetic resonance spectroscopy
IM	Internal mixer
ISO	International organization for standardization
KBr	Potassium bromide
MA	Maleic anhydride
MDPt	Moving die processability tester
Mins.	Minutes
MNR	Maleated natural rubber
Mw	Molecular weight
NBR	Acrylonitrile-butadiene rubber
NR	Natural rubber
NSBR	Acetyl styrene butadiene rubber
OTES	Octyltriethoxysilane
phr	Parts per hundred rubber
PP-g-MA	Maleic anhydride-grafted polypropylene

RPA	Rubber process analyzer
RSS3	Rubber smoked sheet, grade no.3
SBR	Styrene-butadiene rubber
SDT	Bis-(ethylhexylthiophosphoryl) polysulfide
SEM	Scanning electron microscopy
Sq	Squalene
T.S.	Tensile strength
TDAE	Treated distillate aromatic extract oil
TESPD	Bis-(triethoxysilylpropyl) disulfide
TESPT	Bis-(triethoxysilylpropyl) tetrasulfide
TMQ	Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline
TMSMT	Bis-(trimethylsilylmethyl) tetrasulfide
TP	Dibutyldithiophosphate zinc salt
TRM	Two roll mill
VTMS	Vinyltrimethoxysilane
XNBR	Carboxylated acrylonitrile-butadiene rubber
ZnO	Zinc oxide

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 # The letters: P- or Pee- and N- or Nong-, prefixed to Thai names are personally informally used to call elder and younger persons, respectively.

Wisut

CURRICULUM VITAE

Wisut Kaewsakul was born on July 18th, 1984, in Nakhon-Si-Thammarat, Thailand. He received his B.Sc. degree on Rubber Technology in 2007 and M.Sc. degree on Polymer Technology in 2009, from Prince of Songkla University, Pattani campus, Thailand. The subject of his master project was “Thermoplastic elastomer based on modified natural rubber and EVA blends”. After M.Sc. graduation, he immediately continued his Ph.D. study under a joint program between Prince of Songkla University and University of Twente. He studied and worked in Thailand for 2.5 years and in the Netherlands for 1.5 years, on a project entitled “Silica-reinforced natural rubber”.

“Being deeply learned and skilled, being well-trained and using well-spoken words; these are good luck”

Lord Buddha

“การเป็นผู้เรียนรู้อย่างลึกซึ้ง ฝึกฝนทักษะให้มีความเชี่ยวชาญ และรู้จักใช้คำพูดที่ดี เหล่านี้คือโชคดี”

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