Plasma Coating of Silica: A key to improved dispersion and properties of reinforced elastomer blends

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Plasma Coating of Silica: A key to improved dispersion and properties of reinforced elastomer blends

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With references – With summary in English and Dutch

Cover designed by Sheetal Tiwari, which gives an example of plasma in nature (the violent spark of lightning); The AFM image shows the co-continuous phase morphology of plasma silica filled SBR/EPDM blend.

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PLASMA COATING OF SILICA: A KEY TO IMPROVED DISPERSION AND PROPERTIES OF REINFORCED ELASTOMER BLENDS

DISSERTATION

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on the authority of the rector magnificus,
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on account of the decision of the graduation committee,
to be publicly defended
on Thursday, 2nd December 2010 at 16:45 hrs.

by

Mukund Tiwari

born on 5th August 1978
in Farrukhabad (Uttar Pradesh), India

This dissertation has been approved by:

Promotor: prof. dr. ir. J.W.M. Noordermeer
Co-promotor: dr. W. K. Dierkes

To my loving father

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Chapter 1

General Introduction

1.1 Historical overview

Christopher Columbus was probably the first European ever to handle a piece of rubber. According to the eminent historian Antonio de Herrera, who recounts the voyages and conquests of the Castillians, it was during his second voyage to America (1493-1496) that Columbus learned of a game played by the natives of Haiti with a ball made of a kind of elastic resin. The game had, in fact, been known to the Indians for centuries, as revealed by excavations intended to throw light on the Maya civilizations, which goes at least as far back as the 11th century. A piece of ground specially reserved for playing this game was discovered, the game itself consisting of throwing a rubber ball, the same size as a modern football, into a hole in a vertical wall by means of the shoulder or the thigh[1].

It was only in 1615, however, that certain useful applications of rubber were revealed by Juan de Torquemada in his book *Monarquia Indiana*[1], where an account is given of the manufacture of a substance known to the natives of Mexico as *ulei* and prepared by them from the latex of a tree known as *ule* for the purpose of waterproofing articles of clothing. However, the interest later to be shown in Europe in this substance and its many practical applications, as well as and the role it was destined to play in the economy, was only aroused much later by two French scientists: La Condamine and Fresneau[1]. La Condamine had been sent to South America by the Paris Academy of Sciences to measure a meridian in the neighborhood of the equator. La Condamine sent some lumps of a dark, resin-like substance from Quito to the Academy of Sciences. This material came from a tree known to the Indians as *heve*, the bark of which, when incised, exuded a white milky liquid which gradually solidified and darkened on exposure to air. He also reported the various uses made of the substances by the natives, and observed that the same tree was found growing on the banks of the Amazon river. The material was known to the Maya Indians as “caoutchouc,” a word derived from caa (wood) and o-chu (to flow or weep)[2]. In 1762 the name *Hevea guianensis* was given to the tree described by Fresneau. It was then quickly realized that rubber trees were not exclusively American plants and that others capable of producing the same material existed. The various types of rubber latex-bearing plants are very numerous and are found almost all over the world, especially in the intertropical zone. However, not all of these are suitable for industrial exploitation, and when the collection of rubber from wild trees was supplemented by large scale cultivation, the choice fell on Hevea brasiliensis. It is from this tree that all of the natural rubber on the market is obtained nowadays[1].

To make use of the valuable resin from the weeping tree, as it was imported into Europe as dried sheets, it was first necessary to discover a liquid capable of dissolving this solid rubber, which could then be recovered, with its original properties intact, by simple evaporation of the solvent. Almost another century was to elapse before two fundamental discoveries, mastication and vulcanization, gave rise to the rubber industry.

In 1819, Hancock had discovered the mastication of rubber. However, rubber is, in fact, degraded by this mastication; according to the degree of plasticizing, it is more or less deprived of its original properties. It was only at this price that the incorporation of ingredients and molding could be achieved. But it remained to discover a means of achieving the full elastic properties of the rubber, without which practical applications would be impossible. The full properties were therefore only obtained some 20 years later, after an essential complementary discovery in 1839 by Charles Goodyear had been made, namely vulcanization. The term vulcanization was named after Vulcan, the Roman god of fire. In 1839 he made an observation which was to revolutionize the industry - he found that if crude rubber was treated with sulfur above the melting point of the latter, it undergoes a change which produces a marked improvement in its mechanical properties and also in its ability to withstand changes in temperature[2].

From that time, thanks to the discoveries of Hancock and Goodyear, the tremendous field of applications of rubber was open. Since then, considerable progress has been achieved in manufacturing processes, and modern rubber mixes contain many ingredients whose purpose is to confer on them a variety of properties. The most important discoveries have unquestionably been accelerators of vulcanization, antioxidants, and reinforcing fillers.

The standardized definition of rubber is: an “elastomer which can be, or already is, modified to a state in which it is essentially insoluble (but can swell) in a boiling solvent, such as benzene, methyl ethyl ketone and ethanol-toluene azeotrope.

A rubber in its modified state, free of diluents, retracts within 1 minute to less than 1.5 times its original length after being stretched at room temperature (18 to 29°C) to twice its length and held for 1 minute before release”[3].

Rubber and rubber like materials are distinguished from other substances by a remarkable combination of two characteristics:

- In the first place, they are capable of sustaining large deformations without rupture; a maximum elongation of five to ten times the unstretched length is common among typical rubbers;
- Secondly, the deformed rubber possesses the capacity to recover spontaneously very nearly to its initial dimensions, no appreciable fraction of the deformation remaining permanently after removal of the stress.

In the modern society, rubber is as indispensable as steel and wood and cement. Automobiles, trains and aircrafts rely on it for safety and comfort. Industry uses it to produce tires, hoses, belts, gaskets and moldings[4]. Rubber in the modern world is omnipotent. Rubber basically has two sources: natural and synthetic. Natural Rubber is siphoned from cultivated trees on plantations in Asia, Africa and South America. Synthetic rubber is man-made and is produced around the world in manufacturing plants that synthesize it from crude oil. Whether it’s natural or synthetic, rubber in its native form is virtually useless. But after addition of chemicals, it gets properties that make it “totally unlike” any material the world has ever known. Depending on the chemicals used, products made of rubber can be as soft as a sponge, as resilient as a rubber band, or as hard as a bowling ball. Natural Rubber has been available for centuries, synthetic rubber for just hundred years. Although experimenting with synthetic rubber began in 1906, it was not until after World War II that the quality was improved to the point that it rivaled that of Natural Rubber. Wartime necessity became the impetus for the emergence of synthetic rubber on a large-scale basis, when governments began building plants to offset

Natural Rubber shortages. Synthetic rubber plants were built around the world after 1945, primarily in Europe, North America and Japan. In 1960 the use of synthetic rubber surpassed that of Natural Rubber for the first time. Synthetic rubber has maintained a small lead ever since[5].

As mentioned before in this chapter, rubber compounding was first developed by Goodyear and Hancock and it continues to develop as new materials and new variations on old ones appear in the marketplace. It starts with the raw gum elastomer such as Natural Rubber (NR), Ethylene Propylene Diene Terpolymer (EPDM), Butadiene Rubber (BR), Styrene Butadiene Rubber (SBR), Acrylonitrile Butadiene Rubber (NBR), or Chloroprene Rubber (CR). The raw gum elastomer itself has very limited use, of which adhesives provide one example. Most are mechanically weak and subject to significant swelling in liquids, and will not retain their shape after molding. In general, elastomers are little used in a pure state. The principal components of compounds are large amounts of solid particulates such as carbon black and silica, and substantial amounts of oils. Often, blends consisting of different elastomers are used rather than single elastomers. Finally, crosslinks are introduced during the vulcanization process, the molecular weight between cross-links being typically of the order of 5000 to 10000. Vulcanization changes the material from a deformable, viscoelastic substance to a highly elastic product capable of returning essentially to its original shape following very large deformations.

In 1888, John Boyd Dunlop invented the pneumatic rubber tire[6]. The first tires consisted of a rubber tube sheet covered with fabric. The first person to consider air filled tires for cars was a man named André Michelin. Due to many flat tires with his type of tire, this tire was declared a failure. In 1911, the Hardman company was the first to produce a combination of a tire and tube. An air filled inner tube was surrounded by a hardened rubber tube, which was reinforced with fabric. The automotive rubber tire had finally been born. In the following years, many improvements and developments have been made on tyres[6]. The latest major development in the tire industry focused on reduction of fuel consumption of cars. Tire producers have therefore been concentrating on the development of tires with low rolling resistance[7].

Rolling resistance contributes between 18 and 30% of the resistance to the forward motion of a passenger car[8,9]. The rolling resistance accounts for between the 5-15% of the fuel consumption[7]. This means, that a 30%

reduction in rolling resistance results in approximately 1.5% reduction of fuel consumption[10]. This may go as high as around 4.5%. Hysteresis within the tire cords and rubber is the largest contributor to rolling loss and is responsible for 85 to 95% of the total loss[10,11]. Consequently, modification of the viscoelastic behavior of tire materials is an effective way to decrease rolling resistance[9].

A major problem facing tire designers has traditionally been the compromise between low rolling resistance, high wet grip and high wear resistance. Lowering the rolling resistance commonly results in a reduction in wet grip performance and vice versa. The balance in this “Magic Triangle of Tire Technology” depends on the choice of (blends of) rubber polymers and reinforcing fillers. A major step in solving this problem can be achieved by the replacement of carbon black by silica as the reinforcing filler in the tire tread compound. This has enabled tire producers to produce tires, which provide improved wet grip properties, better winter performance and lower rolling resistance[12]. It has been found that the use of highly dispersible precipitated silica in combination with a coupling agent allows the tire manufacturers to produce a tire tread that decreases the tire rolling resistance by approximately 20%. This corresponds with a decrease of 3-4% in fuel consumption of the car[13].

Although a lot of research has already been done in the past on this subject[14-23], it is generally felt that improvements of this technology can still be made by a further study of the silica compatibilization with the rubber matrix by using a new surface modification technique i.e. plasma polymerization.

1.2 Objective of this research

Apart from blends of rubber types with similar polarities like NR, SBR and BR used in balancing the “Magic Triangle of Tire Technology”, blends of rubber polymers with different polarities have gained limited practical importance because of the technical difficulties involved. Each different rubber to be applied in a blend needs its own specific package of reinforcing fillers and curatives for the vulcanization, for full deployment of the rubber properties. Consequently, for blends of elastomers with different polarities to be practically feasible, three requirements need to be fulfilled:

1. a fine homogenous dispersion of the different rubber polymers in each other;
2. at vulcanization temperature the same curing rate and amount of crosslinks for the various rubber phases;
3. a proper distribution of reinforcing fillers over the phases.

The different rubber polymers to be applied in a blend possess by virtue of their chemical composition different polarities, which limit the compatibility of the separate rubber phases with each other.

Silica is considered to be one of the most important reinforcing fillers for rubber. However, silica is hydrophilic and polar of nature, and that causes strong agglomeration of the particles by interparticle forces, which results in poor dispersion within the elastomer matrix and gives low mechanical and dynamic properties to the filled elastomers. Presently, a coupling agent is used to overcome these problems and this is an absolute prerequisite for a proper performance of a silica reinforced rubber compound.

The main objective of the present project is the development of a plasma surface-modification technique for silica to be used for reinforcement in rubber blends. In this way the surface energies of the filler particles may be matched with the different rubber components, so as to selectively compatibilize these to those phases in the rubber blend where they have to arrive during the mixing operation.

1.3 Concept of this thesis

The research described in this thesis comprises the surface modification of silica by a plasma polymerization technique and its reinforcing effect in several straight rubber polymers and their blends. The thesis is divided into 9 chapters as outlined hereunder:

Chapter 2 serves as an introduction to those subjects, which are relevant for the work of this thesis. The properties of silica which are crucial for the application as filler in rubber are described, and the reinforcement of rubber by silica is discussed. The incompatibility of fillers and elastomers in a blend is addressed and different approaches to improve the compatibility are discussed. This chapter also gives an overview of the work done so far in the field of surface modification of fillers by plasma polymerization in order to achieve an improved compatibility with different elastomers.

Chapter 3 deals with the surface modification of precipitated silica powders by using a plasma-polymerization process. The monomers used for the plasma-polymerization are acetylene, pyrrole and thiophene, chosen due to the different chemical moieties in their structure which might be active in the vulcanization process of the elastomers.

In ***Chapters 4***, ***5 and 6***, the plasma modified silica's with acetylene, thiophene and pyrrole monomers are blended with solution-SBR, EPDM and NBR. Further, their dispersion and reinforcing effects are investigated with different measurement techniques. As references, untreated and silanized silica are used.

Chapters 7 and 8 deal with the properties of 50/50 rubber blends based on SBR, EPDM and NBR, filled with untreated, plasma-acetylene, -pyrrole and -thiophene treated silica as well as silanized silica. Both chapters focus on the compatibilization effect of the different silica modifications for the incompatible polymers SBR, EPDM and NBR.

Chapter 9 discusses the morphology of compounds filled with the different silica fillers based on S-SBR, EPDM, NBR and their blends. The micromorphology is measured with the aid of Atomic Force Microscopy (AFM) and is related to the different properties of the straight rubbers and their respective blends as used in the study.

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Chapter 2

Elastomer Reinforcement and Influence of Plasma-Coating of Silica on Elastomer Blends, A Literature Review

This chapter introduces the different topics that are relevant for the work described in this thesis. The properties of silica which are crucial for the application as filler in rubber are described, and the reinforcement of rubber by silica are discussed. The incompatibility of fillers and elastomers in a blend is addressed and different approaches to improve the compatibility are discussed. Special attention is given to mixing of silica-filled rubber compounds, in particular the reactions that take place in the presence of the silane coupling agent. This chapter also gives an overview of the work done so far in the field of surface modification of fillers by plasma polymerization in order to achieve an improved compatibility with different elastomers. The mechanistic aspects of plasma polymerization and other details of the process are reviewed.

2.1 Introduction

Powders, including carbon black, silica, zinc oxide, iron oxide, titanium oxide, pigments and zeolites, are useful raw materials in the rubber, electronic, paint, and petrochemical industries. The surface characteristics of powders or pigments are a very important factor when they are used in many forms of industrial applications. Flow behavior, dispersion, adsorption properties and adhesive forces between the powder particles and towards other materials are all dominated by the surface characteristics of the powders. An important property of filler powders is the structure in which primary particles are arranged into aggregates and agglomerates. However, these two characteristics are often contradictory; therefore the modification of surface characteristics without altering the bulk properties is often desirable or even necessary. Such a process has the potential of creating novel materials with property profiles hitherto not known. The properties of powders that may be tailored by surface modification include compatibility, adsorption, wettability, triboelectricity, barrier and insulation effects, adhesion, diffusion, friction, corrosion, dispersion, flow behavior, to mention only a few.

2.2 Elastomer blends

2.2.1 Introduction

Polymer blends are of practical interest as micro–structured materials. The phenomenon that most polymers do not readily blend is due to repulsive interactions combined with low entropy of mixing. Since this combinatorial entropy is small for blending of high molecular weight polymers, the majority of such blends, including most commercially utilized rubber mixtures, possess phase-separated morphologies. The control of the phase separation process of binary mixtures gives the possibility to adjust the resulting phase morphology[1]. The range of miscible rubbers based on hydrocarbons is therefore very limited.

All straight rubbers have shortcomings in one or more properties. This is the technical reason for combining different polymers in a blend. The advantages of blending different polymers are:

- the possibility to obtain combined properties for the blends;
- easier processing.

2.2.2 Thermodynamics of polymer blends

In general, two components (solid, liquid or gas) mix with each other when the Gibbs free energy decreases. Complete miscibility in a mixture of two polymers requires that the following condition is fulfilled:

$$\Delta G_m = \Delta H_m - T\Delta S_m < 0 \tag{2.1}$$

where ΔG_m, ΔH_m and ΔS_m are the Gibb's free energy, the enthalpy and entropy of mixing at a certain temperature T. For a stable one-phase system, a criterion for phase stability of binary mixtures of composition φ at fixed temperature T and pressure P are:

$$\Delta G_m < 0, \left(\frac{\partial^2 \Delta G_m}{\partial \varphi^2}\right)_{P,T} > 0 \tag{2.2}$$

A miscible polymer blend is characterized by homogeneity down to molecular level and associated with a negative value of the free energy of mixing. The domain size is comparable to the dimensions of the macromolecular statistical segments. The value of $T\Delta S_m$ is always positive since there is an increase in entropy on mixing, however small due to the macro-molecular nature of the polymers. Therefore, it depends on the ratio of the ΔH_m- and $T\Delta S_m$- values whether the ΔG_m is positive or negative: The polymer pairs form a single-phase only if the entropic contribution to the free energy exceeds the enthalpic contribution, which nearly never happens, or if:

$$\Delta H_m < 0 \tag{2.3}$$

Starting point for most of the theoretical interpretations of polymer solutions and blends is the Flory-Huggins lattice theory. It is basically an extension of the concept of regular solutions to polymer solutions. Thus the model restrictions are:

- no change of volume during mixing (incompressible model);
- the entropy of mixing is entirely given by the number of rearrangements during mixing (combinatorial entropy);

- the enthalpy of mixing is caused by differences in the interactions of different segments after the dissolution compared to interactions of the same type of segments. It is a mean-field model, i.e. only average interactions are taken into consideration.

The main problem is to quantify the entropy of mixing because polymer blends show significant deviations from values expected for ideal solutions. Assuming a rigid cubic lattice model, this problem was independently solved for polymer solutions by Huggins and Flory. The lattice theory for the enthalpy of mixing in polymer solutions can be formally applied to polymer mixtures, which provides a rough estimation of the miscibility of the polymers[2,3]. Assuming random mixing of two polymers and no volume change, $\Delta V_m = 0$, the well-known expression for the combinatorial entropy of mixing ΔS_m of the Flory-Huggins theory can be derived:

$$\Delta S_m = -R\left[\frac{\varphi_1}{r_1}\ln\varphi_1 + \frac{\varphi_2}{r_2}\ln\varphi_2\right] \qquad (2.4)$$

where φ_i (i = 1, 2) is the volume fraction of the component i, r_i is the number of polymer segments, and R is the gas constant. It can be seen that the entropy of mixing decreases with increasing molar mass (r_i is proportional to the degree of polymerization) and vanishes for infinite molar masses.

2.2.3 Interaction parameter

Applying the concept of regular solutions and taking into consideration all pair interactions in the framework of a mean-field theory, yields for the enthalpy of mixing ΔH_m:

$$\Delta H_m = RT\chi\phi_1\phi_2 \qquad (2.5)$$

For binary systems, the Flory-Huggins equation can then be expressed in the following form[4,5]:

$$\Delta G_m = RT\left[\frac{\varphi_1}{r_1}\ln\varphi_1 + \frac{\varphi_2}{r_2}\ln\varphi_2 + \chi\phi_1\phi_2\right] \tag{2.6}$$

where χ is the so called Flory-Huggins binary interaction parameter. For polymers having infinite molar mass (i.e. r_i is infinite), the entropic contribution is very small and the miscibility or immiscibility of the system mainly depends on the value of the enthalpy of mixing (Equation 2.5). Miscibility can only be achieved when the interaction parameter χ is negative. This parameter depends on temperature, concentration, pressure, molar mass, molar mass distribution and even on model parameters such as the coordination number of the lattice and segment length.

For polymers, miscibility can only be achieved when $\chi < \chi_{cr}$. The χ parameter at the critical point χ_{cr} is defined as follows:

$$\chi_{cr} = \frac{1}{2}\left(\frac{1}{\sqrt{r_1}} + \frac{1}{\sqrt{r_2}}\right)^2 \tag{2.7}$$

where r_i is the number of polymer segments, as before. It should be mentioned that Equations 2.6 and 2.7 are based on the assumption that χ is not a function of composition but is determined by the magnitude of the interaction energy, while χ_{cr} is determined by the molecular weight and concentration of the components. Within the assumptions of the lattice theory, for a given pair of polymers, χ is fixed, while χ_{cr} can be adjusted to control the phase morphology. In regular solutions and mixtures, Upper Critical Solution Temperatures (UCST) are expected, since χ is inversely proportional to temperature, reflecting the fact that the driving force for miscibility, the contribution of the combinatorial entropy to the free energy of mixing, is proportional to the temperature.

2.2.4 Solubility parameter

The Hildebrand Solubility Parameter concept, widely used for liquid-liquid miscibility, has also been used for polymer-solvent studies as well, as it is a simple tool for predicting the miscibility of polymers with solvents[6] and swelling of vulcanized rubber in organic liquids[6]. Hildebrand and Scott[6] developed a theoretical expression for regular solutions of polyelectrolytes by assuming that a solution process involves replacing similar molecules with dissimilar ones. On this basis, they developed a relationship between ΔH_m and the square root of the energy of vaporization, usually known as the solubility parameter δ. This is given by the following equation:

$$\frac{\Delta H_m}{V_1} = K\,(\delta_1 - \delta_2)^2 \varphi_1 \varphi_2 \qquad (2.8)$$

where,
V_1= the average molar volume of the two liquids;
K = constant (nearly equal to 1);
δ_1, δ_2 = solubility parameters of component 1 and 2;
ϕ_1, ϕ_2 = volume fraction of component 1 and 2.

There are advantages in using the solubility parameter concept in predicting polymer-solvent and polymer-polymer miscibility, namely[7]:

1. For most organic liquids, the solubility parameter δ can be estimated from accessible data such as energy of vaporization, boiling point, refractive index, surface tension, etc.
2. For most polymers, the solubility parameter δ has been estimated by measuring solubility, swelling, or viscosity in a number of solvents.
3. For most solvents and polymers, δ can be estimated by a group contribution approach from the knowledge of the chemical structure and molar volume of the molecules (in case of a liquid) or repeating units (in case of a polymer) and existing empirical data on group contributions[8].

Mangaraj[9] found that the solubility parameter correlation is valid only when the solvents belong to a homologous series and have a chemical structure similar to the polymer. Hansen and Paint[10] further elaborated this concept and showed that δ can be described in terms of three components: δ_d, the contribution from dispersive interactions, δ_p, the contribution from polarity, and δ_h, the contribution from hydrogen bonding. The total solubility parameter,

δ_t is the root mean square of the three components as presented in Equation 2.9:

$$\delta_t^2=\delta_d^2+\delta_p^2+\delta_h^2 \tag{2.9}$$

The attempt to obtain the three components of δ_t and to apply them for determining polymer-solvent and polymer-polymer miscibility has met limited success. It may be stated that the solubility parameter concept is limited and can never predict a negative ΔH_m, nor does it predict a very small positive ΔH_m accurately, often associated with miscible polymer systems. However, in spite of this limitation, the solubility parameter concept provides a simple tool for estimating approximate values of ΔH_m, which can assist in understanding the polymer-polymer miscibility and predicting the same with limited accuracy.

Molecular weight also plays an important role in polymer-polymer mixing for slightly endothermic systems. In facilitating miscibility, it is important to match the solubility parameters of the candidate polymers as closely as possible. A difference of 0.1 or more in the solubility parameter values of a polymer pair can already lead to immiscibility.

Polarity also plays an important role in polymer-polymer miscibility. For polar polymer pairs, chemical moieties in the main chain or side groups interact with each other, providing an exothermic heat of mixing, the driving force for the miscibility. Paul and Barlow[11] attributed the existence of a number of miscible polymer pairs to exothermic interaction (negative ΔH_m). Exothermic interactions are often referred to as “specific interactions”. In some cases, this interactive dissimilarity is the driving force for the miscibility. The term “complementary dissimilarity” is also often used in reference to the specific interactions that lead to the miscibility. These are “attractive” interactions such as hydrogen bonding. Miscibility of polymer pairs such as polyvinyl chloride (PVC) / acrylonitrile-butadiene-rubber (NBR), polymethyl methacrylate (PMMA) / polyvinylidene fluoride (PVDF), polystyrene (PS) / polyvinyl methyl ether (PVME), ethylene vinyl acetate (EVA) / polychloroprene rubber (CR) and styrene acrylonitrile copolymer (SAN) / polycaprolactone (PCL) is ascribed to the existence of specific interactions and negative enthalpy of mixing[6]. It may be stated that for a pair of polymers with a small difference in solubility parameters (smaller than 0.1) or with specific interactions, there is a potential for miscibility. Otherwise, most polymer blends are immiscible, except at very extreme compositions.

2.2.5 Phase separation

In a blend of immiscible polymers (generally the case for elastomers), the morphology is usually not at equilibrium, due to the sluggishness of macromolecular diffusion. Equilibrium thermodynamics can provide an indication of the degree of miscibility expected in a polymer mixture. The structure may be invariant, however, due to slow diffusion or crosslinking. In the preparation of miscible mixtures, equilibrium conditions will be obtained easier and the resulting morphology is relatively insensitive to the details of the method of blend preparation.

One of the predominant effects of polymer-polymer immiscibility is phase separation, i.e. when the two polymers exist in discrete domains both in the liquid and solid phases. Figure 2.1 illustrates the phase diagram of a typical polymer blend as a function of temperature[6].

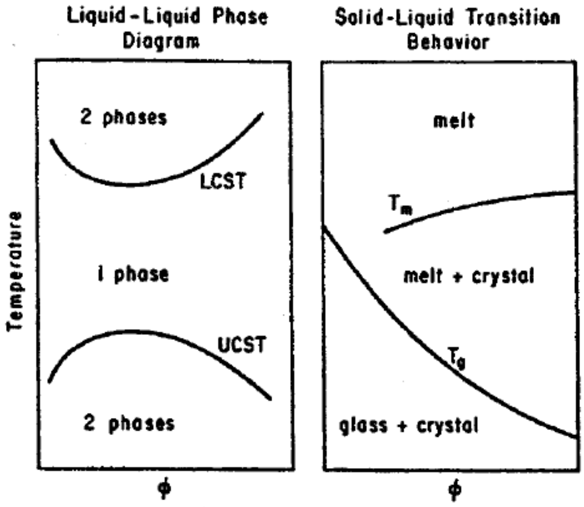

Fig. 2.1: Possible phase transition behavior in polymer blends[6].

The diagram represents a miscible polymer blend, having a single glass transition temperature (T_g). As the temperature is increased, the two polymers which are immiscible at lower temperature, become miscible. The temperature for complete miscibility, the Upper Critical Solution Temperature (UCST) is lower for the blend compositions with excess of one component than for equal percentages of the components. As the temperature is raised further, the miscible blends often separate, indicating the existence of a Lower Critical Solution Temperature (LCST). At this temperature, miscible blends of a certain composition become immiscible and separate into two phases. Most polymer pairs, which are miscible due to a negative enthalpy change on mixing, become immiscible at higher temperatures.

Other factors which may contribute to the existence of a Lower Critical Solution Temperature (LCST) are a negative volume change on mixing and positive excess heat capacities[12]. Lower Critical Solution Temperature (LCST) behavior is not affected by molecular weight above a certain critical molecular weight for each polymer pair[13]. This confirms that the entropic contribution to the Lower Critical Solution Temperature (LCST) behavior is minimal.

Most elastomers in their commercial form are very high molecular weight polymers, much larger than thermoplastic polymers. They are masticated in a Banbury or open roll mixer so that their molecular weights are sufficiently lowered to provide good mixing due to enhanced entropy change. In the case of elastomer blends, the state of mixing is stabilized by crosslinking at higher temperatures. However, if the temperature of vulcanization is either greater than the LCST or lower than the UCST, the uniform dispersion of the two elastomers will be hampered, giving an inhomogeneous blend. The dissimilarity in polarity which leads to immiscibility of elastomer blends also affects other aspects of elastomer technology, particularly the distribution of compounding ingredients prior to vulcanization and the crosslink density, once the compound is vulcanized[14].

The solubility parameter concept as discussed in the previous section is used to predict polymer-solvent and polymer-polymer miscibility. It also plays an important role in estimating the critical molecular weight (M_c) above which phase separation takes place. The estimated M_c values for all rubbers are far below the molecular weight of the commonly used rubber grades used in the industry. The solubility parameters of typical elastomers are given in Table 2.1[15]. The temperature dependence of the solubility parameter δ of EPDM, NR, BR and emulsion SBR is equal.

Table 2.1 Solubility parameter of elastomers[15].

	Hildebrand Solubility Parameters ($MPa^{½}$)	Hansen Solubility Parameters ($MPa^{½}$)		
Elastomer	δ	δ_d	δ_p	δ_h
Acrylonitrile butadiene copolymer*				
- 18 %	18.0			
- 25 %	19.0			
- 30 %	20.0			
- 39 %	21.0	18.6	8.8	4.2
Styrene-butadiene copolymer	18.1	17.4	2.9	6.8
Ethylene-propylene copolymer	18.5	16.6	8.2	
Ethylene propylene-diene terpolymer (ethylidene norbornene)	17.1			
Polyisobutylene	16.5	14.5	2.5	4.7
Polyisoprene	16.7	16.6	1.4	-0.8
Natural rubber	16.9			

*acrylonitrile content

The domain size is an important parameter to measure heterogeneity in rubber blends. The domain size of the minor component d is proportional to $\Delta\delta$, the difference of the solubility parameters of the components. The domain size of NR with BR, high-vinyl BR, emulsion-SBR, solution-SBR and EPDM are given by the following correlation[7]:

$$d = 1260[\Delta\delta - (-0.204)] \qquad (2.10)$$

For NR/SBR blends with different styrene contents, $\Delta\delta$ changes and the distribution of the domains becomes heterogeneous, finally breaking into a binary distribution. The aspect ratio (AR) of the domains is defined in Equation 2.11[7]:

$$\text{Aspect Ratio (AR)} = 0.671 + 0.178\,\Delta\delta \qquad (2.11)$$

The aspect ratio of the domains in the blend is increasing with decreasing degree of compatibility[7].

2.2.6 Formation of heterogeneous blends

Rubber blends can be prepared by a variety of methods, including in situ polymerization, by latex or solution blending, and by mechanical mixing. The morphology of immiscible rubber blends is dependent on the mixing procedure and rheological properties of the blend components and on their degree of compatibility as reflected in the interfacial energy. Blends of components with similar viscosities and concentrations are more likely to show co-continuity of the phases[11]. The usual structure of a heterogeneous blend is a dispersion of one component in a continuous matrix of the other. As seen in Figure 2.2, the rubber of lower viscosity constitutes the continuous phase, provided it is present at a sufficiently high concentration[16]. Another approach is to compare the interfacial tension between the two phases: It has been suggested that the phase with the larger stress function will form the dispersed particles[17]. Correlations between the morphology of a blend and the relative magnitude of the interfacial and surface tensions have been reported by Hobbs et al.[18].

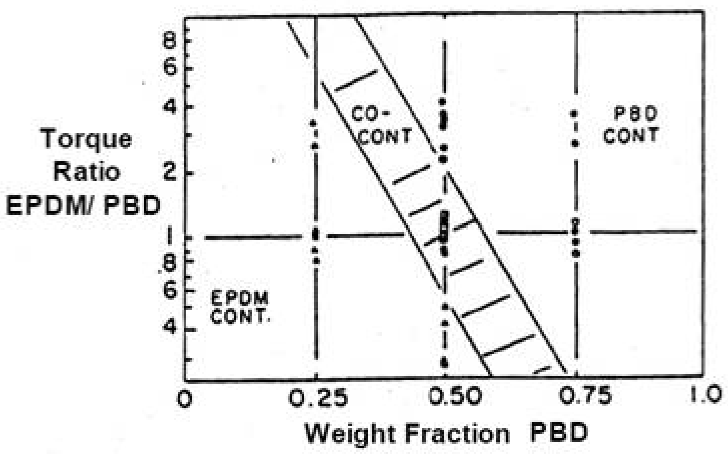

Fig. 2.2: The dependence of the phase structure on composition for EPDM/BR blends, at various relative viscosities of the components[16].

During mechanical mixing of rubber blends, the dispersed domains are deformed during passage through the high shear regions of the mixing vessel and, under the proper circumstances, will fracture to produce smaller particles. Simultaneously, these flowing particles collide and often coalesce to form larger dispersed domains. The blend morphology represents this competition between dispersion of the rubber particles and their flow-induced coalescence[19,20]. Attempts to predict the morphology of rubber blends from the consideration of the competition between breakup and coalescence have been made by assuming an energy criterion for particle fracture[19]. The breakup is related to the stress level exerted on the particle by the flowing matrix, and how effectively this stress can sustain particle deformation. The number of particles produced upon breakup is a function of the stress level as well as the relative viscosities of the components[21].

Homogeneity at a fairly fine level is necessary for optimum performance, but some degree of microheterogeneity is usually desirable to preserve the individual properties of the respective polymer components[22]. In rubber blends, “technological compatibility” is very important to obtain better properties of the product. For example EPDM, a copolymer of ethylene, propylene and a minor portion of a diene monomer, has particularly good resistance to the degrading effects of oxygen or ozone. However, unvulcanized EPDM rubber has poor tack properties and is consequently unsuited for the assembly of tires. High-diene hydrocarbon rubbers such as natural rubber and synthetic polyisoprene, polybutadiene and copolymers of butadiene with other monomers have better tack, but are much more susceptible to oxygen and ozone degradation due to the relatively high number of double-bonds in their molecular backbones. Blends of a mono-olefin rubber (e.g. EPDM) with a high-diene rubber (e.g. natural rubber) should combine the good properties of each component. Unfortunately, simple blends of these two materials have not been successful, except those in which only a small amount of one of the components was present. These two types of rubber are “technologically incompatible”, differing in properties such as viscosity, surface energy, and vulcanization rate.

It can be concluded that the most pertinent property pertaining to rubber blends is the homogeneity (phase morphology). Most blends of elastomers are immiscible because mixing is endothermic and the entropic contribution is small because of their high molecular weights. Homogeneity is favored by similarity in polymer viscosities and solubility parameters[1,16].

2.3 Elastomer reinforcement

2.3.1 Introduction

Particulate fillers such as silica and carbon black are generally used as reinforcing materials for rubber to improve their physical properties such as modulus, tensile strength, abrasion resistance, tear properties and dynamic properties. The selection of the filler used in a rubber formulation is based on the property requirements of the end-product. For that purpose, active fillers like silica or carbon black are of special interest as they lead to a strong modification of the elastic properties of the rubber compared to a mere addition of hard, randomly dispersed particles. Typically, silica and carbon black act as reinforcing fillers which enhance the strength characteristics, the term "reinforcement" refers to the changes in the stress-strain properties brought about by the presence of reinforcing particles in the vulcanizate. Reinforcement of elastomers with particulate fillers depends, to a large extent, on the polymer properties, filler characteristics (particle size or specific surface area, structure and surface activity) and processing conditions. The maximum efficiency is attained when a continuous, structured network of the filler, homogeneously dispersed within the polymeric matrix, is formed.

Donnet[23] summarized the basic work of Payne on elastomer reinforcement as the simple concept of "additive effects" as shown in Figure 2.3. He described the enhancement of mechanical properties due to the presence of fillers as the result of a hydrodynamic effect superimposed by different kinds of interactions: polymer to filler and filler to filler interactions and the rubber network.

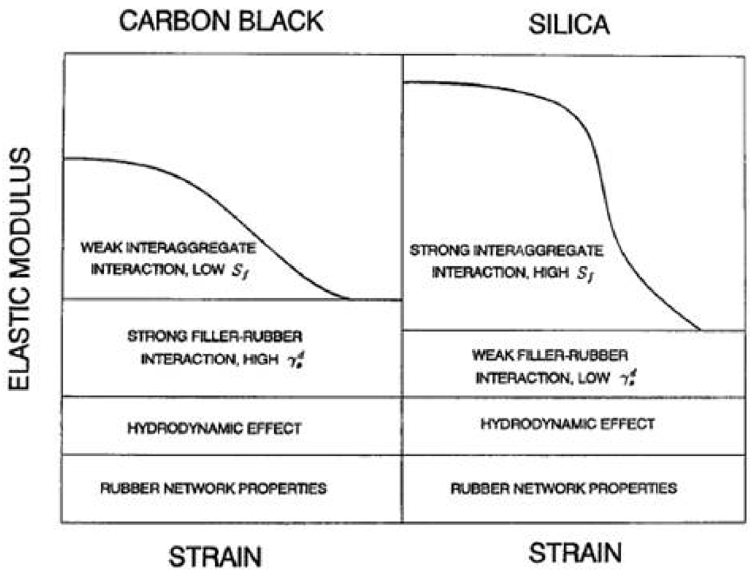

Fig. 2.3: Payne concept of reinforcement[24].

2.3.2 Surface energy of solids and filler-polymer interactions

A molecule interacts with its neighbors resulting in different types of cohesive forces. Within the bulk of the material, the resultant of the forces is zero. On the surface, however, the resultant is not equal to zero, but is directed towards the interior of the particle[25]. The surface free energy or surface tension, γ, is therefore defined as the work, W, necessary to increase the surface by one unit area as presented in Equation 2.12:

$$\gamma = \left(\frac{\partial \mathrm{W}}{\partial \mathrm{A}} \right)_{\mathrm{T,P}} \tag{2.12}$$

where A is the surface area, T the temperature and P is the pressure. This definition cannot be used for solids, because the molecules lack mobility. In this case, the surface energy of the solid, γ_s, can be defined as half of the energy necessary to reversibly cleave a unit plane parallel to the surface, $W_{cleavage}$. Thus for a unit surface of a solid, the surface energy of the solid is:

$$\gamma_s = \frac{W_{cleavage}}{2} \tag{2.13}$$

In the case of all cohesive forces involved in independent ways, the surface free energy can be expressed as the sum of several components each corresponding to a specific type of interaction. Since the effect of dispersive forces is universal, the dispersive component of the surface free energy, γ_s^d, is particularly important. If a substance is able to exchange only dispersion interaction with its environment, its surface free energy would be:

$$\gamma_s = \gamma_s^d \tag{2.14}$$

For most substances however, the surface free energy is the sum of the dispersive part γ_s^d and the specific part γ_s^{sp}:

$$\gamma_s = \gamma_s^d + \gamma_s^{sp} \tag{2.15}$$

It is known that the possible interaction between two materials 1 and 2 is determined by their surface energies. When only dispersive forces are responsible for the interaction, the energy of adhesion between these two materials would correspond to the geometric mean value of their specific surface energies, according to Fowkes' model[26]**:**

$$W_a^d = 2(\gamma_1^d \gamma_2^d)^{1/2} \tag{2.16}$$

where W_a^d is the dispersive component of the adhesive energy. Similarly, the polar component of the adhesive energy, W_a^p, can be described by the polar component of their surface energy as presented in:

$$W_a^p = 2(\gamma_1^p \gamma_2^p)^{1/2} \tag{2.17}$$

Hence, the total adhesive energy, W_a, can be given by:

$$W_a = W_\mathrm{a}^\mathrm{d} + W_\mathrm{a}^\mathrm{p} + W_\mathrm{a}^\mathrm{h} + W_\mathrm{a}^\mathrm{ab} \tag{2.18}$$

or

$$W_a = 2(\gamma_1^d \gamma_2^d)^{1/2} + 2(\gamma_1^p \gamma_2^p)^{1/2} + W_a^h + W_a^{ab} \tag{2.19}$$

where W_a^h is the adhesive energy due to hydrogen bonding and W_a^{ab} the adhesive energy due to acid-base interactions. It can therefore be concluded that the polymer-filler and filler-filler interaction in a given polymer system, which is related to the filler networking, are determined by the filler surface energy and chemical nature, particularly when physical interaction is concerned.

From the above equation, the total change in adhesive energy, ΔW, in the agglomeration process is given by:

$$\Delta W = 2\gamma_f^d + 2\gamma_f^p + 2W_f^h + 2W_f^{ab} + 2\gamma_p^d + 2\gamma_p^p + 2W_p^h + 2W_p^{ab} - 4(\gamma_f^d \gamma_p^d)^{1/2} - 4(\gamma_f^p \gamma_p^p)^{1/2} - 4W_{fp}^h - 4W_{fp}^{ab} \qquad (2.20)$$

where γ_f^d and γ_f^{p} are the dispersive and polar components of the surface energy of the filler; γ_p^{d} and γ_p^{p} the dispersive and polar components of the surface energy of the polymer; W_f^h, W_p^h, and W_{fp}^h the hydrogen bonding work of the filler, of the polymer and the filler-polymer interaction; and W_f^{ab}, W_p^{ab}, and W_{fp}^{ab}, the work from acid-base interactions between filler surface, polymer surface, and between filler and polymer surfaces, respectively.

Rearranging the above equation results in:

$$\Delta W = 2[\gamma_f^d + \gamma_p^d - 2(\gamma_f^d \gamma_p^d)^{1/2}] + 2[\gamma_f^p + \gamma_p^p - 2(\gamma_f^p \gamma_p^p)^{1/2}] + 2[W_f^h + W_p^h - 2W_{fp}^h] + 2[W_f^{ab} + W_p^{ab} - 2W_{fp}^{ab}] \qquad (2.21)$$

Therefore, the following equation may be given:

$$\Delta W = 2[(\gamma_f^d)^{1/2} - (\gamma_p^d)^{1/2}]^2 + 2[(\gamma_f^p)^{1/2} - (\gamma_p^p)^{1/2}]^2 + 2[W_f^h + W_p^h - 2W_{fp}^h] + 2[W_f^{ab} + W_p^{ab} - 2W_{fp}^{ab}] \qquad (2.22)$$

The above model, which is given by Wang**[25]**, is based on the kinetic model for the change in adhesion energy described by Medalia**[27]**:

$$\Delta W = W_{ff} + W_{pp} - 2W_{fp} \qquad (2.23)$$

where ΔW is the change in the adhesion energy, W_{ff} is the adhesion energy between the fillers, W_{pp} is the adhesion energy between the polymers, and W_{fp} is the adhesion energy between filler and polymer.

If

$$\gamma_f^{\mathrm{d}} = \gamma_p^{\mathrm{d}} \tag{2.24}$$

$$\gamma_f^{\mathrm{p}} = \gamma_p^{\mathrm{p}} \tag{2.25}$$

$$W_f^h = W_p^h = W_{fp}^h \tag{2.26}$$

$$W_f^{ab} = W_p^{ab} = W_{fp}^{ab} \tag{2.27}$$

then

$$\Delta W = 0 \tag{2.28}$$

In this case, the attractive potential between filler particles in contact with polymers disappears. From a thermodynamic point of view, the dispersed filler in a polymer matrix is only stable provided the energy characteristics of the filler surface and polymer are identical or the adhesive energies between polymer and filler surface are very high. In this case, they are able to overcompensate the effect of the difference in surface energies between polymer and filler and cohesive energies of the filler and polymer themselves. The greater the difference in surface energies and the lower the specific interactions in terms of hydrogen bonding and acid-base interaction between filler and polymer, the higher is the tendency for filler-filler interaction.

When $\Delta W > 0$, the aggregates tend to de-mix and form agglomerates dispersed in the rubber matrix, and when $\Delta W < 0$, the aggregates have a strong tendency to disperse in the rubber matrix without forming agglomerates.

2.3.3 Characteristic properties of polymer-filler composites

2.3.3.1 Hydrodynamic reinforcement

Several fundamental models can describe the mechanical reinforcement of rubber compounds. Amongst these, the simplest one describes the hydrodynamic displacement of filler particles. Table 2.2 shows the evolving description of the hydrodynamic effect. In 1906[28], Einstein proposed the first straight theoretical relation for viscosity increase in a Newtonian flow, as seen in Equation 2.29. ϕ is the volumetric concentration and η_0 and η the viscosity of the pure liquid and of the suspension, respectively.

One of the first steps taken in order to apply this effect to elastomers was the assumption that the modulus of rubber would behave similar to the viscosity of a liquid. This was postulated by Smallwood[29], with the assumption that the particles were spherical, dispersed, wetted and under low shear stress. However, since fillers do not meet these ideal conditions, further modifications were required, as shown in Table 2.2. For the practical application, the equation needed to be modified for higher filler fractions causing filler-filler interactions: introduction of the φ^2 terms. Guth and Gold[30] took into account the interaction of spherical fillers by adding an term in the power-series expansion. Equation 2.30 has been modified in several ways to account for deviations of the fillers from the ideal case. In practice, fillers are not spherical but asymmetric consisting of complex branched structures. Furthermore, the hydrodynamic effect is limited to small strains with rigid fillers providing the reinforcement and to low volume fractions to avoid filler-filler interactions. Guth introduced the form factor f in Equation 2.31 to take into account the deviation of the filler shape from a sphere. Medalia modified this equation by using an effective volume ϕ_{eff} in place of $f\phi$.

Wolff, Donnet, Wang, and coworkers published many papers that discuss the hydrodynamic effect in rubbers[31-33]. Wolff and Donnet[32] replaced the modulus in Equation 2.32 with the stress σ of the rubber under tensile stress-strain conditions. Using the data from stress-strain experiments for rubbers filled with silica and carbon black, they came up with values for the factor f as a function of filler volume fraction (up to $\phi = 0.22$), temperature and surface activity. Medalia[27] related the modulus E of the rubber to the surface area of the filler. Vilgis and Heinrich[34] reviewed rubber reinforcement and emphasized, that no consistent model exists that may be used to explain rubber reinforcement. Eggers and Schümmer[35] discussed the Thomas equation, Equation 2.33, showing that it fits a much broader range of filler loading ($0.1 < \phi < 0.5$) than the previous forms of the Guth-Gold equation.

Table 2.2: Historical development of the description of the hydrodynamic effect.

Eq. Nr.	Equation	Comments	Ref.
(2.29)	$\eta = \eta_0(1 + 2.5\,\phi)$	-	**28,29**
(2.30)	$E = E_0(1 + 2.5\,\phi + 14.1\,\phi^2)$	Expanded ϕ^2 term	**30**
(2.31)	$E = E_0(1 + 2.5 f\phi + 14.1 f^2\phi^2)$	f=form factor, or $\phi_{eff} = f\phi$	**27**
(2.32)	$G = G_0(1 + [G]\,\phi + \vartheta\phi^2)$	-	**36**
(2.33)	$f = \frac{\eta}{\eta_0} = 1 + 2.5\varphi + 10.05\varphi^2 + A\exp(B\varphi)$	A, B constants, A = 0.00273, B = 16.6	**37**

The hydrodynamic effect accounts for the increase in modulus under the conditions of low strain and low volume fraction. When the strain goes beyond a critical value, the major contribution to the modulus is attributed to the rubber itself. When the volume fraction of the filler increases, filler-filler interaction increases resulting in a filler network: a reinforcement mechanism different from the simple hydrodynamic phenomenon.

2.3.3.2 Polymer-filler interactions: Bound rubber formation

The bound rubber phenomenon has been extensively studied for many years, since it is considered an important factor in filler reinforcement of rubber, a measure of filler surface activity and polymer-filler interactions[38-44]. A number of authors have published theories to describe this phenomenon[45-48]. Several models explain the exclusion of rubber from the matrix, and Figure 2.4 illustrates these models for carbon black as a filler[49]. In case a), the rubber chains are attracted either physically or chemically to form a rubber shell on the surface of the primary carbon black particle. The rubber that is directly attached to the carbon black molecule is much stiffer than the rubber molecules in the matrix, all the way to glassy-like. In case b), the rubber shell that is shown for the primary particle in a), is extended for a filler aggregate. As in a), the rubber chains closest to the aggregate are the stiffest. In this shell, bridging of the bound rubber in the aggregates leads to a higher bound rubber fraction. In case c), rubber is arranged around the aggregate and the rubber shell to form an outer layer of occluded rubber. This layer is not tightly bound to the filler aggregate but does experience decreased mobility near the surface of the aggregates. In case d), rubber is trapped between aggregates which have formed an agglomerate. This rubber experiences little stiffness increase and becomes 'free' once the aggregate structure breaks apart during deformation.

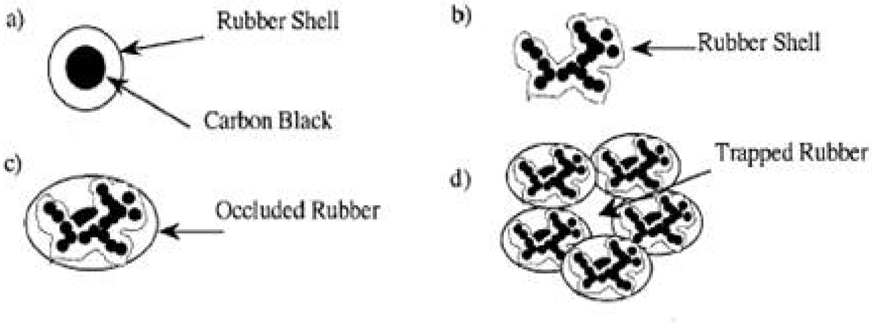

Fig. 2.4: Models of rubber excluded from the matrix[50]*.*

Nuclear magnetic resonance imaging (NMR) studies confirmed the existence of a rubber shell around filler particles[50]. This bound rubber affects the properties of the compounds by contributing to the filler volume to form an 'effective' filler volume fraction: ϕ_{eff}. Meissner[51] critically reviewed the existing theories and concluded that the most complete explanation of available experimental data is offered by a random adsorption model.

In general, the bound rubber content increases with higher loadings of filler. The filler particles with adsorbed polymer chains cannot be dissolved by a solvent, but form a coherent mass called polymer-filler gel. There are many factors influencing the bound rubber formation as shown in Table 2.3[52]:

Table 2.3: Factors influencing bound rubber formation.

i. Filler

- ❑ Concentration
- ❑ Aggregate size (structure)
- ❑ Surface area
- ❑ Chemical composition
- ❑ Surface Activity
  - Free radicals (aggregate breakdown)
  - Functional groups
  - Heat treatment
  - Surface treatments
    - ▪ coupling agents
    - ▪ hydrophobic agents
    - ▪ surface active agents

ii. Elastomers

- ❑ Chemical composition
- ❑ Unsaturation
- ❑ Stability
  - Thermal
  - Mechanochemical
  - Oxidative

iii. Chemical additives

- ❑ Free radical quenchers
- ❑ Processing promoters
- ❑ Coupling agents
- ❑ Surface active agents

2.3.3.3 Dynamic mechanical reinforcement

Dynamic mechanical analysis is frequently used to measure the reinforcement of rubber by fillers. Wang reviewed several studies on filler reinforcement using dynamic mechanical analysis[25]. The major factors for dynamic reinforcement are filler structure, filler loading and filler-rubber interactions. G' (shear storage modulus), G'' (shear loss modulus), and tan δ (loss factor) are the important parameters for the dynamic mechanical properties, and their dependence on temperature and dynamic strain amplitude provides information about the filler network structure and filler rubber interactions. Figure 2.5 shows a plot of the storage modulus versus temperature for rubbers with high, medium, and no filler loading.

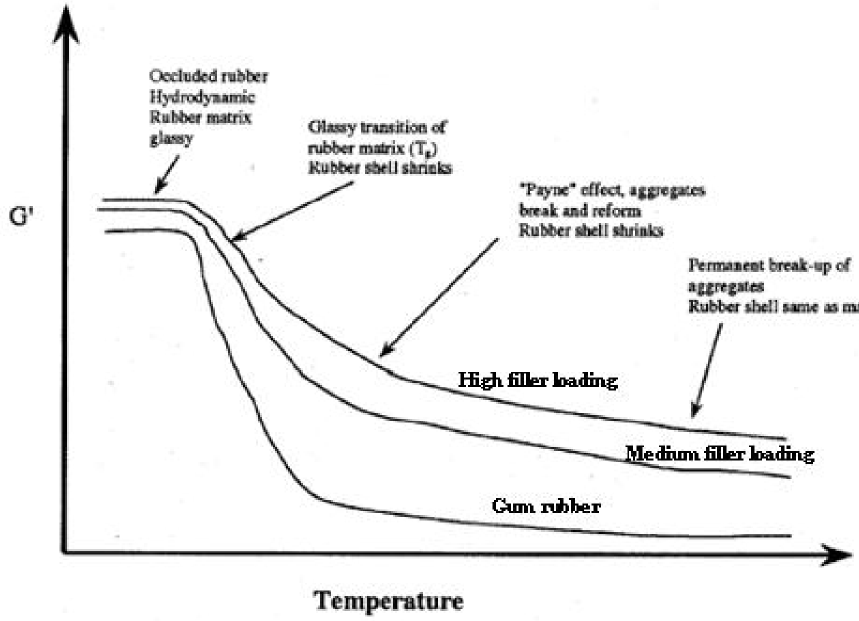

Fig.2.5: The temperature dependence of the storage modulus G' for filled and unfilled rubbers[25].

The classical models and most of the related theories ignore the important role of filler polymer interactions, caused by the large aggregates and their associated large surfaces. Ample evidence exists for both, physical and chemical interactions, each capable of giving rise to reinforcement effects[49]. The filler network formation in the polymer matrix is determined by attractive forces between filler particles or aggregates, as well as the interaction between filler and polymer. Generally, the total interaction between particles is the sum of contributions from various interactions: dispersion, induction (induced dipole-dipole), orientation (dipole-dipole), hydrogen bonding, acid-base interaction, chemical bonding, and repulsion (see 2.3.2). If the particles are surrounded by a medium, the attractive force between filler aggregates would be substantially reduced. In this case the filler network formation may be estimated from surface energies of the filler and polymer which also originate from intermolecular interactions.

2.3.4 Silica reinforcement in rubbers

2.3.4.1 Production

In the past decade, much attention was devoted to the use of silica. There are mainly three categories of commercially available silicas: Precipitated, fumed, and surface treated products[53]. The precipitated silica types are the most common types for general rubber use and are commonly called ‘silica’ as a generic term. Fumed silicas are used primarily in silicone rubber and compounds with special polymers or cure systems. The surface treated silicas are specialty products used in certain niche applications.

Precipitated silica is made by acid precipitation of sodium silicate, also called ‘water glass’. The sodium silicate solution is usually produced by combining high purity sand and sodium carbonate (soda ash) in a high temperature furnace, followed by dissolving the molten ‘glass’ in water. The particles of precipitated silica are filtered, washed and dried. The dried powder may be packaged as it is, milled to a fine powder, or granulated for easier handling.

Fumed silica, also called ‘pyrogenic’, ‘colloidal’ or ‘anhydrous’ silica, is produced by a high temperature gaseous process and is more expensive than the precipitated silicas. Their application in rubber is limited due to the high costs and difficulty in mixing: too fluffy. They are primarily used in silicone rubber and specialty polymer applications.

2.3.4.2 Surface properties

In relation to high structure carbon blacks, silica fillers may be categorized as having a low ‘permanent’ structure due to hydrogen bonding among particles which forms loose clusters or aggregates, but a much stronger ‘secondary’ structure network that has a profound effect on mixing, processing and in-rubber performance properties. Silica is an amorphous material and the functional groups are randomly located on the filler surface as shown in Figure 2.6[25]. The surface of silica is covered with silanol groups [Si-OH] that readily form hydrogen bonding ‘bridges’ with neighboring particles, water molecules (moisture), or other polar substances. The silanol groups are formed by hydration of SiO_2 on the surface. Precipitated silica is available in a range of surface areas from 40 to greater than 200 m^2/g. The high surface area silicas can have a drastic effect on the cure rate and crosslink density of a rubber compound due to interactions with other compounding ingredients. Like the precipitated silicas, fumed silicas also form aggregates of amorphous silica particles that further agglomerate via hydrogen bonding. They also have silanol groups on the surface, but the silanol group density is lower compared to precipitated silicas. The moisture level as well as the affinity for moisture is reduced. Commercial fumed silicas are available with average ultimate particle sizes of 7-40 nm and with the surface areas ranging from 50-400 m^2/g. The reduced moisture sensitivity contributes to their use in some specialty elastomer compounds, e.g. silicones[25].

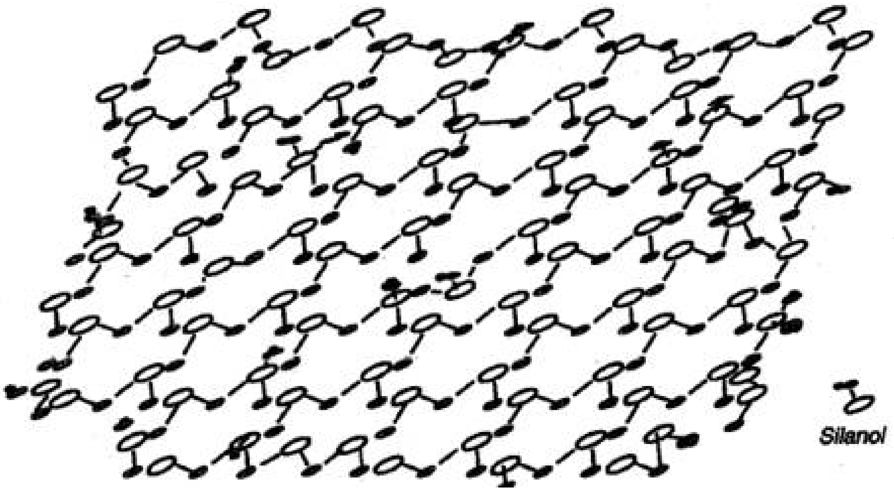

Fig. 2.6: Surface chemistry of silica[25].

2.3.4.3 Effects of silica surface modification on rubber properties

The chemical compounds used for surface treatments of silica fillers can be divided into ‘hydrophobic’ and ‘coupling’ treatment groups - with the latter referring to treatments that enable stable covalent chemical bonds to the polymer as well as to the silica surface. Commercial ‘hydrophobic’ silicas - both precipitated and fumed silica types - are used in silicone rubber compounds and in some rubber compounds that are sensitive to moisture or acidic materials. Silicas with ‘coupling’ pre-treatments have limited usage in rubber compounding. The in-situ silane modification of precipitated silicas during mixing of the compound is far more common. Silane chemicals are effective agents for modifying the surface of silica and other non-black fillers via chemical attachment[25].

The random distribution of silanol groups on the surface of silica fillers facilitates the modification with a silane coupling agent. The proposed mechanism of the linkage of bi-functional organosilanes through covalent bonding, resulting in a chemical “coupling” between the silica on one side and the polymer on the other side of the molecule is illustrated in Figure 2.7[25].

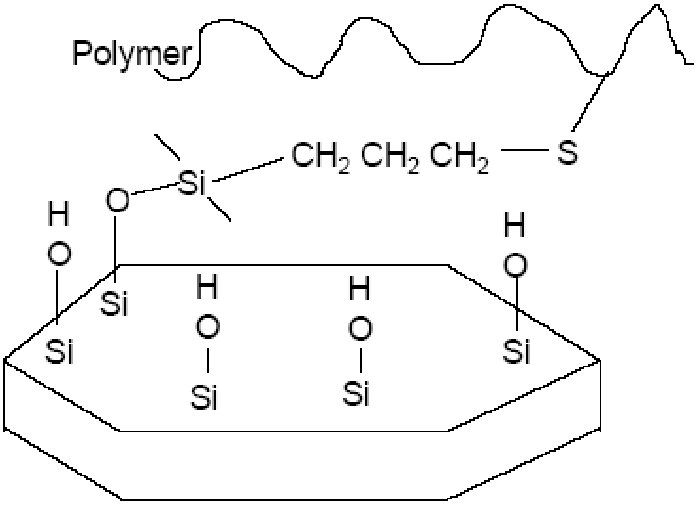

Fig. 2.7: Schematic illustration of the proposed silane coupling[25].

The coupling agents react with the silanol groups on the filler surface and also contain a functional group that will bind to the rubber during vulcanization. The result is an additional filler-polymer bonding that brings about an increase in the modulus and tensile strength, and improves abrasion resistance. Modification of the filler surface also improves polymer wetting and dispersion, and reduces the tendency to adsorb ingredients of the cure system. The modified silica has a reduced filler-filler network attraction and thus gives lower viscosity compounds with improved processing characteristics. Silane coupling agents that are commonly used in sulphur-cured compounds filled with non-black fillers include mercaptosilane, thiocyanatosilane and bis-(3-triethoxysilylpropyl)tetrasulfane (TESPT). These coupling agents commonly have ethoxy-groups which can react with the silanol groups on the surface of silica, silicate, or clay particles during mixing to give a strong bond. They also have a sulphur-containing group that reacts during vulcanization resulting in a bond to the polymer. A thorough investigation on the coupling mechanism and impact on the material properties was done by ten Brinke, Reuvekamp and Dierkes[54-56]. However, the improvements achieved with the silane system are accompanied by problems like ethanol formation, as well as limitations in the processing temperatures for achieving a sufficient silanization rate and to avoid scorch reactions. The plasma polymerization can be regarded as another approach to modify the surface of silica and to improve its reinforcement in the rubber compounds: see later in this chapter.

2.3.5 Distribution of fillers in rubber blends

The physical properties of a polymer blend are in general strongly influenced by the heterogeneity of the blend and the distribution of additives, especially reinforcement fillers in each of the polymer phases. This is especially true for elastomer blends. With filled elastomer blends, controlled blend structure, i.e. controlled filler and curative distribution in the individual rubber phases, is of primary importance[57].

Over the last years, the interest in silica reinforcement of rubbers for various applications has grown, especially for tread compounds in tires. However, the strong interparticle forces of silica are a drawback in obtaining a good dispersion within the polymer matrix[58-62]. The surface of precipitated silica carries on average 5-6 silanol groups per nm^2, therefore it exhibits a hydrophilic character. The active silanol groups at the silica surface are responsible for formation of particle aggregates and agglomerates. The hydrophilic nature of the silica surface and the tendency to form hydrogen bonds are the cause of strong filler-filler interactions which prevent easy dispersion during mixing and, as a consequence, influence the final physical properties[63].

The surface polarity of silica due to the presence of silanol groups is an important factor which influences its distribution even more in elastomer blends. The surface activity of fillers has an important effect on the interaction between the filler surface and the polymer matrix. In a physical sense, variations in surface energy determine the adsorptive capacity and energy[64]. The surface activity of silica aggregates in elastomers, especially in hydrocarbon rubbers, can be tailored by modifying the filler surfaces in order to obtain the same or better reinforcing properties compared to other active fillers like carbon black. Wolff et al.[65] have determined the characteristic features of silica:

1. A relatively low dispersive component of the surface energy;
2. A very high specific or polar component of surface energy.

The reinforcement markedly depends on the extent of interaction between the silica surface and the rubber matrix, and the extent of interaction can be controlled by varying the characteristics of the silica surface[66]. Chemical modification of silica with silanes is a method to reduce the specific component of the surface energy. This modification increases the compatibility of silica with hydrocarbon elastomers, hence improves the filler dispersion, compound processability and vulcanizate properties. The ability of different elastomers in a blend to accept the fillers is generally accepted to be an important factor in attaining good dispersion, which in turn influences reinforcement and ultimate performance properties.

Wang et al.[67] demonstrated atomic force microscopy as a useful technique to study filler dispersion and rubber morphology at microscopic level. They concluded that compared to carbon blacks, silica has a poor dispersion even in presence of a coupling agent. In the case of elastomer blends, the phase detection mode can reveal microphase morphology and preferential location of the fillers in one of the phases[68].

2.4 Plasma polymerization

2.4.1 Introduction

Plasma polymerization is a process, in which gaseous monomers, stimulated through a plasma (fourth state of aggregation), condense on freely selectable substrates as highly cross-linked layers. The precondition for this process is the presence of chain-producing atoms, such as carbon, silicone or sulfur, in the working gas. The monomer molecules mostly become shattered into reactive particles in the plasma, and the remaining molecules are only partially disintegrated with part of the original structure preserved. The active molecules result in the formation of cross-linked and disordered structures.

Plasma polymerization is a very complex process that is so far not well understood. The structure of plasma-deposited films is highly complex and depends on many factors, including reactor design[69], power level[70], substrate temperature[71], frequency[72], monomer structure and pressure[73], as well as monomer flow rate[74,75]. Generally, two types of polymerization reactions can occur simultaneously:

- Plasma-induced polymerization;
- Polymer-state polymerization.

In the former case, the plasma initiates a polymerization reaction at the surface of liquid or solid subtrates[76]. For this to occur, monomers must contain polymerizable structures, such as double bonds, triple bonds, or cyclic structures. In the latter case, polymerization occurs in a plasma in which electrons and other reactive species have enough energy to break any bond. The rates at which monomers polymerize are relatively similar regardless of the structure of the monomer. Yasuda has shown that for various pairs of monomers with similar chemical structure but with and without vinyl double bonds, the difference in the rate of polymer deposition is very small[77].

Plasma polymerization is a unique technique for modifying polymeric and other material surfaces by depositing a thin polymer film[78-90]. Plasma deposited films have many special advantages:

1. A thin film with a thickness of a few tenths of nanometers to one micrometer can easily be prepared.
2. Films can be prepared with unique physical and chemical properties. Such films, highly cross-linked and pinhole-free, can be used as very effective barriers.
3. Films can be formed on practically any kind of substrate including polymers, metal, glass, and ceramics. In general, good adhesion between the film and substrate can be achieved.

2.4.2 General mechanism of plasma polymerization

Yasuda[77] represented plasma polymerisation by a bicyclic step-growth mechanism as shown in Figure 2.8:

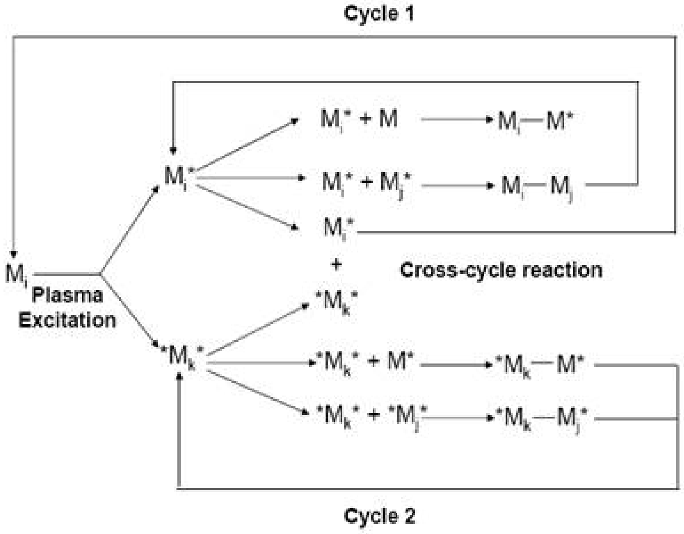

Fig. 2.8: Bicyclic step-growth mechanism of plasma polymerization[77]*.*

where i, j, and k indicate the difference in the size of species and M* represents a monofunctional reactive species which can be an ion of either charge, an excited molecule, or a free radical, produced from neutral species M, but not necessarily retaining the molecular structure of the starting material. M can be a fragment, or even an atom detached from the original starting material. *M* represents a bi-functional activated species.

As shown in the above cycles, the overall reaction contains two major routes of rapid growth. Cycle 1 is based on repeated activation of the reaction products from mono-functional activated species. Cycle 2 contains bi-functional or multifunctional activated species, which produce very possibly branches or crosslinks in the polymer structure. This explains why plasma polymers are usually crosslinked.

The total reaction rate shown in the above cycles is a function of electron density and electron energy and can be expressed as:

$R_{total} = f(N, E)$

where R_{total} is the total reaction rate, N the electron density and E the electron energy.

Plasma polymerization is a plasma-enhanced chemical vapor deposition process and proceeds in the vapor phase. As the polymerization proceeds, the growing polymer cannot remain in the vapor phase and diffuses to a surface. Reactive species in the gas phase, such as ions and free radicals, may simultaneously interact with surfaces inside the plasma reactor that have been activated by the impact of the glow discharge to form ions or free radicals from the surface molecules of substrates.

2.4.3 Plasma reactor types

Two different processes are used for plasma treatment based on the pressure in the reactor: low pressure plasma and atmospheric pressure plasma.

2.4.3.1 Low pressure plasma reactors

All types of low pressure plasma reactors have a number of internal parameters that define the plasma activity. These internal parameters are shown in Table 2.4, and they are determined by the external parameters and the plasma reactor operation conditions[91-97]. Low Pressure Plasma (LPP) presents many important advantages over ambient plasma for the treatment of surfaces, and some reactors have already been adapted to modify powdery materials. The high versatility of this type of reactors being able to change gas feed ratios, gas flow, time of treatment, power density amongst others, allow to tailor surface properties in a wide range.

Table 2.4: Internal and external parameters for low pressure plasma characterization[91-97].

Internal parameters	External parameters
- Fragmentation degree of the gas	- Pressure
- Density of neutral species	- Feed composition, flow rate, leaks
- Density and energy distribution of electrons	- Field frequency
- Ionization degree	- Power density
- Residence time of the species	- Reactor configuration, materials, electrode geometry
- Process homogeneity	- Substrate position
- Deposition, etching, treatment rate	- Substrate temperature
- Contaminations	- Substrate bias potential

Feed composition, flow rate, power density and substrate position are the most frequently studied parameters for a given reactor system which consequently affect internal parameters such as fragmentation degree, residence time of the species, or ion bombardment. For the generation of the plasma, most plasma sources use a radiofrequency at 13.56 MHz or 27 MHz. Another source that is also commonly used is microwaves at 2.53 GHz. Microwaves allow operating at higher pressures and giving higher plasma densities[91-97].

The most frequently used low pressure plasma reactors for powders are bell-jar reactors[93], down-stream reactors[94,95], rotary drum reactors[96], and fluidized bed reactors[97]. Figures 2.9 and 2.10 show the schematics of the bell-jar and down-stream reactors.

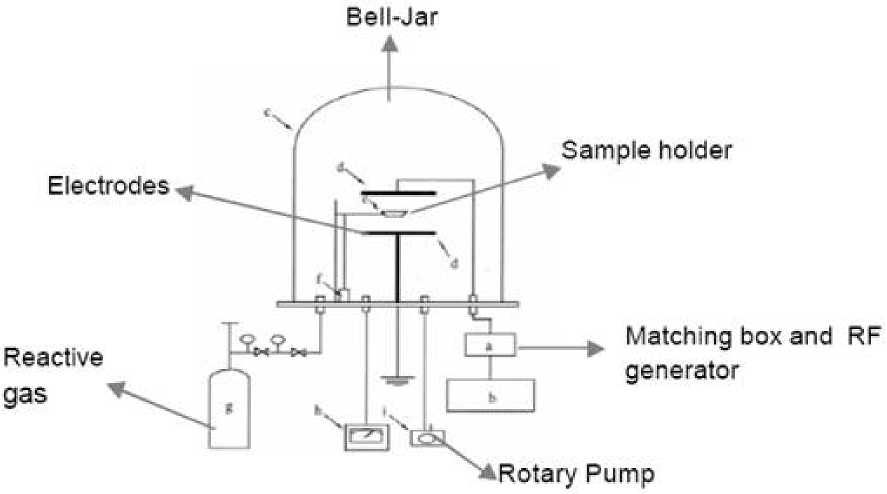

Fig. 2.9: Bell-jar reactor with vibrating device[93].

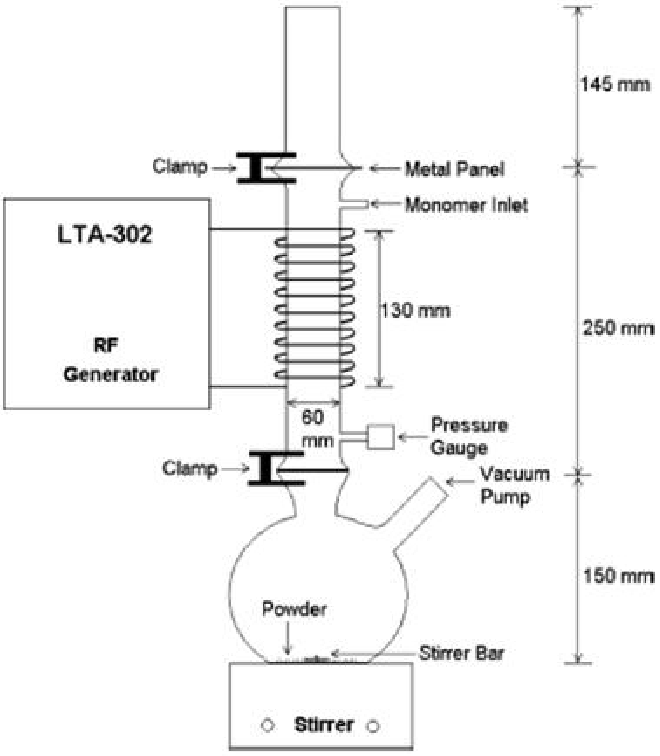

Fig. 2.10: Schematic view of vertical plasma reactor (down-stream reactor)[94,95].

2.4.3.2 Atmospheric pressure plasma reactors

Atmospheric Pressure Plasma (APP) fields are an attractive alternative to LPP processes, as the latter are difficult to scale up, especially in the case of continuous processes, and rather cost intensive. The main advantages of APP are the elimination of vacuum systems, reduction of costs, the possibility to use continuous systems and treatment of materials with high vapor pressure. However, these systems have drawbacks such as the glow instability and the inhomogeneity of the treated surfaces. Despite these problems, APP has been successfully used already in some fields such as etching, surface activation, ozone production and decontamination amongst others[98,99].

2.4.4 Effect of plasma polymerized surface coated rubber additives in rubber compounds

In terms of reinforcing fillers, there are some critical factors affecting the extent of reinforcement including the size of the filler particles, uniformity of dispersion in different phases of a blend and filler-polymer interactions. A high degree of reinforcement can be obtained with a high extent of polymer-filler interaction and uniform dispersion of fillers in the polymer matrix[100]. Wang stated that filler-filler interaction can be depressed by changing the surface characteristics, especially by a reduction of the surface energy. An alternative is the increase of the filler-polymer interaction and compatibility. Nah et al.[101,102] found that a surface modification of silica by plasma polymerization strongly affected the dispersion in an styrene-butadiene rubber (SBR) matrix and the physical properties of the vulcanizate. Akovali and Ulkem[103] conducted studies on plasma polymerization coating of carbon black. They reported improved mechanical properties such as tensile strength for SBR filled with plasma coated carbon black. Roh et al.[104] reported an enhanced mechanical strength of epoxy moulding compounds by acetylene plasma polymerization coating of silica. Vidal et al.[105] modified the surface of the accelerator N-cyclohexyl-2-benzothiazolesulfenamide (CBS) by a plasma polymerization process and found a change in the reactivity of CBS leading to a modification of the scorch time.

Little work was done on plasma polymerized silica fillers in elastomer blends: Van Ooij et al.[106,107] investigated two different types of pyrrole plasma polymerized silica fillers in a 70/30 natural rubber/styrene-butadiene rubber

(NR/SBR) blend. Partial replacement of silica by the plasma treated filler leads to an increase in viscosity, especially in comparison with silane-treated silica. Moduli were lower compared to the silanized silica, but tensile strength was not significantly influenced. Lee[108] observed that the surface modification of organo-clay by plasma polymerization strongly affected the dispersion and physical properties of an SBR vulcanizate.

2.5 Summary and focus of the project

In this chapter, the plasma polymerization technique and its role in surface modification of a substrate is discussed. By plasma polymerization, the surface properties of powders can be modified in order to improve various properties such as compatibility with different matrix materials, sorption, wettability, triboelectricity, barrier and insulation properties, adhesion, diffusion, friction, corrosion, dispersion, or flow behavior. Plasma polymerization is an environmentally friendly technique as it does not require any solvents and does not create problematic residues.

The reinforcement of elastomers by fillers is an important measure to improve the final vulcanizate properties. Silica is considered one of the most important reinforcing fillers for rubber. However, silica is hydrophilic and polar of nature, and that causes strong agglomeration of the particles by interparticle forces, which results in poor dispersion within the elastomer matrix and gives lower mechanical and dynamic properties to the filled elastomers. Presently, a coupling agent is used to overcome these problems and this is an absolute prerequisite for a proper performance of a silica reinforced rubber compound.

Another important aspect is the incompatibility of silica with different elastomers, which also affects the properties of the final vulcanizate. For full deployment of the rubber properties, each elastomer in a blend requires its own specific reinforcing fillers. Consequently, a proper distribution of the reinforcing fillers over the different elastomer phases is a requirement.

Based on the above discussion, the research described in this thesis focuses on the following points:

- surface modification of silica fillers with different monomers by using a plasma polymerization technique in order to reduce the surface energy;

- effect of plasma modified silica on the dispersion of the filler in different elastomer matrices in comparison to unmodified and silane-modified silica;
- selective compatibilization of silica and elastomers by matching the surface energy of the silica and the different elastomers in a rubber blend;
- a morphology study of the dispersion of silica.

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Chapter 3

Surface Modification of Silica by Plasma-Polymerization: Preparation and Characterization of Silica Coated with Different Monomers

Surface modification of precipitated silica powders was done by using a plasma-polymerization process. The monomers used for the plasma-polymerization were acetylene, pyrrole, and thiophene, chosen due to the different chemical moieties in their structure which might be active in the vulcanization process of the elastomers. Plasma film deposition was applied in order to improve the performance of silica in straight polymers such as S-SBR, NBR and EPDM as well as in their blends by better matching the surface energies of the silica filler and the rubbers. The uncoated and coated fillers were analyzed by immersion tests, water penetration measurements, determination of the relative surface area (CTAB), thermo-gravimetric analysis (TGA), time of flight- secondary ion mass spectroscopy (ToF-SIMS) and scanning electron microscopy with elemental analysis by energy dispersive X-ray spectroscopy (SEM/EDX). All techniques give evidence of film deposition on the surface of silica.

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M. Tiwari, W. K. Dierkes, J. W. M. Noordermeer, W. J. van Ooij, Polym. Adv. Technol., 19, 1672 (2008);

M. Tiwari, R. N. Datta, A. G. Talma, J. W. M. Noordermeer, W. K. Dierkes and W. J. van Ooij, Rubber Chem. Technol., 82, 473 (2009).

3.1 Introduction

Carbon black is considered an universal filler in a wide variety of elastomers. In an effort to further improve the final property profile of filled elastomers and to reduce the costs, several alternative materials have been tried as fillers. Research is reported on the substitution of carbon black by other fillers like silica, without adversely affecting the mechanical properties[1,2]. Nowadays, non-black fillers such as silica are gaining more importance compared to carbon black in the reinforcement of elastomers, especially in the tire industry due to their low hysteresis, resulting in a lower rolling resistance of tires at equal wear resistance and wet grip[3].

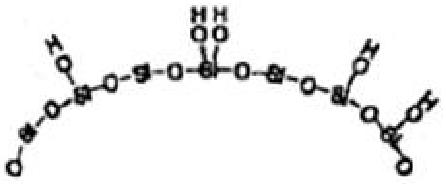


Fig. 3.1: Surface chemistry of silicas[4].

Figure 3.1 shows various functional groups which are detected on silica surfaces[4]. The polar surface of the filler particles enhances filler–filler interactions resulting in strong interparticular hydrogen bonds between silanol groups of the filler[5-7]. Besides, there is a considerable polarity difference between silica and the polymers. This causes two problems: First, the compounds are difficult to mix due to a low dispersibility of silica particles in the rubber matrix and a high viscosity of silica filled compounds[4,7-12]. Second, it results in poor reinforcement, giving e.g. inferior tensile properties and abrasion resistance.

Discussing structure and properties of silica filled rubber composites, the main focus is on the interaction between silica particles and between silica particles and rubber molecules. Wolff and Wang[12] studied the effect of differences in surface energy of fillers on rubber reinforcement, and reported that the surface energy of silica is characterized by a dispersive and a specific component. The high specific component of the surface energy leads to a high viscosity of the rubber composites due to strong interactions amongst silica particles. The low dispersive component causes weak filler-rubber interactions, leading e.g. to a lower content of bound rubber in the composites.

In this study, plasma-polymerized acetylene-, pyrrole- and thiophene-films are deposited onto the surface of silica filler aggregates by using a plasma-polymerization technique. The change in surface properties of the aggregates due to the film formation is investigated by immersion tests, water penetration measurements, thermo-gravimetric analysis (TGA), time-of-flight secondary ion mass spectrometry (TOF-SIMS), scanning electron microscopy (SEM), and energy dispersive X-ray (EDX) analysis.

3.2 Experimental

3.2.1 Materials

Conventional precipitated silica (Ultrasil VN3, Degussa GmbH) obtained in fluffy form was used as reinforcing filler in untreated as well as in surface-modified form. The monomers used for the surface modification in this study are shown in Table 3.1.

Table 3.1: Monomers used in the study.

Chemical name	Source
Acetylene (C_2H_2), 99.9 % purity	Wright Brothers, Inc.
Pyrrole (C_4H_5N), 99.9 % purity	Sigma-Aldrich GmbH
Thiophene (C_4H_5S), 99.9 % purity	Sigma-Aldrich GmbH

3.2.2 Plasma-polymerization of silica

For the surface modification of silica, a radiofrequency (13.56 MHz) electrodeless tumbler plasma reactor was used. The design of the reactor is shown in Figure 3.2.

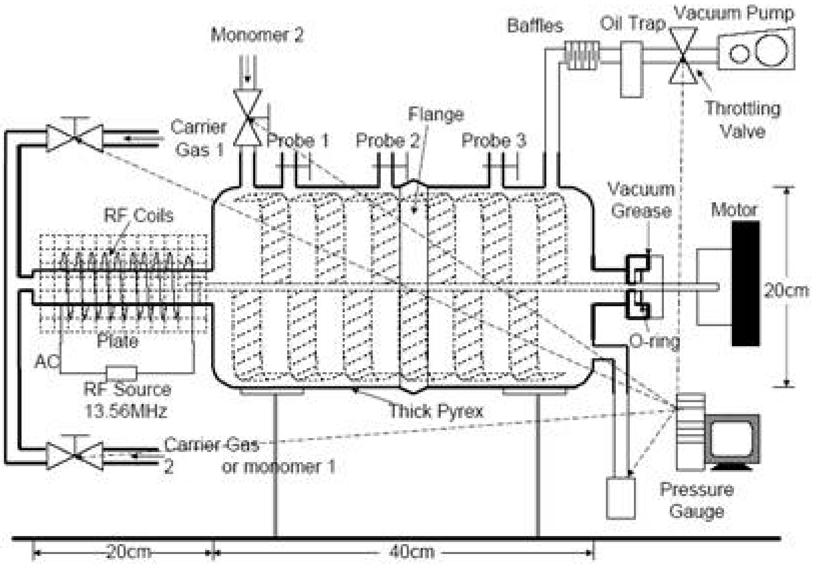


Fig. 3.2: Schematic representation of the tumbler RF plasma reactor for plasma-polymerization for the deposition on powders.

This reactor consisted of a Pyrex cylinder chamber of 40 cm in length and 20 cm in diameter, with a motor-driven shaft at its centre, and two vanes running in opposite direction and attached to the shaft for refreshing the powder surface exposed to the plasma phase, as well as a manual impedance matching system. The reactor was based on a horizontal mixing principle and was capable of treating approx. 350 g/batch.

Plasma-polymerization was carried out after charging 100 g of dried silica into the reactor, pumping down to 13 Pa and introducing plasma gases or monomer vapours for further plasma-polymerization. The operating pressure was adjusted by varying the monomer gas or vapour flow through a needle valve. The conditions for the plasma- polymerization of acetylene (PA), pyrrole (PPy) and thiophene (PTh) are presented in Table 3.2. The sample designations are also listed in Table 3.2.

Table 3.2: Plasma-polymerized acetylene-, pyrrole- and thiophene-film deposition conditions used for the surface modification of silica filler powders.

Designations	Power (W)	Monomer Pressure (Pa)	Time (min)
PA-silica	100	53	90
PPy-silica	100	33	90
PTh-silica	100	20	90

3.2.3 Characterization techniques used for plasma modified silica powders

3.2.3.1 Hydrophobicity: immersion test and water penetration measurements

A simple test to assess the changes in hydrophobicity of the filler surface is the immersion test. This test is done to check the hydrophilic or hydrophobic nature of powders by pouring a small amount of powder onto the surface of a liquid: the powders either floats or sinks in the liquid. This gives an indication of the change in the surface energy of powders. Liquids such as toluene, formamide, ethylene glycol, glycerol, n-hexane, cyclohexane, and water were used.

Another method for a more quantitative measurement of the hydrophobicity is the water penetration method: A glass column is packed with 5 mg of the filler, and one opening is sealed by a very fine nylon mesh (pore size: 20µm). The sealed end of the column is placed in water, and the change in weight over time is measured with a balance[13].

3.2.3.2 Specific surface area: CTAB-measurements

The determination of the specific surface area was done by the cetyltrimethyl ammonium bromide (CTAB) adsorption method, according to ISO 6810. This method allows measuring the external surface area which is considered to most readily correspond with the accessible surface of silica for elastomer molecules.

3.2.3.3 Deposited material: Thermo-Gravimetric Analysis (TGA)

A Perkin-Elmer instrument (TGA 7) was used for the thermal analysis. The heating temperature was varied from 50ºC to 600ºC at a rate of 10ºC/min, and air was used as purging gas. These measurements provide information about the weight of the plasma-polymer coating per unit weight of the filler.

3.2.3.4 Chemical structure of the film: Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS)

Secondary ion mass spectroscopy (SIMS) is one of the most sensitive techniques for surface characterization of complex materials. The information obtained from SIMS describes the chemistry of the surface layer. Static SIMS produces molecular ion fragments that are indicative of the particular chemical structure being analyzed prior to primary ion beam modification of the sample. The TOF-SIMS analysis was performed on a CAMECA ION-TOF Model IV spectrometer. This instrument was equipped with a reflection-type Time-of-Flight mass analyzer and a pulsed 25 kV primary source of monoisotopic $^{69}Ga^{+}$ ions, with a minimum beam size of 500 Ǻ.

3.2.3.5 Morphology: Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy (SEM/EDX)

A Philips Environmental-SEM/EDX (Philips XL30) was used to measure the morphology of untreated and plasma-polymer film deposited silica filler powders. The powders were fixed on the sample holder by double conductive adhesive aluminum tape, and then gold-coated. Secondary electron images were recorded by the scanning electron microscope using a 15 keV acceleration voltage. EDX data were obtained at the same time.

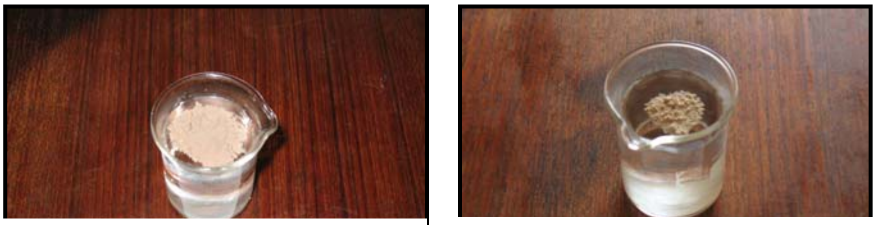
3.3 Results

3.3.1 Immersion test and water penetration measurements

Before plasma-treatment, the silica powder was highly hydrophilic and immediately sank in water. After PA-, PPy- and PTh-film deposition, the material floated on the water surface for several hours as shown in Figure 3.3.

Untreated silica powder

Plasma-acetylene treated silica powder



Plasma-pyrrole treated silica powder

Plasma-thiophene treated silica powder

Fig. 3.3: Immersion test of untreated, plasma-polymerized acetylene-, pyrrole-, and thiophene-coated silica.

The immersion test of silica samples in liquids of known surface tension gives an indication of the surface energy of the different silica samples. The change in surface energy of untreated and plasma-treated samples is shown in Figure 3.4. After the deposition of plasma-polymerized acetylene-, pyrrole- and thiophene-film on the silica surface, a significant reduction in surface energy compared to untreated silica is found: while untreated silica has a surface tension higher than that of water, the three coated samples have values in the range between toluene and ethylene glycol.

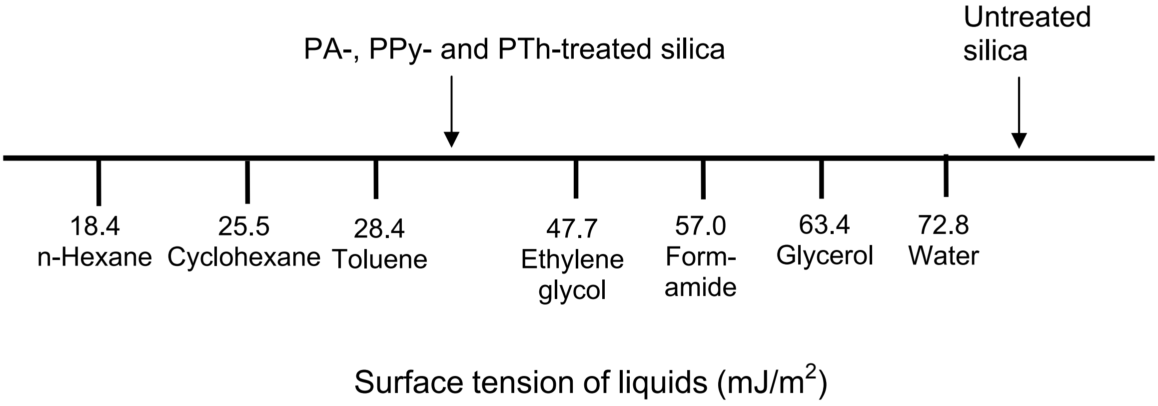


Fig. 3.4: Surface tension of untreated, plasma-polymerized acetylene-, pyrrole-, and thiophene-coated silica.

The results of water penetration into powder beds of untreated and plasma-treated silica are shown in Figure 3.5: The untreated silica absorbs water very fast, whereas the PA-, PPy- and PTh-silica show a significantly decreased water penetration rate. The lowest rate is found for the PTh-silica. This is another more quantitative indication that the surface energy of the silica was decreased by the plasma coating.

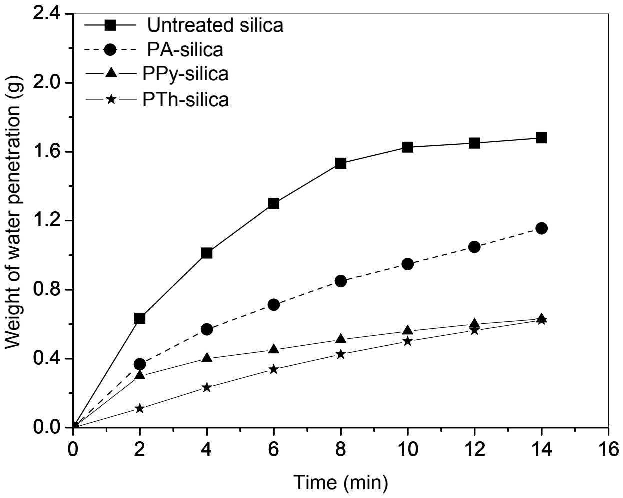


Fig. 3.5: Water penetration into powder beds of untreated, plasma-polymerized acetylene-, pyrrole- and thiophene-coated silica.

3.3.2 CTAB-measurements

The specific CTAB surface areas of untreated and treated silica powders are listed in Table 3.3: There is only a slight difference between the specific surface areas of untreated and PPy and PTh-silica: the relative surface area is reduced by app. 5%. PA-silica has an intermediate position between these silica types.

Table 3.3: CTAB results for untreated and treated silica fillers.

	Untreated silica	PA-silica	PPy-silica	PTh-silica
CTAB surface area (m^2/g)	232	226	219	218

3.3.3 Thermo-Gravimetric Analysis (TGA)

The TGA curves of untreated, PA-, PPy-, and PTh-polymerized silica are shown in Figures 3.6-3.8. The difference in weight loss between coated and untreated silica corresponds to the weight of the plasma-polymerized film deposited on the surface. The untreated silica looses 5 wt% in two stages while heating up to 600°C. The initial weight loss of 2.3% between 50°C to 150°C is due to the evaporation of loosely bound water molecules. The hydroxyl groups start to condense and thus to liberate water when silica is heated above 150°C[14]. In the case of PA-, PPy- and PTh-silica, an extra weight loss is observed: In the temperature range between 50 and 600°C this extra weight loss is 5 wt% for PA-silica, 1.1 wt% for PPy-silica, and 3 wt% for PTh-silica compared with untreated silica. In Figures 3.6-3.8, the weight loss seems to be not completed upto 600°C. This is due to the presence of crystal water in silica, which continues to be removed by heating silica to even higher temperatures than 600°C. It causes a problem to use this technique for real quantitative analyses of the amounts of coatings deposited.

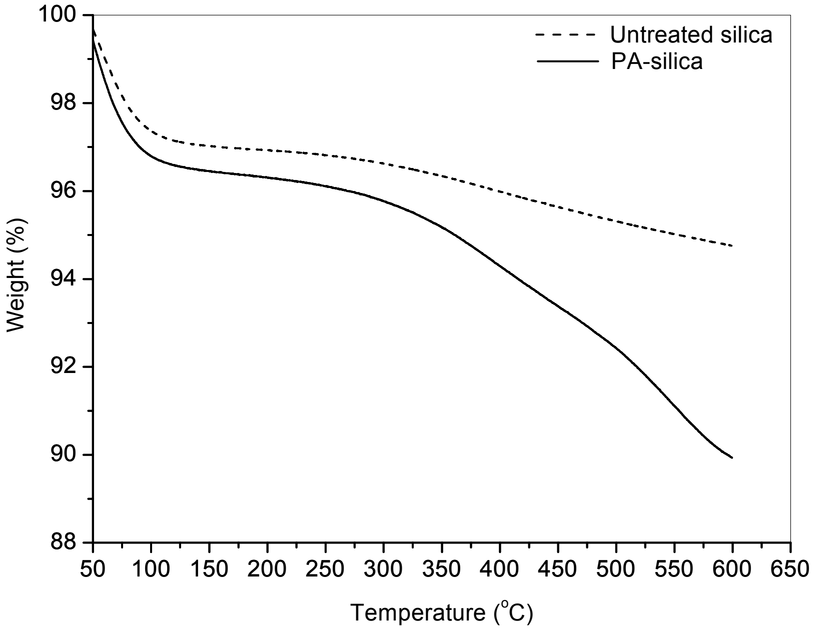


Fig. 3.6: TGA analysis of untreated and plasma-polymerized polyacetylene (PA) coated silica.

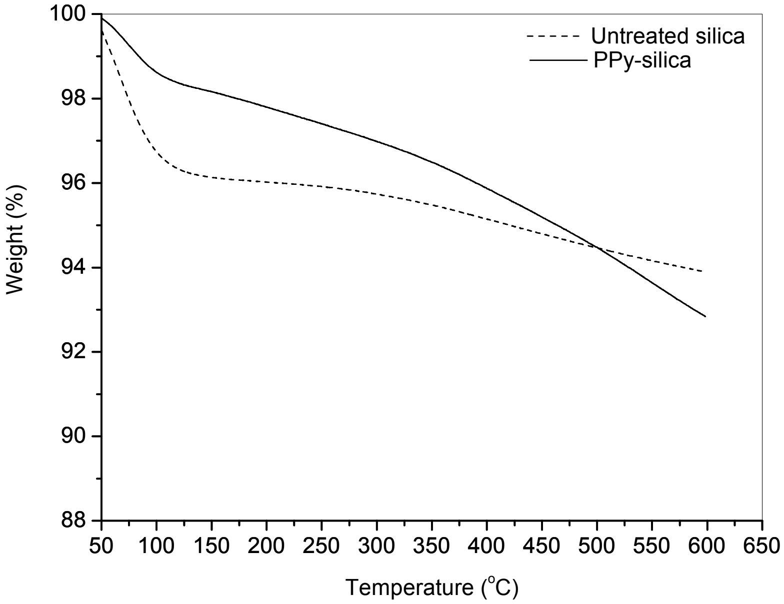


Fig. 3.7: TGA analysis of untreated and plasma-polymerized polypyrrole (PPy) coated silica.

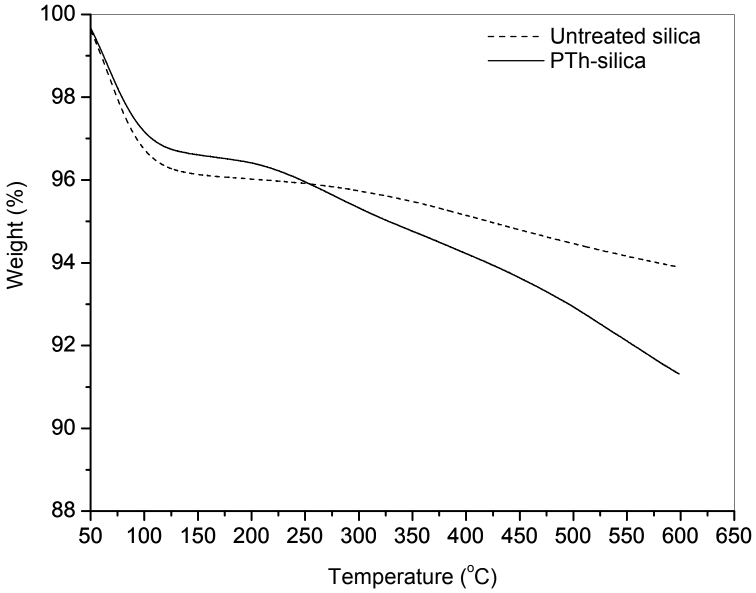


Fig. 3.8: TGA analysis of untreated and plasma-polymerized polythiophene (PTh) coated silica.

3.3.4 Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS)

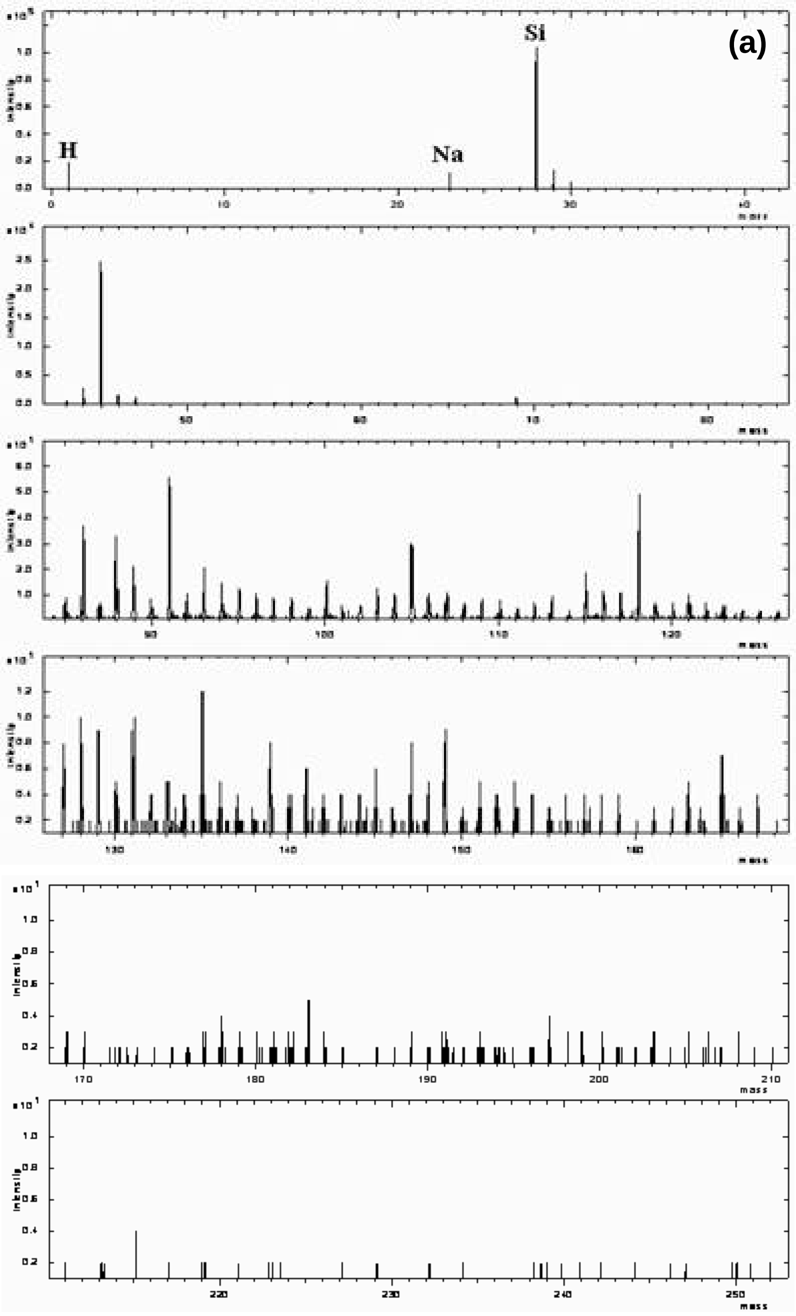
The TOF-SIMS spectra were recorded of the untreated and treated silicas. The peak assignments for some significant peaks are listed in Table 3.4[15]. Figures. 3.9 and 3.10 show the deposition of a complex structure of a plasma-polymerized acetylene film on the silica surface. Positive and negative spectra are shown for both samples.

Table 3.4: Ion fragments in positive ToF-SIMS spectra.

Mass (a.m.u.)	Composition
Positive Spectrum	
+ 1	H^+
+ 15	CH_3^+
+ 23	Na^+
+ 27	$C_2H_3^+$
+ 28	Si^+
+ 29	SiH^+; $C_2H_5^+$
+ 39	$C_3H_3^+$
+ 41	$C_3H_5^+$
+ 43	$C_3H_7^+$
+ 130	$C_{10}H_{10}^+$
+ 169	$C_{12}H_{25}^+$
+ 171	$C_{13}H_{15}^+$
+ 172	$C_{13}H_{17}^+$
+ 175	$C_{13}H_{19}^+$
+ 178	$C_{14}H_{10}^+$
+ 183	$C_{13}H_{27}^+$
+ 185	$C_{14}H_{17}^+$
+ 187	$C_{14}H_{19}^+$
+ 189	$C_{14}H_{21}^+$
+ 191	$C_{15}H_{11}^+$
+ 193	$C_{15}H_{13}^+$
+ 195	$C_{14}H_{27}^+$
+ 197	$C_{14}H_{29}^+$
+ 201	$C_{15}H_{21}^+$
+ 202	$C_{16}H_{10}^+$
+ 215	$C_{16}H_{23}^+$

In Fig. 3.9 (a), the spectra of the untreated silica sample, no specific peaks in the low mass region up to 150 a.m.u. (atomic mass units) such as related to $C_2H_3^+$, $C_{10}H_{10}^+$, and no cluster peaks in the higher mass region are found. In Figure 3.10 (a), the acetylene-monomer treated sample shows specific plasma-polymerized acetylene peaks in the low mass region and strong acetylene-cluster peaks in the higher mass region, indicating a polymeric surface coating on the silica powders.

The spectra of the negative ions of untreated and PA-coated samples are shown in Figures 3.9 (b) and 3.10 (b). In Figure 3.9 (b), the spectrum from the untreated silica powders have no specific peaks such as related to C^-, CH^- in the mass range of 0-40 a.m.u. In Figure 3.10 (b), the sample shows C^- peaks in this mass region as another proof of the surface coating on the silica powders.



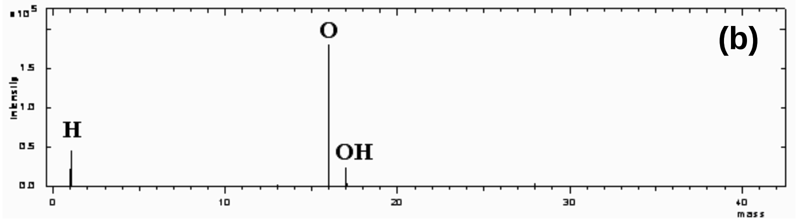
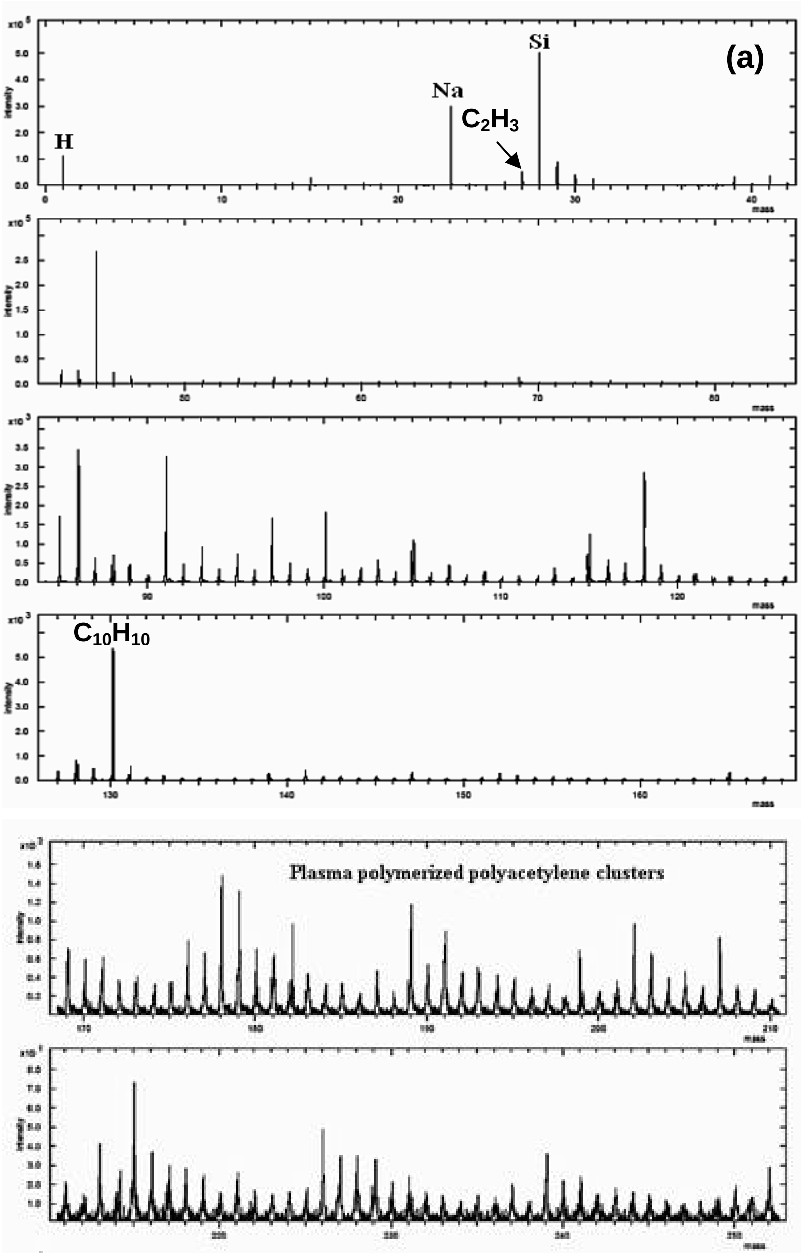


Fig. 3.9: ToF-SIMS spectra of untreated silica (a) positive spectra; (b) negative spectrum.



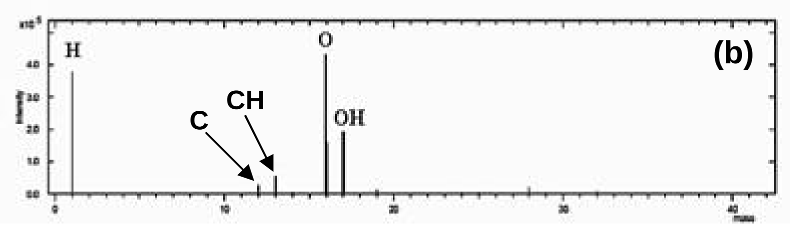
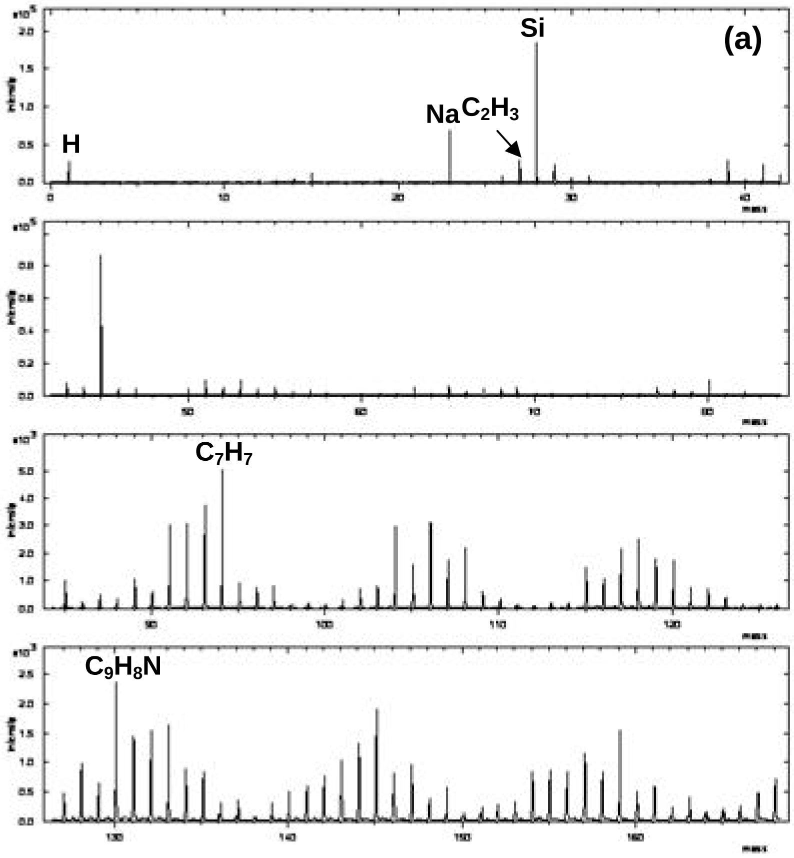


Fig. 3.10: ToF-SIMS spectra of plasma-acetylene coated silica: (a) positive spectra; (b) negative spectrum.

Figure 3.11 (a), the positive spectra of the pyrrole-treated sample, shows the specific plasma-polymerized pyrrole peaks in the low mass region and strong polypyrrole cluster peaks in the higher mass region. This indicates that the surface of the silica powder is covered with a polypyrrole film. Figure 3.11 (b), the negative spectrum of the sample, shows an intense hydrogen peak, a carbon peak at 12 a.m.u., and less intense oxygen and hydroxyl peaks. The presence of nitrogen is detected as the hydrocarbon derivative of nitrogen in the form CN^- at 26 a.m.u.



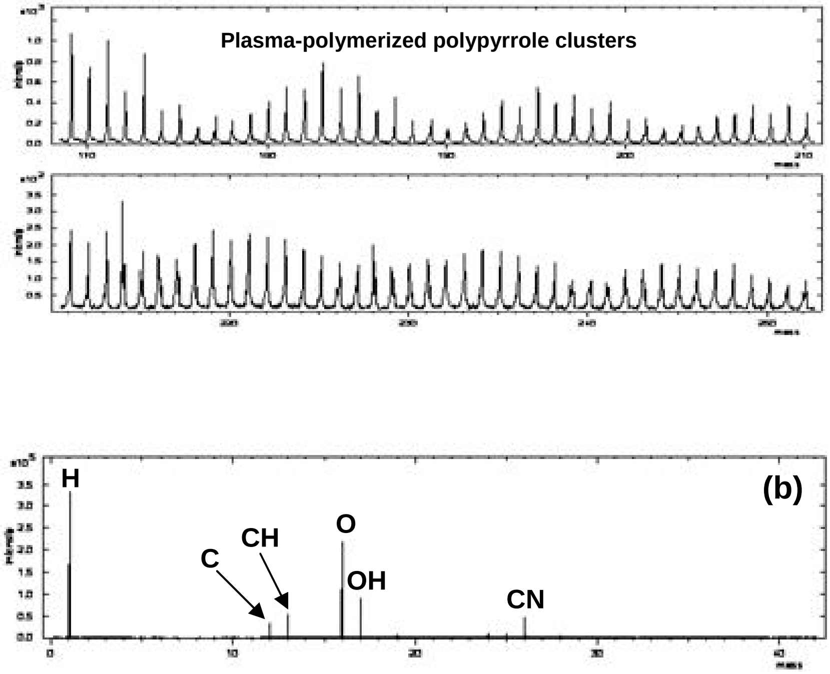


Fig. 3.11: ToF-SIMS spectra of plasma-pyrrole coated silica fillers: (a) positive spectrum; (b) negative spectrum.

In Figure 3.12 (a), again the characteristic peaks prove the presence of a polythiophene coating. In Figure 3.12 (b), the negative spectrum of the sample shows an intense hydrogen peak, as well as a carbon peak at 12 a.m.u., and less intense oxygen and hydroxyl peaks. The presence of sulphur was detected at 32 a.m.u. The result proves the deposition of a polythiophene film on the surface of the silica powders.

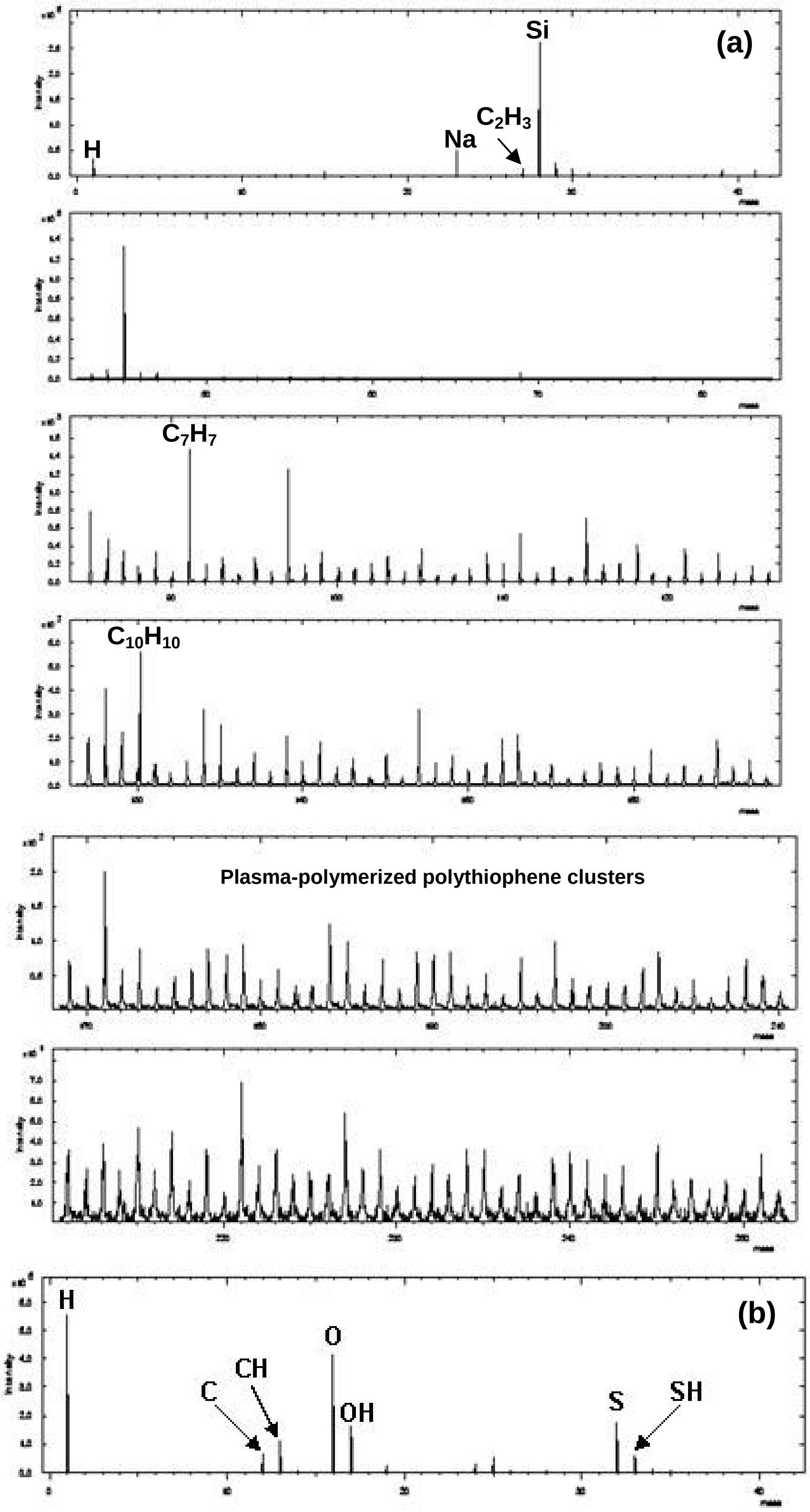


Fig. 3.12: ToF-SIMS spectra of plasma-thiophene coated silica fillers: (a) positive spectrum; (b) negative spectrum.

3.3.5 Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy (SEM/EDX)

From SEM-images, the morphology of the untreated and plasma-treated silicas can be derived. EDX can provide information on the relative amount of different elements present on the surface. SEM images of untreated and acetylene-treated samples are shown in Figure 3.13. The untreated silica is shown in Figure 3.13 (a), where aggregates of different sizes composed of primary particles are visible. Figure 3.13 (b), the PA-sample, shows a clear difference in dimensions in comparison with the untreated silica powder: The film deposition is occurring onto the small-size aggregates, resulting in larger spherical particles connected into an open structure.

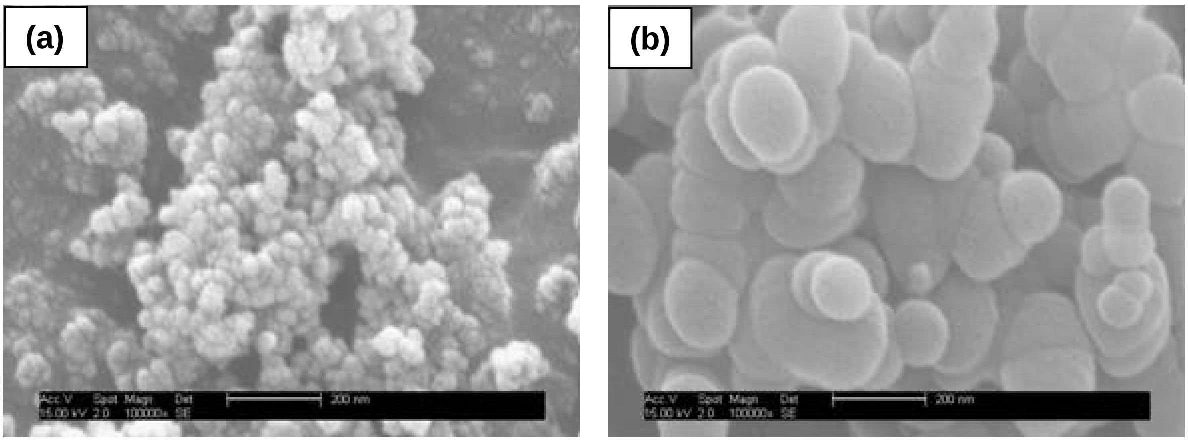


Fig. 3.13: SEM images of untreated and plasma-acetylene coated silica fillers at 100,000X (a) untreated; and (b) PA-treated silica.

Typical percentages of carbon, silicone and oxygen on the surface of untreated and treated samples as measured by EDX are shown in Table 3.5. In Table 3.5, the carbon content increased significantly after the PA-coating, while oxygen and silicone decreased, indicating the deposition of the plasma-polymerized film on the surface. With the PPy- and PTh-coating on the silica surface as shown in Tables 3.5, the carbon content increases sharply in each case, indicating a significant covering with the deposited PPy- and PTh-film. The EDX data show the presence of nitrogen and sulphur as expected from the chemical structure of pyrrole and thiophene. All plasma-polymerized samples in these tables show high contents of carbon, which reconfirms the TOF-SIMS and TGA results.

Table 3.5: Chemical composition of untreated, plasma-polymerized acetylene-, pyrrole-, and thiophene-treated silica.

	Untreated Silica			PA-silica			PPy-silica			PTh-silica		
Element	Atomic (%)	O/C	Si/C	Atomic (%)	O/C	Si/C	Atomic (%)	O/C	Si/C	Atomic (%)	O/C	Si/C
C	15.8	3.1	2.2	59.8	0.5	0.2	76.0	0.17	0.03	71.0	0.31	0.09
O	49.4			28.2			13.0			22.0		
Si	34.6			11.9			2.0			6.0		
N	-			-			9.0			-		
S	-			-			-			0.53		

3.4 Discussion

The morphological properties of active fillers are important aspects for rubber reinforcement. The structure of the filler is characterized by aggregates of primary particles, which form cavities for attachment and penetration of polymer molecules. The SEM-pictures of Figure 3.13 tend to show, that a thick plasma coating covers the fine-structure of the silica-aggregate. The individual primary particles are not visible any more; they are transformed into coarser sub-clusters within the aggregate. However, the three dimensional morphology is basically maintained. Furthermore, the SEM-pictures show that there is no breakdown of aggregates into smaller entities during the plasma process. It indicates that the functionality of silica is maintained during the surface treatment.

The relative surface area of silica aggregates correlates with its reinforcing effect in rubbers. After plasma treatment of silica, the minor reduction in surface area indicates no significant change in the reinforcing potential in rubbers. As the basic structure is also maintained, it is expected that the filler still has its reinforcing potential. TGA measurements show the deposition of PA-, PPy- and PTh-film on the silica surface. In all three cases, the amount of plasma-film deposition is different. The calculated coating thickness as based on the CTAB surface area and the measured weight loss for PA-, PPy- and PTh-film on the silica surface is 2 Å, 0.5 Å and 1.3 Å, respectively. This can be due to different stabilities of reactive species (radicals, ions and neutral species) during the plasma process. The high TGA weight loss for PA-silica indicates an effective film deposition due to a easier formation and higher stability of reactive species during the plasma process compared to pyrrole and thiophene. The thin coating layers as derived from the TGA- and

CTAB-measurements do not seem to correspond with the apparent thick coverage seen in the SEM-picture 3.13. The further tests with these materials in the next chapters may shed some further light on this apparent inconsistency.

The water penetration measurements as shown in Figure 3.2 do not show a correlation with the TGA weight loss values: PPy- and PTh-silica are more hyrdrophobic compared to PA-silica. One explanation can be the structure of the film: a complete coverage by a thin film layer would result in an optimal hydrophobation, in deposition in isolated areas with an island-like structure. Another factor is the presence of different chemical moieties in the complex film structure formed on the silica surface. PPy- and PTh-silica show the presence of a higher amount of carbon with nitrogen and sulfur moieties and less oxygen as measured by EDX compared to PA-silica. The reduction in the amount of oxygen in PPy- and PTh-silica decreases their polarity and thus their interaction with water. This increases the hydrophobicity of PPy- and PTh-silica compared to PA-silica.

3.5 Conclusions

A plasma-polymerized polyacetylene-, polypyrrole- and polythiophene-film could successfully be applied onto silica aggregates. Immersion tests and water penetration measurements showed a significant change in surface energy after film deposition: the PA-, PPy- and PTh-coated aggregates are less hydrophilic compared to untreated silica. The increased weight-loss measured by TGA confirmed the deposition of a plasma-polymer film onto the silica surface. ToF-SIMS spectra showed well-defined polyacetylene, polypyrrole and polythiophene cluster peaks in the higher mass region.

SEM pictures showed that the plasma coating covers the fine-structure of the silica-aggregates. The individual primary particles are not visible anymore, but are transformed into coarser sub-clusters within the aggregates. The individual primary particles are not visible anymore, but are transformed into coarser sub-clusters within the aggregates. The SEM pictures also show that no breakdown of aggregates into smaller entities occurs during the plasma process. This indicates that the functional properties of silica are not significantly changed by the surface treatment, and that the three-dimensional aggregate-structure is maintained. The specific surface area as measured by CTAB absorption and relevant for the polymer-filler interaction was only slightly changed. The elemental analysis by EDX, showing an increased carbon content for all plasma-treated silica's and the presence of nitrogen and sulfur on the surface of the PPy- and PTh-silica, confirm a film deposition on the silica surface.

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Chapter 4

Reinforcement of S-SBR by Plasma-Polymerized Acetylene-, Pyrrole- and Thiophene-Coated Silica

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The filler surface chemistry is a crucial factor for dispersion and filler-polymer interaction in rubber compounds, as they strongly influences the final vulcanized properties of the rubber article. Acetylene, thiophene and pyrrole are used as monomers for plasma-coating of silica, and the surface-treated silica's are blended with S-SBR, and their dispersion and reinforcing effects are investigated. As reference, untreated and silanized silica are used. The relative rankings of reduction in filler-filler interaction: improved dispersion, enhanced polymer-filler interaction, apparent crosslink density and tensile mechanical properties are mutually different: Where the best silica-dispersion and largest reduction in filler-filler interaction is obtained with polyacetylene coating, respectively the worst with polythiophene coating, the tensile properties achieved with the polythiophene coating are far better than all others. Apparently, the sulfur contained in the thiophene moiety enhances the filler-polymer interaction and contributes to the degree of cross-linking. Unmodified silica performs worst in all aspects, also because its acidic nature harms the preferably alkaline vulcanization process. Silane-treatment of silica has a positive effect on reduced filler-filler interaction and improved dispersion, but not on polymer-filler interaction in the still not-vulcanized state. The tensile properties after vulcanization are comparable with polyacetylene- or polypyrrole-coated silica.

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M. Tiwari, W. K. Dierkes, J. W. M. Noordermeer, W. J. van Ooij, Rubber Chem. Technol., 81, 276 (2008);
M. Tiwari, W. K. Dierkes, J. W. M. Noordermeer and W. J. van Ooij, Polym. Adv. Technol., 19, 1672 (2008);
M. Tiwari, R. N. Datta, A. G. Talma, J. W. M. Noordermeer, W. K. Dierkes and W. J. van Ooij, Rubber Chem. Technol., 82, 473 (2009).

4.1 Introduction

The improvement of rubber properties has always been a subject of special interest. Since decades, styrene-butadiene rubber (SBR) has been used in passenger car tire tread compounding. In the case of elastomers like SBR, which do not undergo strain-induced crystallization, the use of fillers improves the mechanical properties, next to improvements in processability, and these fillers reduce the cost of rubber articles. Carbon black is considered as a universal reinforcing filler in elastomers like SBR. However, silica is more and more replacing carbon black, partially or completely[1]. The silica success is based on its ability to provide simultaneously an excellent wet traction and winter performance with a good reduction in rolling resistance of tires in comparison with carbon black[2,3].

The surface of silica contains hydroxyl groups which makes it polar. Therefore, silica can interact very well with polar elastomers, but at the same time, the polar surface of silica enhances filler-filler interactions[4,5]. The hydrophilic nature of the silica surface and the tendency to form hydrogen bonds cause strong filler-filler interactions which prevent easy dispersion during mixing and, as a consequence, negatively influence the final physical properties of the compounds[6]. Furthermore, silica can re-agglomerate after mixing, resulting in a poor dispersion in the elastomeric matrix[7]. To overcome the poor filler-polymer interaction and the strong filler-filler interaction, the silica surface can be modified in a coating process. This can be done either with coupling agents or by coating the filler surface with a suitable polymer. The commonly used coupling agents are bifunctional organosilanes like bis(triethoxysilylpropyl)-tetrasulfide (TESPT)[8]. The silane coupling agents react with silanol groups on the surface of silica and form siloxane bonds.

The silica dispersion in elastomers can thus be improved by surface modification techniques[9]. Plasma polymerization is a proven technology, whose application for filler coating is rather new. The advantage of plasma-polymerization is that it does not affect the bulk properties of the material[10-15]. Plasma polymerization of simple monomers (i.e., hydrocarbons) produces films that are highly crosslinked, thermally and chemically stable, and very adherent to the surface of a substrate. Furthermore, plasma-polymerized films can be prepared from monomers that cannot be polymerized by conventional chemical reactions (i.e., methane, ethane, saturated hydrocarbons, or organo-metallic compounds).

Recently, surface modification by plasma-polymerization received attention as it allows to improve the wettability of reinforcing fillers like carbon black, silica, clay, talc, etc. It is a valuable alternative to existing surface modification techniques as it is an environmentally clean process and causes less pollution than other techniques.

In the previous chapter, the preparation and characterization of a plasma-coating onto silica was described with acetylene-, pyrrole- and thiophene-monomers in order to reduce the surface energy. The purpose of the present study is to understand the reinforcement effect of these plasma-treated silica's based on different monomers with special attention to dispersion and compatibilization. Silane-modified silica is used as a reference in the study.

4.2 Experimental

4.2.1 Materials

Solution SBR (Buna® VSL 5025-0 HM, Lanxess GmbH) containing 25% styrene and 75% butadiene, of which 50% in the vinyl configuration, was used as polymer.

Conventional precipitated silica (Ultrasil VN3, Degussa GmbH) obtained in fluffy form, was used as reinforcing filler in untreated as well as in surface-modified form. High purity acetylene gas, pyrrole and thiophene monomers for the plasma polymerization were obtained from Wright Brothers, Inc and Sigma-Aldrich GmbH. A detailed description of the preparation and characterization of polyacetylene-, pyrrole- and thiophene-coated silica's is given in Chapter 3 of this thesis. Other chemicals used in this study are shown in Table 4.1.

Table 4.1: Chemicals used in the study.

Chemical	Trade name	Source
Toluene (Analytical Reagent grade)	-	Sigma-Aldrich GmbH
Bis-(triethoxysilylpropyl) tetrasulfide (TESPT)	Si69	Degussa GmbH
Sulfur (S)	-	Solvay
N-Cyclohexyl-2-benzothiazolesulfenamide (CBS)	Santocure CBS	Flexsys N.V.
N,N'-Diphenylguanidine (DPG)	Perkacit-DPG	Flexsys N.V.

4.2.2 Preparation of rubber compounds

The basic formulations used for the S-SBR compounds are given in Table 4.2. In the recipe, the amount of sulfur is adjusted to compensate for the presence of sulfur contained in TESPT, to represent equimolar quantities in all cases.

Table 4.2: Basic formulations of silica reinforced S-SBR.

Components	**Samples**				
	SU	**SPA**	**SPPy**	**SPTh**	**ST**
	phr	phr	phr	phr	phr
S-SBR	100	100	100	100	100
Silica	50	50	50	50	50
ZnO	2.5	2.5	2.5	2.5	2.5
Stearic acid	2.5	2.5	2.5	2.5	2.5
Silane (TESPT)	--	--	--	--	4
Sulfur	1.5	1.5	1.5	1.5	1.04
CBS	1.5	1.5	1.5	1.5	1.5
DPG	1.5	1.5	1.5	1.5	1.5

Sample codes: S: *Styrene-butadiene rubber;* ***U:*** *Untreated silica;* ***PA:*** *Plasma-acetylene coated silica;* ***PPy****: Plasma-pyrrole coated silica;* ***PTh:*** *Plasma-thiophene coated silica;* ***T:*** *Silanized silica*

The samples were mixed in three steps: For the first two mixing steps, a 350S Brabender® Plasticorder internal mixer with a mixing chamber volume of 390 ml was used. The mixing procedure for the first two steps is shown in Table 4.3. The starting temperature was 50°C and the cooling medium was kept at a constant temperature of 50°C. The rotor speed was found to be optimal at 85 rpm. Sulfur and accelerators were added in a third mixing step on a Schwabenthan 100 two-roll mill at a temperature setting of 40ºC.

For the reference samples making use of TESPT, the addition of the coupling agent TESPT directly into the internal mixer is commonly applied for modification of the surface of silica. The important parameters to obtain a good silanization reaction with the silica surface are temperature, time of reaction and removal of ethanol[8,16,17]. Rotor speed and mixing time were adjusted to obtain an average dump temperature between 140°C and 155°C for a good silanization reaction to occur with the silica.

Table 4.3: Mixing procedure for 50 phr silica reinforced S-SBR.

Step 1	
Time (min)	**Action**
0	Filling of the chamber of the internal mixer with gum rubber, lowering of the ram.
1	Raising of the ram and adding ZnO, stearic acid, ½ silica and ½ silane (if applicable), lowering of the ram.
2	Raising of the ram and adding ½ silica and ½ silane (if applicable), lowering of the ram.
4	Sweep
6	Dump
Step 2	
Time (min)	**Action**
0	Load compound
5	Dump

4.2.3 Rheological measurements of unvulcanized compounds

Dynamic mechanical measurements were performed using a RPA2000 dynamic curemeter (Alpha Technologies) at a temperature of 100ºC, a frequency of 0.5 Hz and a strain amplitude in the range from 0.56% to 100.04%.

In dynamic mechanical measurements, with increasing strain amplitude, reinforced samples display a decrease of the storage shear modulus G', commonly designated as the Payne effect, due to progressive destruction of the filler-filler network[18,19]. The stronger the filler-filler interaction, the more pronounced the decrease in storage modulus with increasing strain. In the present chapter, the $\Delta G'$-values calculated from the difference in G'-values measured at 0.56% strain and at 100.04% strain in the unvulcanized state are used to quantify the Payne effect.

4.2.4 Bound rubber measurements and TGA measurements on the bound rubber extract

The bound rubber content was measured with toluene as solvent[20,21]. The unvulcanized samples (0.2 g) were cut into small pieces and put into a steel-wire basket of a very fine mesh, which was immersed in 100 ml of toluene at room temperature for 72 hours. The solvent was renewed after 24 hours. The extracts were collected and left for 24 hours in air and 24 hours in vacuo at 105ºC to evaporate the solvent. The amount of bound rubber (BDR) is expressed as a percentage of the total polymer content in the compound.

TGA measurements were performed on the extracted dried material of the BDR-test. A small amount of the dried insoluble rubber material was heated to 600ºC in a thermal gravimetric analyzer (Perkin-Elmer TGA 7) with a heating rate of 10ºC/min. The weight loss values were compared to the bound rubber values measured as described above.

4.2.5 Cure characteristics and curing

The cure characteristics were determined using the same RPA2000 dynamic curemeter (Alpha Technologies). The increase in torque at a temperature of 160ºC, a frequency of 0.833 Hz and 2.79% strain was measured. The optimal vulcanization time, defined as the time to reach 90% of the difference between minimum and maximum torque value (t_{90}), was determined and used for the duration of the curing of the samples in the press.

4.2.6 Reinforcement parameter

The reinforcement parameter (α_F)^{22} was determined according to equation 4.1:

$$\frac{S'_{max} - S'_{min}}{S'^{0}_{max} - S'^{0}_{min}} - 1 = \alpha_F \cdot \frac{m_F}{m_p} \qquad (4.1)$$

where:

$S'_{max} – S'_{min}$ = curemeter torque difference of silica filled compounds;

$S'^{0}_{max} – S'^{0}_{min}$ = torque difference of the gum compound without silica;

m_F/m_P = filler loading, where m_F and m_P correspond to the mass fractions of filler and polymer, respectively;

α_F = a filler specific constant which is independent of the cure system and is closely related to the morphology and reinforcing power of the filler.

The value is measured by comparing the cosslinking isotherms of a filled and an unfilled elastomer compound using torque measurements in a curemeter. The α_F-value can be correlated with the dispersion of fillers in the elastomer matrix, as the viscosity of the compound strongly depends on the degree of dispersion of the filler.

4.2.7 Apparent crosslink densities

The apparent crosslink density was determined by swelling of a weighed sample of vulcanized compound in toluene. The vulcanized sample of 2mm * 2mm size was cut from a sheet with a thickness of approx. 2 mm and immersed in 100 ml toluene at room temperature for 72 hours[23]. The solvent was renewed after 24 hours. The sample was removed, blotted quickly with filter paper, and weighed in a tared weighing bottle. The samples were collected and left for 24 hours in vacuo at 105ºC to evaporate the solvent. The swelling value Q, defined as grams of toluene per gram of rubber hydrocarbon, was calculated as:

$$Q = \left(\frac{\text{swollen weight} - \text{dried weight}}{\text{original weight}} \right) \text{formula weight X } \frac{1}{100} \qquad (4.2)$$

Where:

Formula weight = total weight of the rubber plus compounding ingredients based on 100 parts of rubber.

The apparent crosslink density was calculated as the reciprocal swelling value, 1/Q[24].

4.2.8 Mechanical properties

Samples were cured in a Wickert laboratory press WLP 1600/5*4/3 at 160ºC and at a pressure of 100 bar (10 MPa) according to the t_{90} of the samples. The cured specimen dimensions were 90 mm * 90 mm and 2 mm in thickness. The stress-strain properties of the cured samples were measured using a Zwick Z020 tensile tester according to ISO-37, tensile bar Type 2 at a crosshead speed of 500mm/min.

4.3 Results

4.3.1 Filler-filler interactions and filler-polymer interactions

The Payne effect of the still unvulcanized S-SBR compounds filled with unmodified, acetylene-, pyrrole- and thiophene-coated as well as silane-treated silica samples are shown in Figure 4.1.

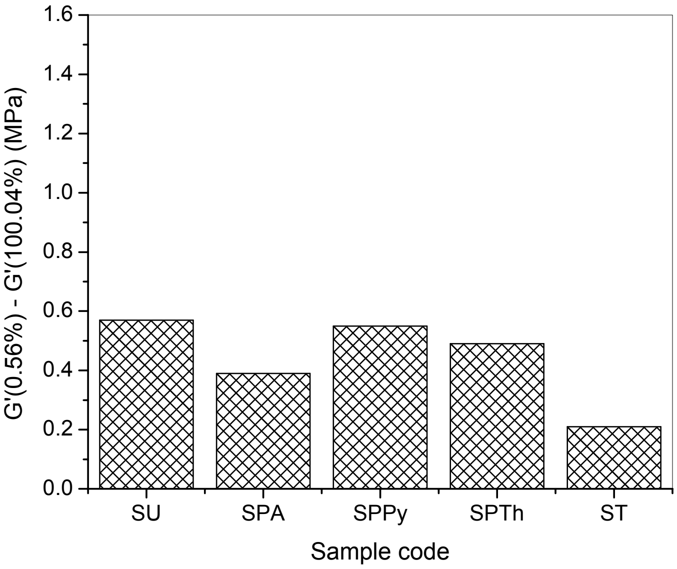

Fig. 4.1: Payne effects of unmodified, plasma-polymerized acetylene-, pyrrole-, thiophene-coated and silane-treated silicas in S-SBR.

There is a significant difference in the Payne effect between the samples with untreated (SU) and acetylene plasma-treated (SPA) silica. Pyrrole plasma-treated silica in SBR (SPPy) shows only a slight decrease in the Payne effect compared to the untreated silica (SU). The thiophene plasma-treated silica is in between. The silane-treated silica (ST) shows the lowest Payne effect of all, which is an indication of the lowest remaining filler-filler interaction between the silica-particles achieved by the silanization.

The level of rubber-silica interaction can be investigated by bound rubber measurements. Figure 4.2 shows the bound rubber content of the unmodified, plasma-coated and silane-treated silica-filled compounds.

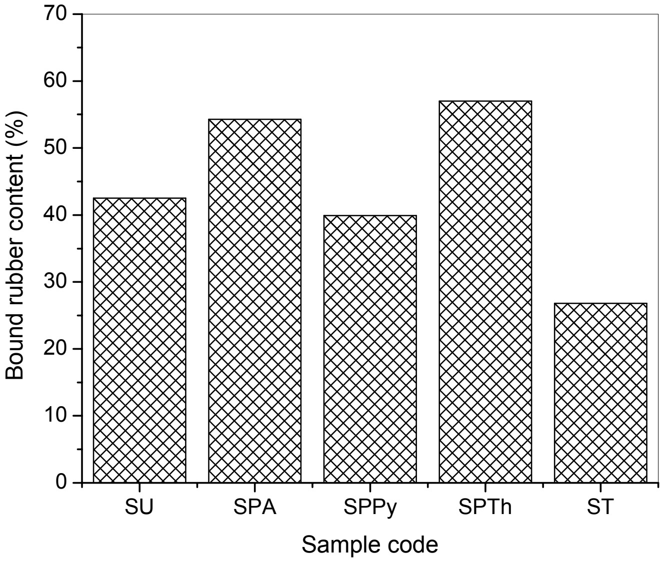

Fig. 4.2: Bound rubber content of unmodified, plasma-polymerized acetylene-, pyrrole-, thiophene-coated and silane-treated silicas in S-SBR.

Plasma-thiophene and –acetylene treated silica show the highest bound rubber contents, while pyrrole-coated silica shows a slightly lower bound rubber content even than unmodified silica. In qualitative terms, the rankings in this test are opposite to the rankings with respect to filler-filler interactions, as depicted in Figure 4.1. However, polythiophene coated silica results in the highest amount of bound rubber, even though it did not result in the lowest filler-filler interaction. Silane-treated silica before the vulcanization apparently does not lead to a large amount of bound rubber, even though it performed best in reducing filler-filler interactions. Figure 4.3 shows the results of TGA measurements performed on the dried filled rubber material after extraction: the filler with attached bound rubber.

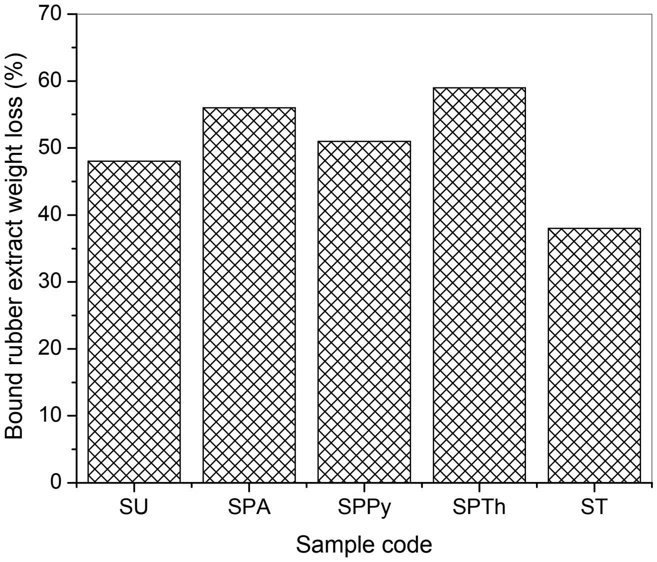

Fig. 4.3: TGA weight loss of the bound rubber extract of S-SBR with unmodified, plasma-polymerized acetylene-, pyrrole-,thiophene-coated and silane-treated silicas.

As expected, the values follow the same trend as the bound rubber contents shown in Figure 4.2, merely confirming these results.

4.3.2 Reinforcement parameter and filler dispersion

Basically, a lower reinforcement parameter α_F (eq. 4.1) indicates a better dispersion of a filler in a polymer. In Figure 4.4, the unmodified silica filled sample SU shows a high value of the reinforcement parameter, which indicates a low degree of dispersion of the filler in the rubber matrix. S-SBR with PA-treated (SPA) and silane-treated (ST) silica show the lowest values, which corresponding to the best dispersion in the polymer matrix in both cases compared to the other fillers.

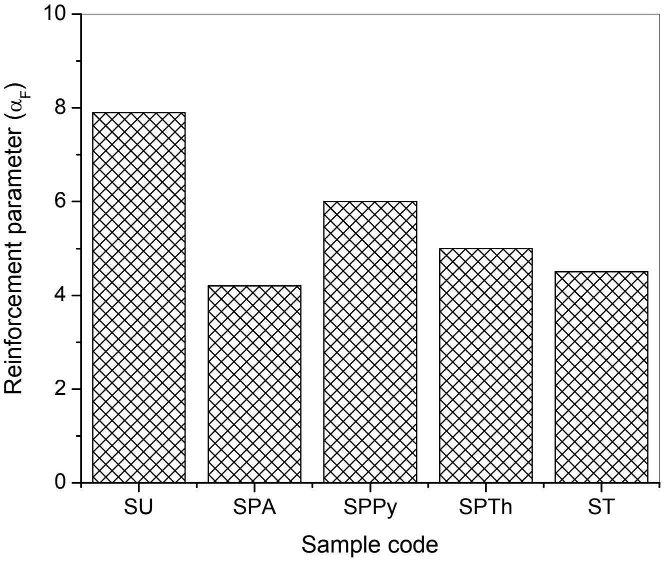

Fig. 4.4: Reinforcement parameter of the reinforced S-SBR with unmodified, plasma-polymerized acetylene-, pyrrole-, thiophene-coated and silane-treated silicas.

4.3.3 Tensile properties and apparent crosslink density

The stress-strain curves of vulcanizates of unmodified, PA- , PPy-, PTh-coated and silane–treated silica filled S-SBR vulcanizates are represented in Figure 4.5. Particularly in the case of PTh-silica filled S-SBR (SPTh), the moduli as well as tensile strength are much higher than for all other samples. SPA, SPPy and ST show all more or less similar values of tensile strength and elongation at break, and slightly higher moduli values for high strains than the untreated silica sample.

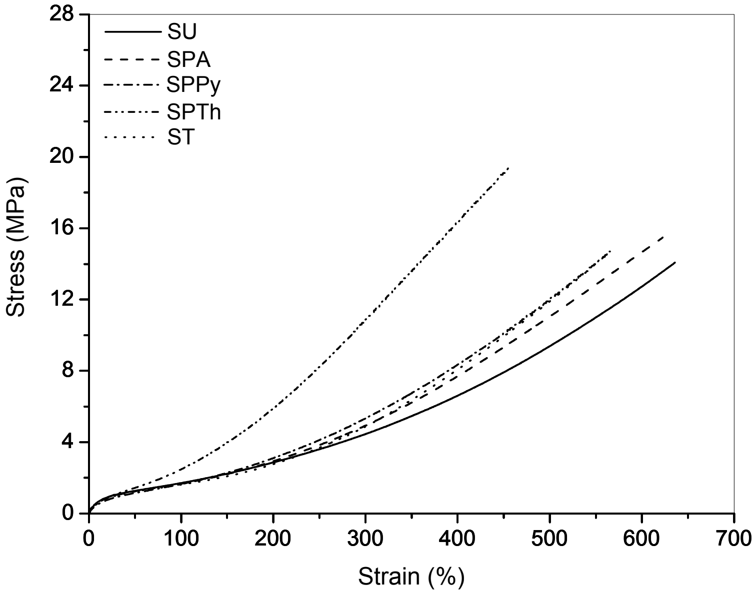

Fig. 4.5: Stress-strain curves of reinforced S-SBR with unmodified, plasma-polymerized acetylene-, pyrrole-,thiophene-coated and silane-treated silicas.

The apparent crosslink density of the unmodified, PA-, PPy-, PTh-coated and silane-treated silica filled S-SBR vulcanizates are shown in Figure 4.6. PTh-silica filled S-SBR clearly shows the highest crosslink density; all other crosslink densities are significantly lower and show only minor differences. Unmodified silica performs the worst in tensile properties as well as in apparent crosslink density.

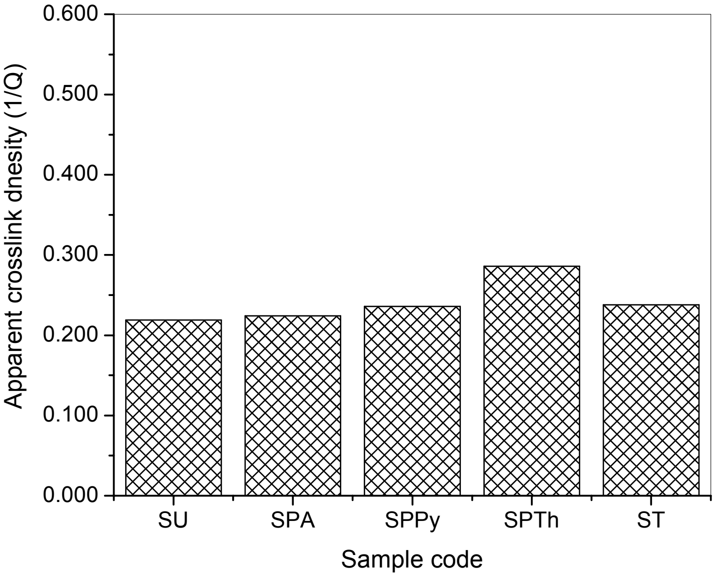

Fig. 4.6: Apparent crosslink density of unmodified, plasma-polymerized acetylene-, pyrrole-, thiophene-coated and silane-treated silicas in S-SBR.

4.4 Discussion

The ability to chemically change the surface of silica in a controlled manner without changing the filler structure makes it possible to study the effects of these changes on reinforcement. The physical or chemical interaction of the elastomer with the filler surface improves dispersion and prevents formation of secondary structures due to re-agglomeration. The consequence of reduced filler-filler interaction and enhanced filler-polymer interaction is a decrease in low-strain stiffness and an improvement in the ultimate vulcanizate properties: tensile strength and elongation at break. The reinforcement parameter, Figure 4.4, shows that the plasma coating clearly improves the compatibility and thus the dispersion of silica in the polymer. This is also confirmed by the lower Payne effect of the PA- and PTh-coatings on silica, as shown in Figure 4.1. The compound with SPPy-coated silica shows a higher Payne effect compared to both other compounds with plasma-coated silica: This indicates a lower compatibility of plasma pyrrole-coated silica with S-SBR. The modification of the polar silica surface by silanization leads to the lowest Payne effect combined with a low reinforcement parameter, apparently due to the strongest decrease in polarity and hydrophilicity of all.

On the other side, complete wetting and good filler-polymer interaction of high surface area silica’s are very essential elements for a good reinforcement in hydrocarbon elastomers. The bound rubber results stand out positively for all plasma coated monomers: Figures 4.2 and 4.3, with a slightly higher value for thiophene as monomer compared to acetylene and pyrrole. This indicates the trend of increasing filler-polymer interactions due to a better match of their surface energies, which improves the compatibility of S-SBR with the different plasma-coated silica’s. Contrary to what might have been expected, the silane-treatment gave the lowest bound rubber values: The filler-polymer interaction in this case is not very strong yet, partly due to the chemical structure of the silane coating and insufficient coverage of the surface by unpolar hydrocarbon groups. And most important in this case, the full filler-polymer interaction is only formed during the vulcanization afterwards. It becomes clear from the comparison of these data, that the relative ranking in reduction in filler-filler interaction cannot directly be translated into a similar opposite ranking in increased polymer-filler interactions. Apparently other factors also still play a role in the phenomena observed.

The reinforcement parameters (α_F) for compounds containing plasma-acetylene, -thiophene and silane-treated silica, Figure 4.4, show the lowest values in this series. This indicates the best dispersion. These samples also show the lowest filler-filler interactions, as seen in Figure 4.1. So, in these cases, higher filler-polymer interaction and improved dispersion do coincide. Plasma pyrrole-coated silica showed a higher reinforcement parameter as it also corresponds with a high Payne effect. This indeed shows the lower degree of hydrophobation of pyrrole-coated silica, with as consequence a lower level of dispersion in the S-SBR matrix. Because the Payne effect and the reinforcement parameter both are related to the status of the filler in the rubber matrix, being it filler-filler interaction or filler dispersion, a correlation between both characterizations for unmodified, plasma-acetylene-, pyrrole-, thiophene-coated and silane-treated silica’s in S-SBR is shown in Figure 4.7. Lower values of the Payne effect, do correspond with a lower reinforcement parameter, but not unequivocally. So, the filler-filler interaction is not the only factor determining the dispersion, as can be seen from the different values for the reinforcement parameters for comparable Payne-effect values in the cases of ST, SPA and SPTh. For higher values of the reinforcement parameter, the

Payne-effect shows an exponential rise: the dispersion is still very sensitive to high filler-filler interaction.

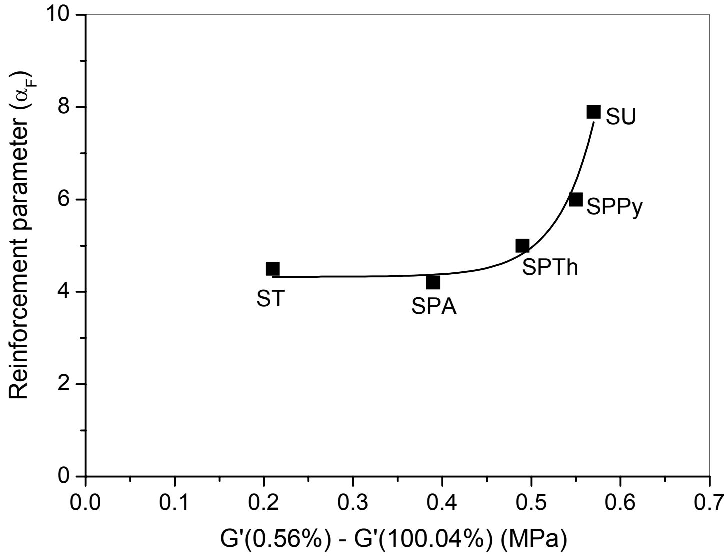

Fig. 4.7: Correlation between the Payne effect and Reinforcement parameter (α_F) of unmodified, plasma-polymerized acetylene-, pyrrole-, thiophene-coated and silane-treated silicas in S-SBR.

Improved dispersion and good surface wetting of reinforcing filler are generally considered to contribute to the stress-strain behavior. However, the question may be raised, which tensile properties are most influenced: moduli, tensile strength or elongation at break? Based on the rubber elasticity theory, it can be anticipated that strong filler-polymer attachments have a similar effect on raising the modulus as increased cross-linking. On the other hand, a seemingly strong filler-polymer attachment will also demonstrate itself in a higher degree of crosslinking. The apparent crosslink densities, 1/Q, therefore encompass elements of real cross-link density, plus polymers attached to the silica surface. Comparing the 1/Q-data with the initial slopes of the curves in the stress-strain diagrams in Figures 4.5 and 4.6, it becomes clear that there is a correlation between the moduli ratio within the range of 100% to 300% strain of the stress-strain curve, and the 1/Q values. Figure 4.8 shows this correlation: the higher the apparent crosslink density, the higher the moduli ratio value or, in other words, the higher the reinforcing effect. The silanized silica might be an exception in this series, as it shows a somewhat lower modulus increase compared to all other silica types, indicating that the reinforcement of the matrix by this silica type is slightly lower. The reason might be the different way of processing: the silane-coating has to be formed during mixing, which might result in a less effective filler-polymer interaction as also seen in Figure 4.2, and thus reduce the reinforcing effect. The tensile strength and elongation at break values are little conclusive in this respect.

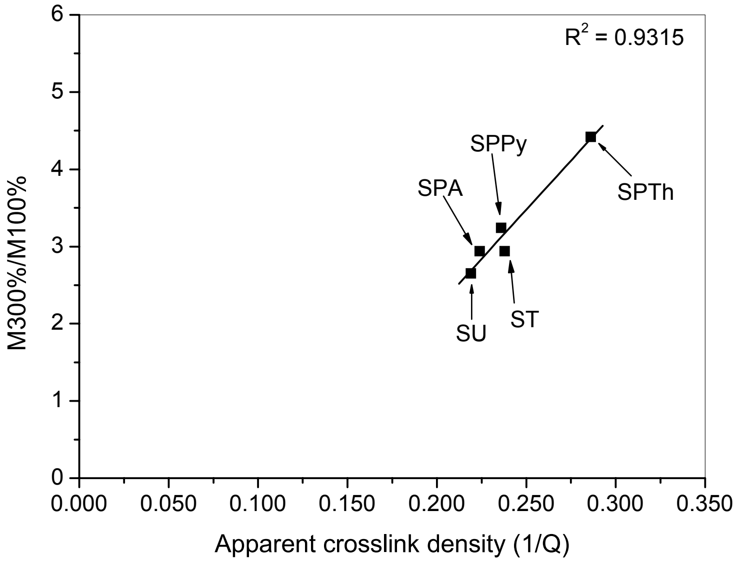

Fig. 4.8: Correlation between the moduli ratio (M300%/M100%) of the stress-strain curve and the apparent crosslink density (1/Q) of unmodified, plasma-polymerized acetylene-, pyrrole-, thiophene-coated and silane-treated silicas in S-SBR.

Most conspicuous is the steep tensile curve for PTh-coated silica in S-SBR. The PTh-silica shows by far the best improvement in tensile properties in terms of tensile strength, moduli at 100%, and at 300%, but lower elongation at break, indicating a strong and dense network. The ranking in tensile properties, moduli and tensile strength, parallels the relative order of the crosslink density values, which is highest for PTh-silica filled S-SBR compared to all other silica types. Most likely, the sulfur contained in the polythiophene-moieties on the silica surface contributes to a more efficient crosslinking in the S-SBR matrix during vulcanization. It even introduces crosslinks in the absence of curatives, as shown in Figure 4.9. The overall poorest performance of unmodified silica, apart from its poor dispersion and strong filler-polymer interaction, which would have positively influenced the reinforcing power, is largely due to its surface acidic nature. The later is quoted to cause adsorption of curatives, resp. denaturation of sulfur vulcanization, which needs an alkaline environment to properly proceed.

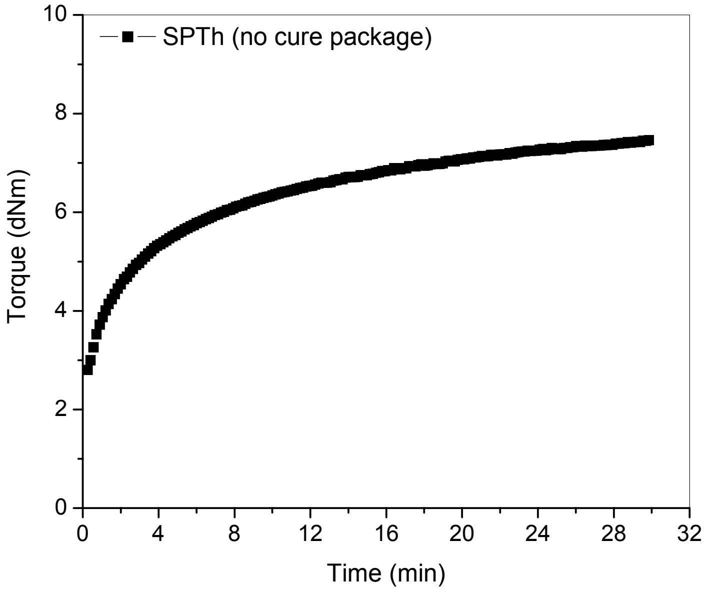

Fig. 4.9: Rheograph of plasma thiophene-coated silica filled S-SBR in absence of a cure package.

4.5 Conclusions

The comparison of the various silica's as reinforcing fillers in S-SBR has shown, that the relative mutual rankings of filler-filler interaction and polymer-filler interaction are not each others reverse. Even the degree of dispersion, as quantified with the reinforcement parameter is not unequivocally related to the remaining filler-filler interaction, as quantified with the Payne effect. In global terms, the various characteristics point in mutually comparable directions, but the individual effects show relative deviations.

Unmodified silica performs worst in all aspects, as was expected due to its large difference in polarity with the rubber, as well as its acidic nature which negatively influences vulcanization. PA- and PTh-coated silica filled samples show lower filler-filler interactions and better filler dispersion compared to PPy-silica and unmodified silica. PPy-coated silica shows practically little improvement cross the board over unmodified silica. Particularly PTh-silica results in high moduli and tensile values in S-SBR, as it performs best in terms of filler-polymer interaction as measured by the bound rubber content; it also gives the highest crosslink densities due to extra cross-links formed by the sulfur contained in the polythiophene moieties on the silica surface. This more than compensates for the fact that polythiophene was not so effective in reducing the silica filler-filler interactions, as for example PA and silane did. Silane in the silica compound effectively reduces the filler-filler interaction and enhances the filler-distribution, but does not provide much polymer-filler interaction yet in the unvulcanized state, as seen in the bound rubber content. It needs a vulcanization temperature treatment to create a solid polymer-filler bond. However, in the final tensile properties it does not gain much anymore relative to PA- and PPy-coated silica samples.

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Chapter 5

Reinforcement of EPDM by Plasma-Polymerized Acetylene-, Pyrrole- and Thiophene-Coated Silica

The surface modification of precipitated silica powders by plasma-polymerization with different monomers in order to improve their performance in EPDM is the subject of this chapter. The properties of EPDM, filled with unmodified, plasma coated polyacetylene-, polypyrrole-, polythiophene- and silane-treated silica, are investigated by measuring the filler-filler interaction, the filler-polymer interaction, the dispersion and the mechanical properties. All modified silica filled samples show a lower Payne effect in EPDM compared to the rubber filled with unmodified silica, indicating a reduced filler-filler interaction. A reduction of the reinforcement parameter for all plasma-treated silicas in EPDM proves a better dispersion and lower degree of agglomeration in comparison to untreated as well as silane-treated silica. The moduli at 100% ad 300% strain of all samples, filled with treated as well as unmodified silica, are determined by the crosslink density of the vulcanized compounds, where the silica-treatment may provide a synergistic positive effect: in the case of silane-treatment, or a negative effect: in the case of polythiophene coating. The ultimate tensile properties: tensile strength and elongation at break, are the result of more homogeneous mixtures with less failure sites, due to reduced filler-filler interaction during mixing for all treated or coated silicas in comparison with unmodified silica.

Part of the work described in this chapter is published in:

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M. Tiwari, W. K. Dierkes, J. W. M. Noordermeer, W. J. van Ooij, Polym. Adv. Technol., 19, 1672 (2008);

M. Tiwari, R. N. Datta, A. G. Talma, J. W. M. Noordermeer, W. K. Dierkes and W. J. van Ooij, Rubber Chem. Technol., 82, 473 (2009).

5.1 Introduction

Filler reinforced ethylene-propylene-diene (EPDM) rubber compounds are of significant commercial importance. Ethylene-propylene-diene rubber is very stable towards oxidative, ozone, thermal and photo-degradation as a result of the saturated main chain, making it very suitable for outdoor applications: automotive and building profiles, roof sheeting, tubes, V-belts, seals and gaskets[1,2]. The reinforcing filler generally used for EPDM reinforcement is carbon black, due to its good compatibility with the polymer. Silica is less compatible with EPDM, as it has a very high polarity due to the presence of silanol groups on the surface. Since EPDM does not have any polar groups in its backbone, a homogeneous dispersion of polar fillers such as silica in EPDM is difficult to obtain. Silica filler dispersion and compatibility with EPDM rubber can be improved by shielding the silanol groups on the silica surface, which can reduce the surface energy or polarity of the silica filler. In this way, a better match of the surface energy of silica and EPDM can be achieved, resulting in a higher compatibility and improvement of the final properties of the vulcanizates.

In this respect, plasma polymerization is a powerful technique to modify the surface energy of silica, as it does not affect the bulk properties of the material[3-10]. This technology is used in various applications for decades already, but has not specially been applied for surface modification of reinforcing fillers like carbon black and silica. Plasma polymerization of well-chosen monomers like acetylene, pyrrole and thiophene onto silica can be done as described in Chapter 3 of this thesis.It is a valuable alternative to existing surface modification techniques such as silanization, with the advantage that the plasma coating is an environmentally sound process compared to other techniques and that a chemical reaction in the rubber mixer can be avoided.

The objective of the present work is to investigate and understand the effect of plasma-acetylene, -pyrrole and -thiophene coated silica on the reinforcement of an EPDM matrix in terms of dispersion and distribution as well as final vulcanizate properties.

5.2 Experimental

5.2.1 Materials

EPDM (Keltan® 4703, DSM Elastomers B.V.) with an ethylidene norbornene content of 9 wt% and an ethylene content of 48 wt%, resp. propylene content of 43 wt%, was used as polymer.

Conventional precipitated silica (Ultrasil VN3, Degussa GmbH) obtained in fluffy form, was used as reinforcing filler in untreated as well as in surface-modified form. High purity acetylene gas (C_2H_2) for the plasma polymerization was obtained from Wright Brothers, Inc. Pyrrole (C_4H_5N) and thiophene (C_4H_5S) monomers for the plasma polymerization were obtained from Sigma-Aldrich GmbH. Other chemicals used in this study are shown in Table 5.1.

Table 5.1: Chemicals used in the study.

Chemical	Trade name	Source
Toluene (Analytical Reagent grade)	-	Sigma-Aldrich GmbH
Bis-(triethoxysilylpropyl) tetrasulfide (TESPT)	Si69	Degussa GmbH
Sulfur (S)	-	Solvay
N-Cyclohexyl-2-benzothiazolesulfenamide (CBS)	Santocure CBS	Flexsys N.V.
Tetramethylthiuramdisulfide (TMTD)	Perkacit TMTD	Flexsys N.V.
Zinc dibenzyldithiocarbamate (ZBEC)	Perkacit ZBEC	Flexsys N.V.

5.2.2 Plasma polymerization onto silica

The surface modification of silica by plasma polymerization, and the characterization of the modified materials are discussed in detail in the experimental part of Chapter 3.

5.2.3 Preparation of rubber compounds

The basic formulations used for the EPDM compounds are given in Table 5.2. The curatives used in the recipes are common for EPDM compounds. In the recipe containing the silane, the amount of sulfur is adjusted to compensate for its presence in TESPT, to represent equimolar quantities in all cases.

Table 5.2: Basic formulations of silica reinforced EPDM.

Components	**Samples**				
	EU	**EPA**	**EPPy**	**EPTh**	**ET**
	phr	phr	phr	phr	phr
EPDM	100	100	100	100	100
Silica	50	50	50	50	50
ZnO	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0	2.0
Silane (TESPT)	--	--	--	--	4
Sulfur	1.5	1.5	1.5	1.5	1.04
CBS	1.5	1.5	1.5	1.5	1.5
TMTD	0.8	0.8	0.8	0.8	0.8
ZBEC	1.5	1.5	1.5	1.5	1.5

Sample codes: E: *Ethylene-propylene- diene rubber;* ***U:*** *Untreated silica;* ***PA:*** *Plasma-acetylene coated silica;* ***PPy:*** *Plasma-pyrrole coated silica;* ***PTh:*** *Plasma-thiophene coated silica;* ***T:*** *Silanized silica*

The mixing procedure of the compounds was discussed in detail in the experimental part of Chapter 4.

5.2.4 Material characterization

Dynamic mechanical measurements were performed using a RPA 2000 dynamic curemeter (Alpha Technologies) at a temperature of 100ºC, a frequency of 0.5 Hz and a strain amplitude in the range of 0.56%-100.04%. Bound rubber measurements and TGA measurements on the bound rubber extract were discussed in detail in the experimental part of Chapter 4, as are the methods to determine the cure characteristics and the relative ranking of crosslink densities.

Further, the mechanical properties are measured on samples, which were cured in a Wickert laboratory press WLP 1600/5*4/3 at 160ºC at a pressure of 100 bar (10 MPa) according to the t_{90} of the samples. The cured specimen dimensions were 90 mm * 90 mm and 2 mm thickness. The stress-strain properties of the cured samples were measured using a Zwick Z020 tensile tester according to ISO-37, tensile bar Type 2 at a crosshead speed of 500 mm/min.

5.3 Results

5.3.1 Filler-filler and filler-polymer interactions

The properties of a mixed compound depend strongly on the dispersion and compatibility of the filler-polymer system. Figure 5.1 shows the influence of the unmodified, plasma-coated and silane-treated silicas on the Payne effect in EPDM rubber, as measured by the difference in storage modulus at 0.56% and 100.04% strain. The plasma-coated silica types (EPA, EPPy and EPTh) exhibit a lower Payne effect compared to the untreated silica (EU). Compared to EPA and EPTh, plasma-pyrrole coated silica (EPPy) shows the lowest Payne effect, or in other words the lowest remaining filler-filler interaction. However, silane-treated silica shows the lowest filler-filler interaction of all silica types used in this study.

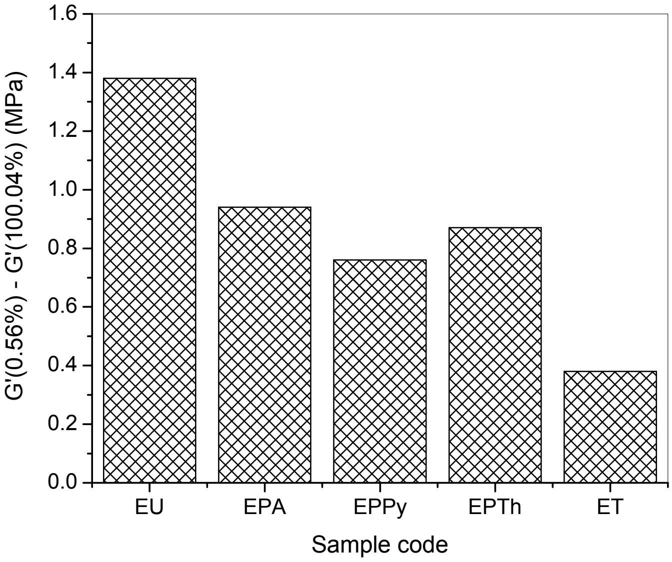

Fig. 5.1: Payne effects of unmodified, plasma-polymerized acetylene-, pyrrole-, thiophene-coated and silane-treated silicas in EPDM.

The level of rubber/silica interaction was studied by bound rubber measurements. Figure 5.2 shows the bound rubber contents of the various silica-filled EPDM compounds. The acetylene-coated (EPA) silica shows a significantly higher bound rubber content compared to all other silicas.

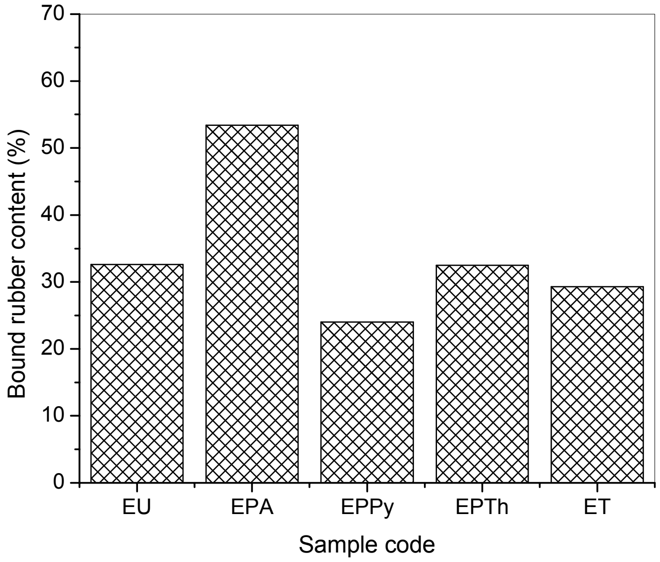

Fig. 5.2: Bound rubber contents of unmodified, plasma-polymerized acetylene-, pyrrole-, thiophene-coated and silane-treated silicas in EPDM.

In Figure 5.3, the TGA measurements performed on the extracted dried materials, which are correlated to the bound rubber contents, are shown. The values follow the same trends as the bound rubber contents shown in Figure 5.2, thus confirming these measurements. Both the bound rubber as well as the TGA weight loss experiment demonstrate a clear affinity of EPDM towards the poyacetylene-coated silica with respect to polymer-filler interaction. This is clearly opposite to the degree with which the coating is able to supress the filler-filler interactions. The behavior for the polypyrrole-coated silica in this polymer is again very different: filler-filler as well as filler-polymer interaction are both low.

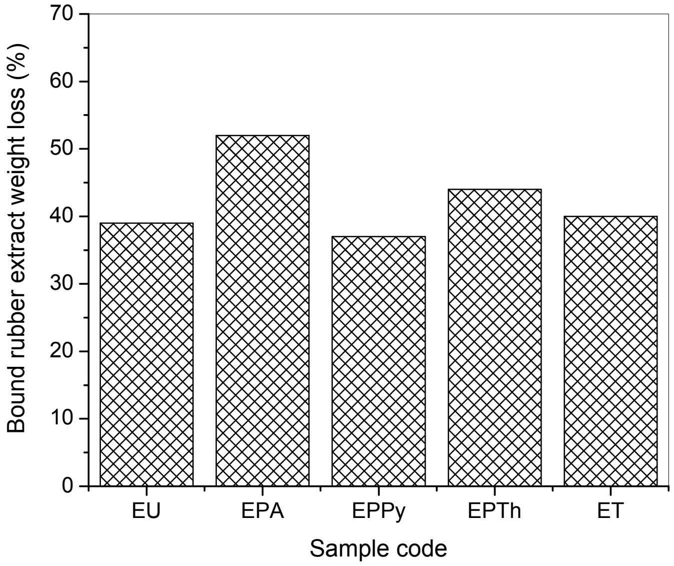

Fig. 5.3: TGA weight losses of bound rubber extract of EPDM with unmodified, plasma-polymerized acetylene-, pyrrole-, thiophene- and silane-treated silics.

5.3.2 Dispersion and reinforcing effects

A lower reinforcement parameter α_F (eq. 4.1) indicates a better dispersion of a filler in a polymer[11]. In Figure 5.4, the untreated silica filled sample EU shows a high reinforcement parameter, which indicates a low degree of dispersion in the matrix. EPDM with PPy-treated (EPPy) and silane treated (ET) silica show similar values, which are only slightly lower than for the compound with untreated silica. This is quite surprising, as both treatments performed best in breaking the filler-filler interactions, as demonstrated in Figure 5.1. Apparently, it did not translate into a better dispersion, respectively reinforcement. EPDM filled with PTh-silica, EPTh, shows the lowest value of the reinforcement parameter with a remarkable difference, which indicates the best dispersion and reinforcement for the polythiophene plasma-treated silica in the EPDM compound. Again surprising, as the polythiophene plasma-coated silica had not shown an exceptionally high affinity for EPDM in the bound rubber experiment.

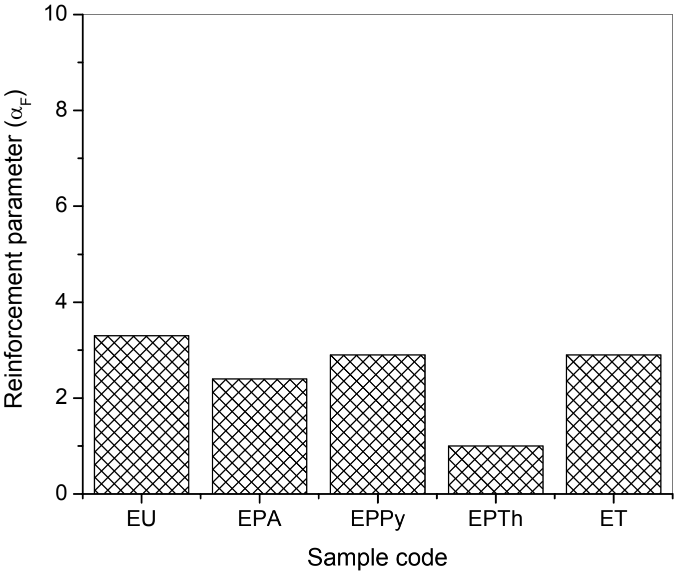

Fig. 5.4: Reinforcement parameter of the reinforced EPDM with unmodified, plasma-polymerized acetylene-, pyrrole-, thiophene- and silane-treated silicas.

5.3.3 Tensile properties and apparent crosslink density

The stress-strain curves of vulcanizates of the various samples are represented in Figure 5.5. Silane-treatment of silica shows a very strong effect in EPDM as evidenced by a much enhanced tensile strength, though lower elongation at break, relative to the other four samples. PA- and PPy-coated silica show somewhat higher moduli relative to untreated silica, while PTh-treatment even results in lower moduli. However, when expressed in ultimate tensile strength and elongation at break, all treatments of silica definitely have a strong positive effect compared to untreated silica. The PTh-coating is even greatly preferred, as it combines a significantly improved tensile strength with a much higher elongation at break.

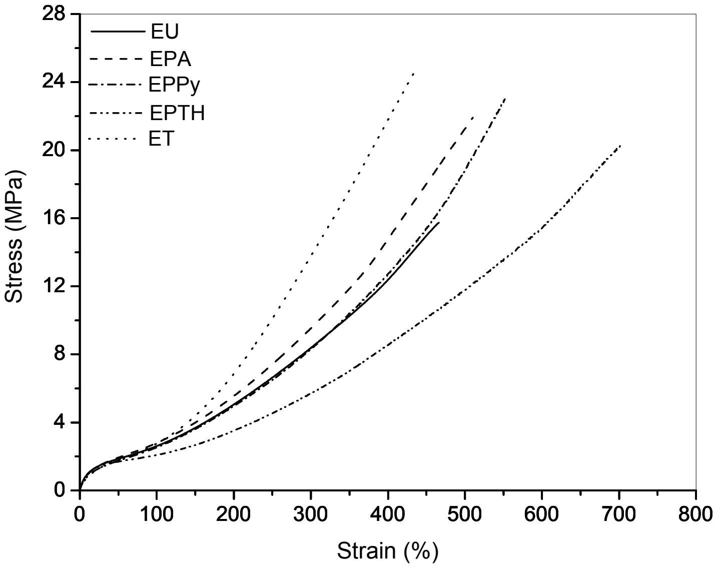

Fig. 5.5: Stress-strain curves of reinforced EPDM with unmodified, plasma-polymerized acetylene-, pyrrole-, thiophene- and silane-treated silicas.

It might be though, that these differences in tensile properties are due to different crosslink densities obtained during vulcanization of the samples. The relative crosslink densities were measured by swelling of the filled vulcanizate samples, and the reciprocal of the swelling value represents the apparent crosslink density. The relative ranking of crosslink densities of the cured samples is shown in Figure 5.6.

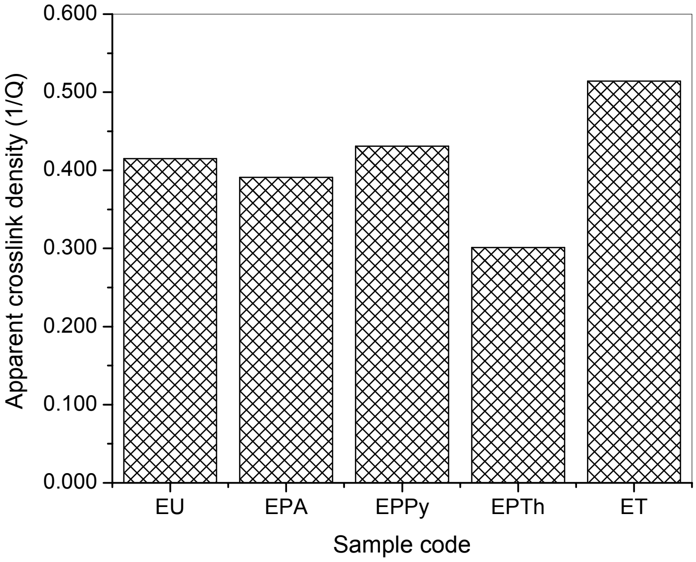

Fig. 5.6: Apparent crosslink density (1/Q) of EPDM with unmodified, plasma-acetylene, -pyrrole, -thiophene and silane-coated silicas.

There is indeed a correlation between the stress-strain properties and apparent crosslink density. At least in terms of the moduli, the lowest value for polythiophene coating does correspond with the lowest relative crosslink density. The highest values for the silane-treated silica correlates with the highest crosslink density. The other three samples, more or less comparable in moduli values, are also similar in apparent crosslink density. Figure 5.7 shows the correlation between the moduli ratio of the stress-strain curve in the range between 100% and 300% strain and the 1/Q values: the higher the apparent crosslink density, the higher the increase in moduli. It is also clear that such a correlation for the tensile strengths and elongations at break does not work.

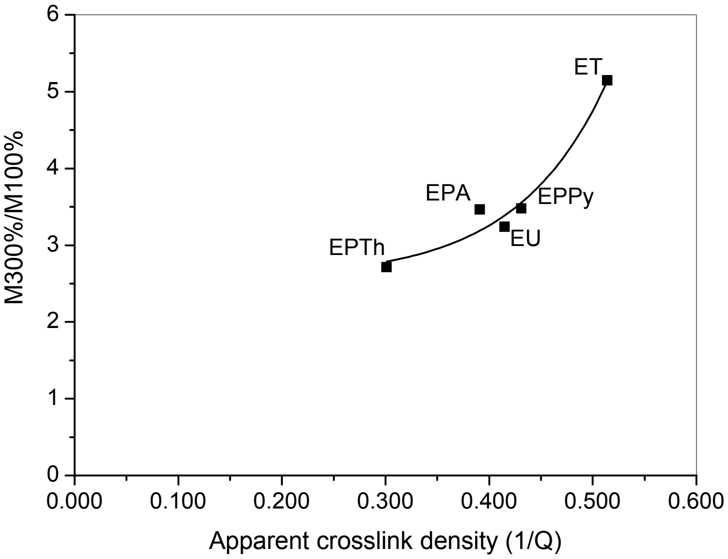

Fig. 5.7: Correlation between the ratio of the moduli at 300% and 100% and the apparent crosslink density (1/Q) of unmodified, plasma-polymerized acetylene-, pyrrole-, thiophene-coated and silane-treated silicas in EPDM.

5.4 Discussion

Large differences in surface energy between filler and polymer, strong interparticle forces as well as high filler loadings can result in a high degree of filler-agglomeration, which is strain dependent: the Payne effect. Figure 5.1 shows that the plasma coating clearly reduces the filler-filler interaction, thus potentially enhancing the dispersion of the filler in this polymer. The plasma-pyrrole treated silica EPPy shows the lowest Payne effect of the plasma-treated silicas. This indicates that the PPy-coating of silica shields the filler surface most effectively in the EPDM-matrix. However, the silane-modification of the polar silica surface apparently leads to the best hydrophobation of the surface and the lowest filler-filler interaction, as indicated by the low Payne effect.

Bound rubber is a parameter which is simple to measure, but difficult to interpret as the factors which influence the results are very complicated. The filler to polymer interaction leading to the formation of bound rubber involves physical adsorption, chemisorption and mechanical interaction. Moreover, bound rubber also shows a dependence on the processing conditions of the compound, such as mixing and storage time. The high amount of bound rubber and weight loss measured by TGA for the acetylene silica filled sample, EPA, demonstrate a strong filler-polymer interaction between PA-silica and EPDM: Figures 5.2 and 5.3. However, the low bound rubber values of EPPy and EPTh are contrary to what would have been expected from the filler-filler interaction: as filler-filler interaction is reduced, the filler-polymer interaction should improve. The bound rubber values for the silane-silica compound are on the level of untreated silica, which is even less expected. The results do indicate that a reduced filler-filler interaction not necessarily improves the filler-polymer interaction. In the present case, all plasma coatings shield the active groups on the filler surface and thus reduce the interaction between filler particles, but they do not necessarily always improve the filler-polymer interaction to the same extent. The fact that the polyacetylene-coated silica stands out so prominently in bound-rubber relative to the others is undoubtedly due to the fact that the polyacetylene coating has a similar chemical structure as the EPDM itself, while the other two plasma-polymers are more polar due to the sulfur- and nitrogen-atoms and have more conjugated double bonds.

The reinforcement parameters for all three plasma-silica filled samples, EPA, EPPy and EPTh, show a positive effect on dispersion compared to untreated silica. PA- and PTh-silica filled EPDM show the best dispersion and reinforcement parameter of all. In the case of polyacetylene, the reason for the good dispersion may again be the chemical similarities of the plasma-polymerized acetylene to the chemical structure of EPDM. In the case of plasma-polymerized thiophene, the sulfur moieties present in the structure might shield the silanol groups on the filler surface very effectively, as also indicated by the reduction of the Payne-effect compared to untreated silica in EPDM.

It is quite surprising though that the effect of polythiophene is so much strange for EPDM than seen in SBR in the previous Chapter. The decrease in modulus for PTh-silica filled EPDM corresponds to the low crosslink density values in Figure 5.6. In this case, there seems to be a negative contribution of the sulfur moieties present on the PTh-silica surface. A possible explanation of this effect might be a deactivation of the double bonds of the EPDM by a reaction with the sulfur. As EPDM has only a low number of unsaturated sites in its chemical structure. The sulfur contained in the polythiophene may reduce the crosslinking sites appreciably till there are practically none left.

The stress-strain curve of the PPy-silica filled compound perfectly matches the curve of EPDM with untreated silica, but it shows a higher tensile strength and elongation at break. An improved dispersion and compatibility of PPy-silica and EPDM must be the factor for improved tensile properties. It is well known the fact, that tensile strength and elongation at break have a strong dependence on the homogeneity of the compounds: tensile bars always break on a stress concentration caused by a large, hard undispersed filler agglomerate particles. The various coatings as well as the silane-treatment apparently all provide a smoother dispersion, with less or not hard particles. High tensile strength cannot unequivocally be related to crosslink density.

When comparing the stress-strain properties as obtained for EPDM in the present chapter, with those measured for S-SBR in Chapter 4, the most conspicuous is the fact that:

- the silane-modified silica for EPDM (ET) gives the highest stress vs. strain, in combination with highest crosslink density;
- the silane-modified silica in S-SBR (ST) gives only a slightly enhanced stress vs. strain and a little increase in apparent crosslink density vs. the unmodified silica;
- the thiophene-coated silica for EPDM (EPTh) gives the lowest stress vs. strain, in combination with the lowest relative crosslink density;
- the thiophene-coated silica for S-SBR (SPTh) gives the highest stress vs. strain combined with the highest apparent crosslink density.

The rankings are reversed; combining the results of both chapters, the following important observations can be summarized:

- Every combination of coated or treated silicas with rubbers shows its own specific behavior.
- Experiences with one rubber are not predictive with other elastomers.
- High moduli at 100% and 300% strain, or otherwise the ratio of moduli at 300% and 100% of the stress-strain curve, are clearly the results of high apparent crosslink density. The specific coating on the silica may have a positive effect on crosslink density:

polythiophene in combination with S-SBR; or a negative: polythiophene with EPDM.

- The moduli are not dependent on the affinity of the coatings or treatment towards the elastomer, as observed in the (uncrosslinked) bound rubber test: EPA versus all other samples. However important bound rubber phenomena may be.
- The ultimate properties: tensile strength and elongation at break, are most prominently the result of reduced filler-filler interaction, as measured by the Payne effect and to a lesser extent the reinforcement parameter. This reduced filler-filler interaction accounts for a smoother mixture with less hard agglomerates of filler left.

It is now very interesting to see how all these silica-coatings will perform in a relatively polar rubber with high unsaturation: Chapter 6.

5.5 Conclusions

In EPDM rubber, the moduli at 100% and 300% strain of plasma-coated or silane-treated silica are primarily determined by the level of crosslink density achieved: by the vulcanization system and/or by synergy with the chemical group embedded in the plasma-coating. Silane-treated silica provides the highest moduli, while thiophene plasma-coated silica results in moduli, which are significantly reduced relative to unmodified silica. The later is probably due to a reaction of the thiophene groups in the plasma-coating with the few unsaturations in EPDM, shielding them later from reaction with the sulfur curing agent.

All types of plasma coating: poly-acetylene, poly-thiophene and poly-pyrrole, as well as silanized silica greatly improve the ultimate tensile properties as tensile strength at break and elongation at break. This is due to a significantly reduced filler-filler interaction relative to untreated silica, enhancing the filler distribution, resulting in more homogeneous compounds with less failure sites due to hard, unmixed filler agglomerates.

There is no evidence that the affinity of the coatings or silane-treatment on the silica towards the EPDM, as quantified with the bound rubber has an effect on the mechanical properties of the vulcanized compounds.

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Chapter 6

Reinforcement of NBR by Plasma-Polymerized Acetylene-, Pyrrole- and Thiophene-Coated Silica

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The performance of NBR filled with untreated, polyacetylene-, polypyrrole-, polythiophene-coated and silane-treated silica, is investigated by measurements of the bound rubber content, the reinforcement parameter (α_F), the Payne effect, the crosslink density and the mechanical properties. The plasma-coated filled NBR samples do not show a reduced filler-filler interaction compared to the unmodified silica-filled elastomer; only the silane-modified silica shows a clearly lower Payne effect. Apparently, all silica samples whether modified or not, already are far more compatible with NBR than with SBR and EPDM. So, not much more compatibilization could be achieved anymore with any of the treatments. A decrease of the reinforcement parameter (α_F) for the PA- and PTh-silica-filled samples indicates a better dispersion compared to PPy-modified and untreated silica-filled samples. The plasma treatment of silica generally also results in a higher bound rubber content due to stronger filler-polymer interactions. All plasma-coated silica filled NBR samples show significantly higher moduli and tensile strength values compared to untreated as well as silane-treated silica, considered to be the result of improved dispersion and compatibilization with NBR as measured with bound rubber and apparent crosslink density. Overall, PA- and PPy-silica show the best improvement in mechanical properties.

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M. Tiwari, W. K. Dierkes, J. W. M. Noordermeer, W. J. van Ooij, Rubber Chem. Technol., 81, 276 (2008);

M. Tiwari, W. K. Dierkes, J. W. M. Noordermeer, W. J. van Ooij, Polym. Adv. Technol., 19, 1672 (2008).

6.1 Introduction

A prerequisite for rubber elasticity is a network, which is generally achieved by blending the polymer with reinforcing fillers and by vulcanization. Among the commonly used fillers, silica is comparable to carbon black in terms of morphology and reinforcing potential, and its use is currently increasing due to improvements in characteristic rubber properties such as transparency, abrasion resistance and dynamic properties[1-3]. Conventional silica's generally are more reinforcing in polar elastomers than in unpolar polymers. Among the various diene rubbers, acrylonitrile-butadiene rubber (NBR) is specific because of its high polarity which is due to the presence of acrylonitrile units[4]. These highly polar moieties make NBR the preferred elastomer for technical rubber goods needing resistance to oils, greases and liquid fuels[4]. A low permanent set, good abrasion resistance, and low gas permeability are also well-known as general characteristics of NBR.

In this chapter, the reinforcement effect of different plasma –polymer-coated silica types in NBR vulcanizates is investigated. Monomers used for the plasma-polymerization are acetylene, pyrrole and thiophene. The effect of a silane coupling agent for the NBR vulcanizate is also studied and compared to the plasma-coated silica's.

6.2 Experimental

6.2.1 Materials

NBR (Perbunan® 3446 F, Lanxess GmbH) containing 34.7 wt% acrylonitrile and 65.3 wt% butadiene, was used as polymer.

Conventional precipitated silica (Ultrasil VN3, Degussa GmbH) obtained in fluffy form, was used as reinforcing filler in untreated as well as in surface-modified form. High purity acetylene (C_2H_2) gas, pyrrole (C_4H_5N) and thiophene (C_4H_5S) monomers for the plasma polymerization were obtained from Wright Brothers, Inc and Sigma-Aldrich GmbH. Other chemicals used in this study are shown in Table 6.1.

Table 6.1: Chemicals used in the study.

Chemical	Trade name	Source
Toluene (Analytical Reagent grade)	-	Sigma-Aldrich GmbH
Bis-(triethoxysilylpropyl) tetrasulphide (TESPT)	Si69	Degussa GmbH
Sulfur (S)	-	Solvay
2,2'-Dithio bis(benzothiazole) (MBTS)	Perkacit-MBTS	Flexsys N.V.

6.2.2 Plasma polymerization onto silica

The surface modification of silica by plasma polymerization with different monomers, and the characterization has been discussed in detail in the experimental part of Chapter 3.

6.2.3 Preparation of rubber samples

The basic formulations used for the NBR compounds are given in Table 6.2. The curing recipe is commonly used for NBR. In the silane formulation (NT), the amount of sulfur is adjusted to compensate for the presence of sulfur contained in TESPT, to represent equimolar quantities in all cases.

Table 6.2: Basic formulations of silica reinforced NBR.

Components	Compounds				
	NU	NPA	NPPy	NPTh	NT
	phr	phr	Phr	phr	phr
NBR	100	100	100	100	100
Silica	50	50	50	50	50
ZnO	2.5	2.5	2.5	2.5	2.5
Stearic acid	2.5	2.5	2.5	2.5	2.5
Silane (TESPT)	--	--	--	--	4
Sulfur	1.5	1.5	1.5	1.5	1.04
MBTS	1.5	1.5	1.5	1.5	1.5

Sample codes: N: *Acrylonitrile-butadiene rubber;* ***U:*** *Untreated silica;* ***PA:*** *Plasma-acetylene coated silica;* ***PPy:*** *Plasma-pyrrole coated silica;* ***PTh:*** *Plasma-thiophene coated silica;* ***T:*** *Silanized silica*

The details of the mixing process for the different samples are described in the experimental part of Chapter 4.

6.2.4 Material characterization

Dynamic mechanical measurements were performed using a RPA 2000 dynamic curemeter (Alpha Technologies) at a temperature of 100ºC, a frequency of 0.5 Hz and strain amplitude in the range of 0.56%-100.04%. Bound rubber measurements, the TGA measurements on the bound rubber extract, the determination of the cure characteristics and the relative ranking of the crosslink densities are discussed in detail in the experimental part of Chapter 4.

Further, the mechanical properties were measured on samples, which were cured in a Wickert laboratory press WLP 1600/5*4/3 at 160ºC at a pressure of 100 bar (10 MPa) according to the t_{90} of the samples. The cured specimen dimensions were 90 mm * 90 mm and 2 mm in thickness. The stress-strain properties of the cured samples were measured using a Zwick Z020 tensile tester according to ISO-37, tensile bar Type 2 at a crosshead speed of 500 mm/min.

6.3 Results

6.3.1 Filler-filler and filler-polymer interactions

The addition of fillers to rubber compounds has a strong impact on the static and dynamic behavior of the material. Different from the strain-independent contributions of the hydrodynamic effect, the filler-to-rubber interaction and the cross-linked network of the polymer molecules, the dynamic storage modulus G’ shows a strong strain dependency at low strains. This stress softening at small deformations, also known as Payne-effect[5,6], can be attributed to breakdown of the filler-filler network, and plays an important role in understanding the reinforcement mechanisms of filled rubber. In the present investigation, the ∆G´-values calculated from the difference of the G´-values measured at 0.56% strain and at 100% strain in the unvulcanized state are used to quantify the Payne effect.

The Payne effects of untreated, plasma-coated and silane-treated silica-filled NBR samples are shown in Figure 6.1.

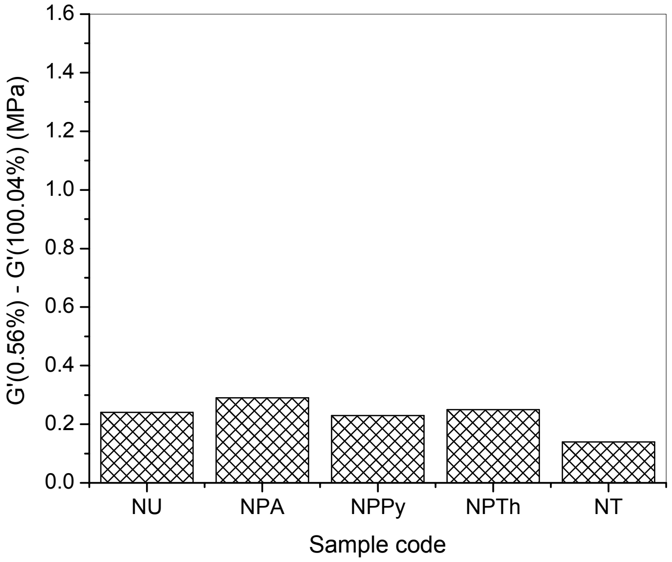

Fig. 6.1: Payne effects of untreated, plasma-polymerized-acetylene, pyrrole-, thiophene-coated and silane- treated silicas in NBR.

In the case of filled NBR, there is no significant difference in the Payne effect values between the samples with untreated and plasma-treated silica's. The silane-treated silica sample (NT) however shows a clearly lower Payne effect compared to all other silica types. Contrary to what was observed for S-SBR and EPDM in the previous chapters, none of the plasma-coatings apparently has an effect on filler-filler interaction in NBR.

The filler-polymer interaction was measured by bound rubber measurements. Figure 6.2 shows the bound rubber contents of the untreated, plasma-coated and silane-treated silica filled NBR compounds. The plasma-acetylene and –thiophene treated silica's show slightly higher bound rubber contents compared to the untreated, plasma-pyrrole and silane-treated silica in NBR. The differences are rather small compared to those seen in the previous chapters for S-SBR and EPDM. The silane-treated silica shows the lowest bound rubber values in this polymer.

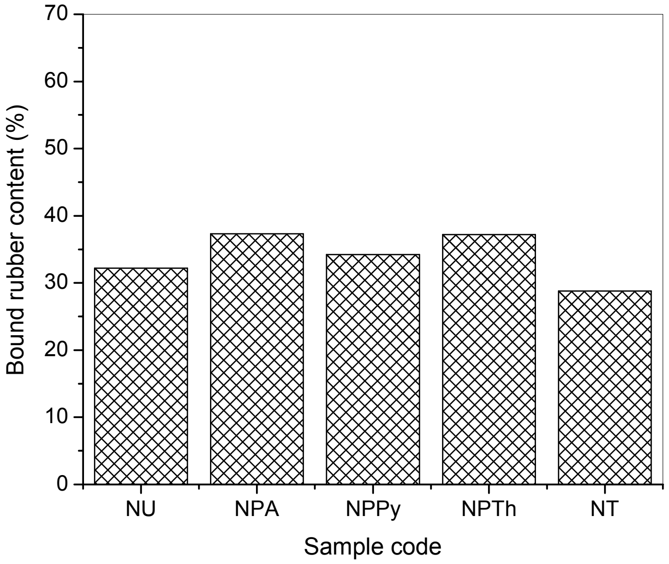

Fig. 6.2: Bound rubber contents of untreated, plasma-polymerized acetylene-, pyrrole-, thiophene-coated and silane- treated silicas in NBR.

Figure 6.3 shows the results of TGA measurements performed on the dried filled rubber material after extraction: this is the filler with attached bound rubber. The weight loss correlates with the bound rubber content, as expected: The values follow the same trend as the bound rubber content shown in Figure 6.2.

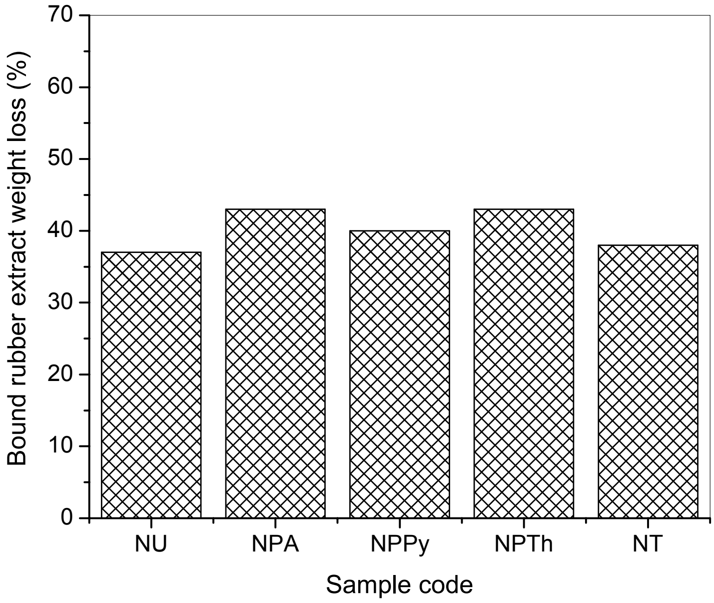

Fig. 6.3: TGA weight loss of bound rubber extract of NBR with untreated, plasma-polymerized acetylene-, pyrrole-, thiophene-coated and silane- treated silicas.

6.3.2 Dispersion and reinforcing effects

Figure 6.4 shows the reinforcement parameter α_F of the different samples. Basically, a lower reinforcement parameter indicates a better dispersion or morphology of the filler in a polymer. According to this measurement, the pyrrole-treated silica has the worst dispersion in NBR. The silane-treated silica shows the lowest value of the reinforcement parameter in comparison with all other types, which corresponds best with the lowest Payne effect in Figure 6.1. It indicates that silane-treatment apparently has the largest effect on compatibilizing the silica with NBR, more than any of the coatings.

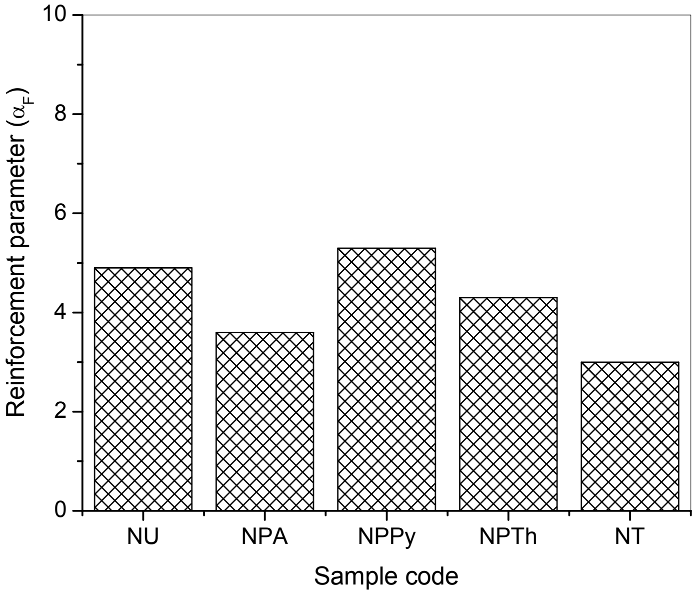

Fig. 6.4: Reinforcement parameter of the reinforced NBR with untreated, plasma-polymerized acetylene-, pyrrole-, thiophene-coated and silane- treated silicas.

6.3.3 Tensile properties and apparent crosslink density

The stress-strain curves of the vulcanizates of NBR with the various silica's are represented in Figure 6.5. In the case of NBR filled with plasma-treated silica's, there is a significant change in the stress-strain curves with considerable increases in ultimate tensile strengths compared to NBR with untreated silica and silane-treated silica. The stress-strain curves became steeper in the series from NPTh over NPPy to NPA. An opposite ranking is found for the elongation at break values: NPTh has the highest value, and NPA shows the lowest elongation at break, although overall the decreases in elongation at break relative to the compound filled with untreated silica are comparatively small.

The differences in the tensile curves are relatively large compared to what would have been expected on basis of the minor variations seen in the previous properties indicative for filler-filler, filler-polymer interactions.

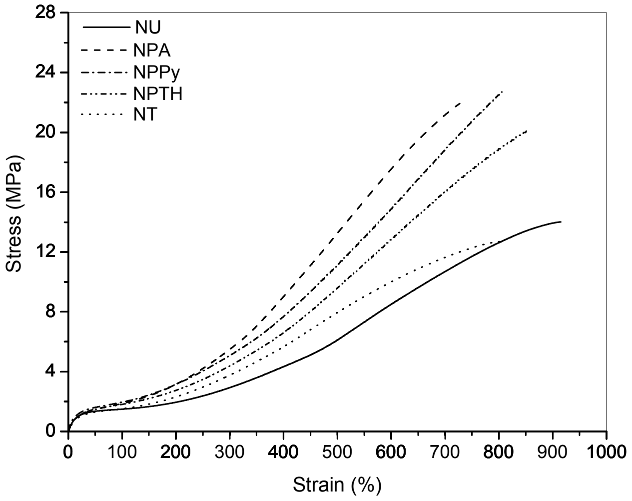

Fig. 6.5: Stress-strain curves of reinforced NBR with untreated, plasma-polymerized acetylene-, pyrrole-, thiophene-coated and silane- treated silicas.

The relative ranking of the crosslink densities of the cured samples is shown in Figure 6.6: There are only slight differences between all samples based on coated and silane-treated silica's and even the difference relative to the untreated silica is minor.

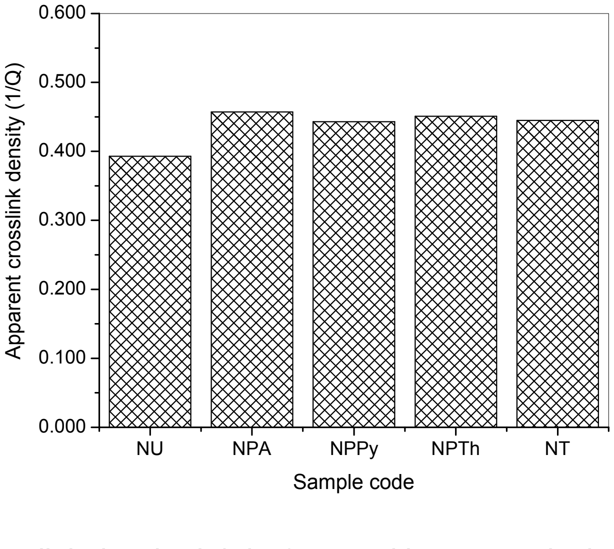

Fig. 6.6: Apparent crosslink density (1/Q) of NBR with untreated, plasma-polymerized acetylene-, pyrrole- and thiophene-coatedand silane-coated silicas.

6.4 Discussion

Figure 6.1 compared to Figures 5.1 and 4.1 as shown in previous chapters, clearly indicates that agglomeration of the filler strongly depends on the polarity match between filler and polymer. The silica-silica interaction measured by the Payne-effect is overall lower in NBR compared to the other polymers due to the fact that the surface energy of filler and polymer match better in this case compared to silica/SBR and silica/EPDM. Consequently, the surface modification of silica with the different monomers shows only a slight influence on the Payne effect. The pyrrole-treated sample NPPy shows a slightly lower Payne effect compared to NU, NPA and NPTh, but the silanized-silica filled sample NT shows the lowest Payne effect within this series, as also seen in the case of S-SBR and EPDM in Chapters 4 and 5. The silane coating is thus very efficient in shielding the silanol groups on the filler surface, thus reducing the filler-filler interaction.

But this effect does not necessarily correlate with the filler-polymer interaction. All plasma-treated silica's show just a slightly higher amount of bound rubber and weight loss measured by TGA as presented in Figures 6.2 and 6.3. Here PA- and PTh-silica have a stronger filler-polymer interaction compared to untreated, NPPy and silane-treated silica. This demonstrates in general a slightly improved compatibility of silica and NBR after the plasma modification. In this particular case, the reduction of the surface energy of silica brings it closer to NBR, resulting in a higher compatibility of the polymer and the filler in comparison to untreated silica and silane-treated silica. Furthermore, unsaturated double bonds are formed on the surface of the plasma treated silica, which in the case of polyacetylene and polythiophene can apparently better interact with the unsaturation of the polymer. The silane coating does not contain any unsaturation, therefore the interaction with the polymer in this case is less pronounced, as long as the compound is not yet vulcanized.

The reinforcement parameters for PA- and PTh-silica filled samples, NPA and NPTh, show a positive effect on dispersion compared to untreated silica, as expected from the higher bound rubber content for these materials. The plasma-pyrrole coating shows a negative effect on dispersion, which again is in line with the lower filler-polymer interaction. However, the silane-treatment of silica shows the strongest positive effect on dispersion in NBR; a consequence of the low filler-filler interaction. This shows that the balance of these three parameters - filler-filler interaction, filler-polymer interaction and dispersion – does determine the final performance of the material. The present results show again, that there is not an unequivocal correlation between these properties.

All plasma-treated silica's show an improvement in the tensile properties in comparison with untreated and silane-treated silica. The PA- and PPy-silica's show the best improvement in terms of moduli and tensile strength. The highest improvement in the tensile properties for PA-silica correlates with the improved dispersion, higher bound rubber content and increased apparent crosslink density. The correlation between moduli and apparent crosslink density does not seem to be generally valid in this matrix. Contrary to what was seen with SBR and EPDM, the cross-link density does not seem to be a dominating factor in combination with filler-polymer interaction for the improvement of the tensile properties in this particular case. In the NBR matrix, the plasma modification of silica with different monomers shows a clear improvement in the vulcanizate properties, which indicates that plasma modification of silica indeed improves the compatibility of filler and polymer in terms of their surface energy.

6.5 Conclusions

All silica samples already show low Payne effect values in NBR compared to SBR and EPDM; therefore no significant further reduction of the filler-filler interaction could be achieved with the plasma PA-, PPy- and PTh-coating of the filler. A reduction of the reinforcement parameter was obtained for PA-, PTh- and the silane-modified silica in NBR, which indicates an improved dispersion of these fillers. The plasma-treated silica- filled samples showed just a little higher bound rubber contents in this matrix than untreated and silane-treated silica. In the vulcanized rubber compounds, the plasma-treated silica types resulted in quite a significant improvement of the tensile properties, with PA- and PPy-silica showing the best mechanical properties, correlating with a combination of improved dispersion, higher bound rubber content and increased apparent crosslink density.

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Chapter 7

Reinforcement of S-SBR/EPDM Blends by Plasma Polymerized Acetylene-, Pyrrole- and Thiophene-Coated Silica

The properties of 50/50 blends based on SBR and EPDM, filled with untreated, plasma-acetylene, -pyrrole and -thiophene as well as silane-treated silica, are investigated by measurement of the Payne effect, the bound rubber content and weight loss related to bound rubber, the reinforcement parameter and the mechanical properties. The pyrrole- and silane-treated silica filled samples show a lower Payne effect in this blend compared to the rubbers filled with PA-, PTh- and unmodified silica, indicating a reduced filler-filler interaction for the first two in the SBR/EPDM blend. The low reinforcement parameter values for all plasma-modified silica types in the blend indicate a better dispersion in comparison to untreated silica. Because PPy-silica filled samples show the best interaction and dispersion properties compared to the other plasma-treated and the untreated silica in the blend, it results in the best mechanical properties with the exception of silane-modified silica. The mechanical properties of the blend filled with plasma-modified silica are significantly improved compared to untreated silica; however, compared to the properties in the straight rubbers all combinations are still largely reduced, as commonly observed for rubber-rubber blends. A proper selection of silica-modification in this blend is shown to be of paramount importance to still obtain the best possible mechanical properties.

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7.1 Introduction

The physical properties of blends of dissimilar rubber polymers are strongly influenced by the heterogeneity of the blends and the distribution of additives, under which the reinforcing fillers, in each of the polymer phases. For filled elastomer blends, a controlled blend structure, i.e. a well-defined distribution of the fillers and curatives in the individual rubber phases, is of primary importance. Generally, reinforcing fillers mainly end up in one of the two phases due to their differences in compatibility with the polymers, leading to over-reinforcement of one and under-reinforcement of the other phase. Interphase transfer of fillers is also observed in blends of highly unsaturated and fully saturated elastomers, explained by a different solvation of the fillers by the polymers in the mixed blends[1].

In recent years, the interest in silica reinforcement for elastomeric applications has grown, especially for tread compounds in tire manufacturing. However, the strong attractive interparticle forces of silica are an obstacle in obtaining a good dispersion within the polymer matrices[2-6]. The surface of precipitated silica carries, on average 5-6 silanol groups per nm^2 and therefore it exhibits a strong hydrophilic character. The hydrophilic nature of the silica surface and the tendency to form hydrogen bonds cause strong filler-filler interactions which prevent easy dispersion during mixing and, as a consequence, influence the final physical properties[7]. Furthermore, extensive transfer of silica from an elastomer with low unsaturation, e.g. ethylene-propylene-diene rubber (EPDM) or isoprene-isobutylene rubber (IIR) to rubbers with high unsaturation (e.g. diene rubbers such as solution-styrene-butadiene rubber, (S-SBR) was found by Jeon et al.[8]**.** Studies in this field demonstrated the preferential take-up of silica by various rubbers, with the silica affinity decreasing in the following order[8]:

NBR > S-SBR > NR ≥ BR > HV- BR > EPDM > IIR

where:

NBR: Butadiene-acrylonitrile rubber
NR: Natural rubber
BR: Polybutadiene rubber
HV-BR: High-vinyl polybutadiene rubber

In the previous Chapters 4, 5 and 6, the reinforcement effect of plasma-treated acetylene-, pyrrole- and thiophene-coated silica in S-SBR, EPDM and NBR was presented. This chapter is focused on S-SBR/EPDM rubber blends, and the effect of the plasma-coated fillers on the structure and mechanical properties of these materials is discussed.

7.2 Experimental

7.2.1 Materials

A detailed description of the materials used for the study can be found in Chapter 4 and 5.

7.2.2 Plasma polymerization of silica

The surface modification of silica by plasma polymerization using acetylene, pyrrole and thiophene monomers was discussed in Chapter 3. In that chapter, a detailed description of the plasma polymerization technique as well as the preparation and characterization of untreated and plasma-treated silicas was reported.

7.2.3 Preparation of rubber samples

The compound formulations used for the 50/50 S-SBR and EPDM blends (S-SBR/EPDM) are given in Table 7.1. In the recipe containing the silane, the amount of sulfur is adjusted to compensate for the presence of sulfur contained in bis-(triethoxysilylpropyl) tetrasulfide (TESPT), to represent equimolar quantities in all cases.

The mixing procedure as discussed in the experimental part of Chapter 4 was applied here as well with the difference, that both polymers were introduced into the mixing chamber at the same time in the very beginning of the mixing cycle.

Table 7.1 Compound formulations of silica reinforced S-SBR/EPDM (50/50) blends.

Components	SEU	SEPA	SEPTh	SEPPy	SET
	phr	phr	phr	phr	phr
S-SBR	50	50	50	50	50
EPDM	50	50	50	50	50
Silica	50	50	50	50	50
ZnO	2.5	2.5	2.5	2.5	2.5
Stearic acid	2.5	2.5	2.5	2.5	2.5
Silane (TESPT)	--	--	--	--	4
Sulfur	1.5	1.5	1.5	1.5	1.04
CBS	1.5	1.5	1.5	1.5	1.5
DPG	0.75	0.75	0.75	0.75	0.75
TMTD	0.4	0.4	0.4	0.4	0.4
ZBEC	0.75	0.75	0.75	0.75	0.75

Sample codes: SE: *Styrene-butadiene rubber/ ethylene-propylene-diene rubber blend;* ***U:*** *Untreated silica;* ***PA:*** *Plasma-acetylene coated silica****; PPy:*** *Plasma-pyrrole coated silica;* ***PTh:*** *Plasma-thiophene coated silica;* ***T:*** *Silanized silica*

7.2.4 Material characterization

The materials were characterized in terms of filler-filler interaction by measuring the Payne effect, and filler-polymer interaction by bound rubber measurements and TGA measurements on the bound rubber extract, as discussed in detail in the experimental part of Chapter 4. The methods to determine the cure characteristics, the apparent crosslink densities and the stress strain properties were also explained in the same chapter.

7.3 Results

7.3.1 Filler-filler and filler-polymer interactions

In dynamic mechanical measurements, reinforced rubber samples display a decrease of the storage shear modulus G´ with increasing strain amplitude, commonly designated as the Payne effect, due to progressive destruction of the filler-filler network[9,10]. The Payne effect values of the S-SBR/EPDM-blend samples filled with untreated, plasma-coated and silane-modified silica's are shown in Figure 7.1.

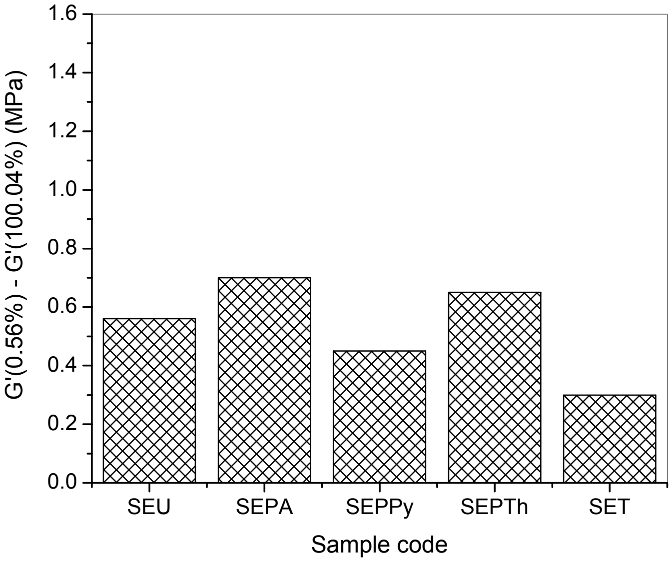

Fig. 7.1: Payne effects of unmodified, plasma-polymerized acetylene-, pyrrole-, thiophene- and silane-coated silicas in S-SBR/EPDM blends.

In these filled S-SBR/EPDM blends, the plasma-acetylene (SEPA) and -thiophene treated silica (SEPTh) show an increase in Payne effect relative to unmodified silica (SEU). Amongst the plasma-treated samples, only the blend containing the pyrrole-treated silica (SEPPy) shows reduced Payne-effect values. And the silane-modified silica shows the lowest filler-filler interaction compared to all other silica's. Comparing these results with those obtained for pure S-SBR in Chapter 4, and pure EPDM in Chapter 5, it is already quite eye-catching that they are totally different! The silane-treated silica still has the lowest Payne effect, just like for S-SBR and pure EPDM.

The level of rubber-silica interaction was further studied by bound rubber measurements. Figure 7.2 shows the bound rubber contents of the various silica-filled S-SBR/EPDM-blend samples. The plasma-treated silica's show in all cases a significantly higher bound rubber content compared to the untreated (SEU) and silane-treated (SET) silica. Comparing these results with those in Chapters 4 and 5, the picture looks most like S-SBR. Except, that pyrrole-treated silica stands out best in this blend-case, while it was the worst of the three coatings in pure S-SBR as well as in EPDM.

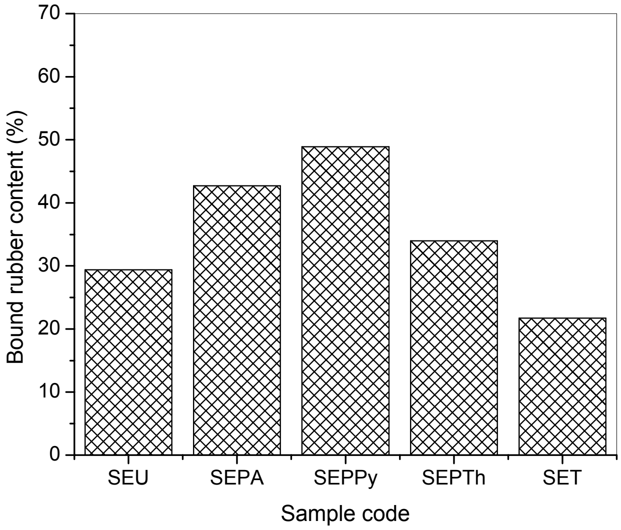

Fig. 7.2: Bound rubber content of untreated, plasma-polymerized acetylene-, pyrrole-, thiophene- and silane-treated silicas in S-SBR/EPDM blends.

In Figure 7.3, the TGA measurements performed on the extracted dried material are shown. These values follow the same trends as the bound rubber contents shown in Figure 7.2, thus confirming these measurements: the same as seen in the previous chapters.

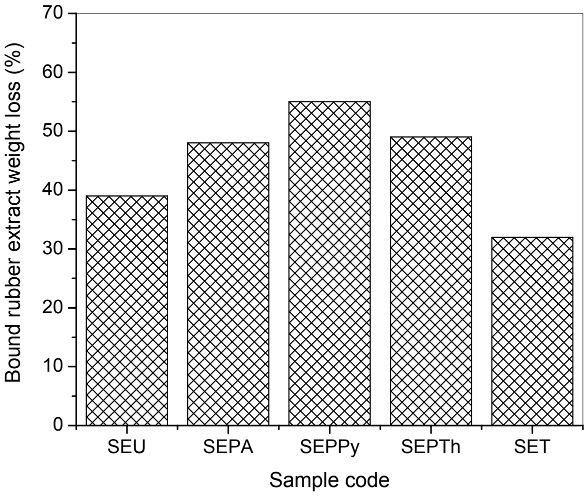

Fig. 7.3: TGA weight loss of bound rubber extract of S-SBR/EPDM blends with untreated, plasma-polymerized acetylene-, pyrrole-, thiophene- and silane-treated silicas.

7.3.2 Dispersion and reinforcing effects

As mentioned earlier, a lower reinforcement parameter α_F (eq. 4.1) indicates a better degree of dispersion of a filler in a polymeric matrix. In Figure 7.4, the untreated silica filled sample SEU shows the highest value for the reinforcement parameter, which indicates the lowest degree of dispersion in the matrix. The silane-treated silica filled blend shows a higher reinforcement parameter than the plasma-silica filled material.

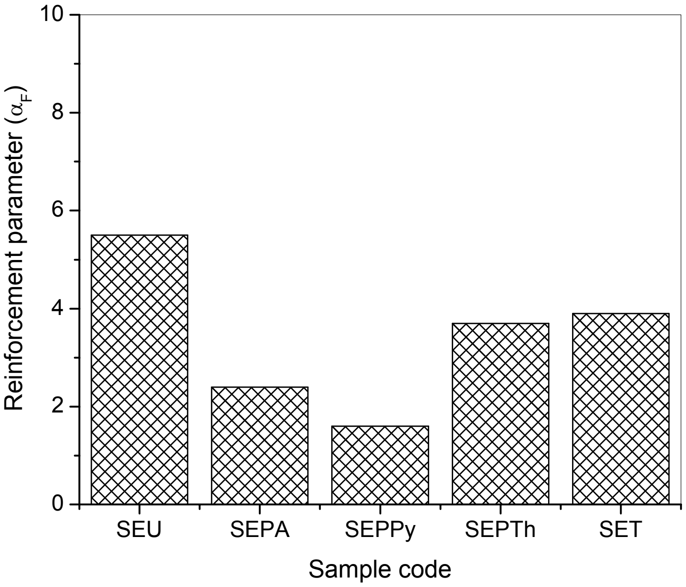

Fig. 7.4: Reinforcement parameter of the reinforced S-SBR/EPDM blends with untreated, plasma-polymerized acetylene-, pyrrole-, thiophene- and silane-treated silicas.

7.3.3 Tensile properties and apparent crosslink density

The stress-strain curves of vulcanizates of untreated, plasma- and silane–treated silica filled S-SBR/EPDM vulcanizates are represented in Figure 7.5. The first thing to notice is the generally lower tensile strengths and elongations at break for all blends, compared to those of the pure polymers: Figures 4.5 and 5.5. It confirms the general problems with rubber-rubber blend properties. The second is the relatively small differences in the moduli of the various samples vs. the large differences seen in the pure polymers.

Incorporation of untreated silica into the blend (SEU) leads to unacceptably low values of moduli, tensile strength and elongation at break. However, there is a significant improvement in tensile properties, when plasma-treated silicas are used. The plasma-acetylene treated silica (SEPA) shows the highest moduli values, but still a comparable tensile strength with SEPPy and SEPTh. The later samples clearly show the highest elongations at break together with the silane-treated silica-filled S-SBR/EPDM blend. Still, the values of tensile strength and elongation at break remain low compared with the pure rubbers.

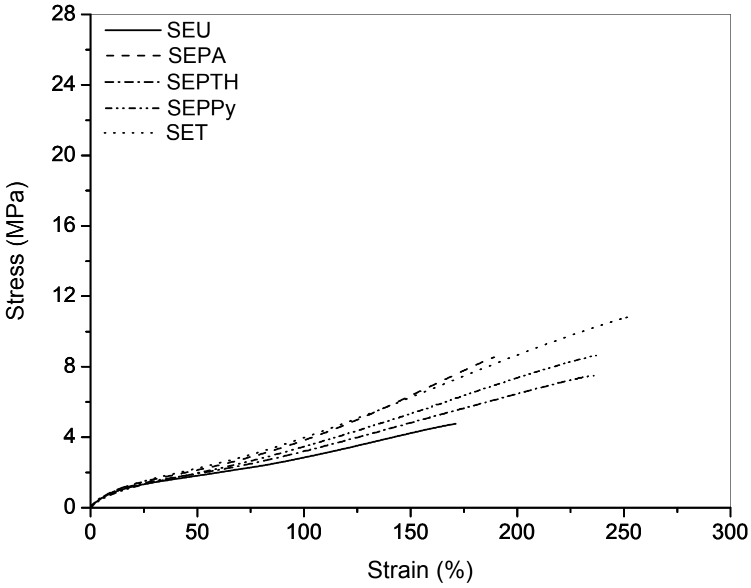

Fig. 7.5: Stress-strain curves of reinforced S-SBR/EPDM blends with untreated, plasma-polymerized acetylene-, pyrrole-, thiophene-and silane-treated silicas.

The apparent crosslink densities (1/Q) of the cured samples are shown in Figure 7.6. SEU, SEPPy and SEPTh show mutually similar values of the apparent crosslink density, which are lower than the crosslink densities of SEPA and SET. The small differences look most like the effects seen in S-SBR in Chapter 4, rather than in EPDM in Chapter 5.

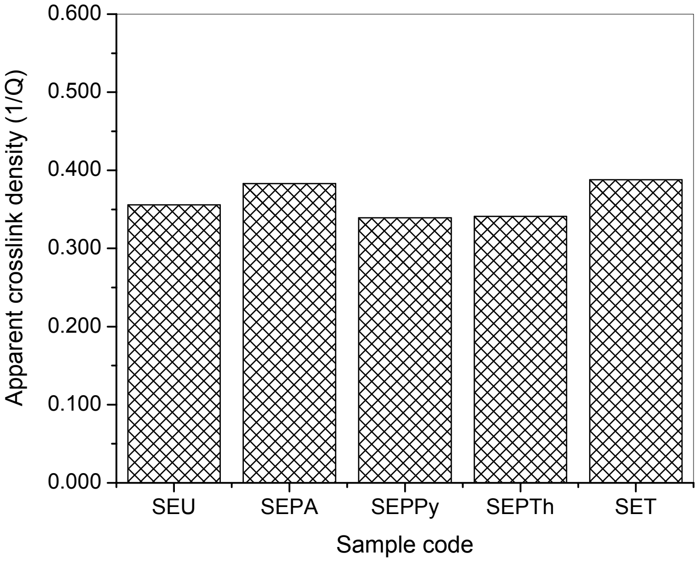

Fig. 7.6: Apparent crosslink density (1/Q) of S-SBR/EPDM blends with untreated, plasma-polymerized acetylene-, pyrrole-, thiophene-and silane-treated silicas.

7.4 Discussion

It is surprizing to see that the various properties in the 50/50 S-SBR/EPDM blend are so different from those seen in the pure polymers. In fact, those in the pure polymers have little if any predictive value for the blend. It illustrates well the general experience in rubber technology that properties of rubber-rubber blends cannot be predicted on basis of the properties of the pure rubbers. It is very seldom to find positive synergistic effects, rather than negative.

Figure 7.1 shows that the plasma-pyrrole coating reduces the filler-filler interaction, thus improving the compatibility and the dispersion of the filler in the polymer blend. Contrary to this, the plasma-acetylene and -thiophene treatment of silica increases the filler-filler interaction in the blend relative to untreated silica. This increase in Payne effect for the SEPA and SEPTh blends relative to the untreated silica is totally unexpected, in comparison with the reduction seen for S-SBR and EPDM in Chapters 4 and 5. It may be explained by the differences in compatibility between the plasma-coatings and the polymers. In the case of PPy-silica, the degree of filler-filler interaction was quite similar in both straight rubber phases, as the Payne effect values were closest as shown in Figures 4.1 and 5.1: 0.55 MPa in S-SBR and 0.75 MPa in EPDM. It may be conceived that this results in a more homogenous distribution of the filler in the blend, with low filler-filler interaction. Compared to untreated silica, PPy-silica has a significantly higher affinity towards EPDM; the Payne effect value of untreated silica in EPDM was 1.4 MPa. Apparently, in the blend using PPy-silica, the EPDM phase dominates the performance.

On an absolute scale, the largest differences in Payne effects were seen in pure EPDM, Figure 5.1, relative to S-SBR. The fact that the absolute values for the blends using PA and PTh are more or less half-way those for the pure rubbers, means that with these silica's there is no clear dominance of either one: a simple blend law.

The higher amounts of bound rubber and weight losses measured by TGA for all plasma-treated silica filled samples, Figures 7.2 and 7.3, demonstrate an improved filler-polymer interaction between all these silica types and the S-SBR/EPDM rubber blends compared to untreated and silane-treated silica. They clearly stand out relative to the pure rubbers. The plasma-pyrrole treated silica filled blend shows the highest filler-polymer interaction compared to all other samples; most probably due to the best match of surface energy of the PPy-treated silica with both polymers as also indicated by the low Payne effect value for this system. The filler-polymer interaction for PPy-silica in the straight rubber matrices was low compared to the other silica samples: Figures 4.2 and 5.2. This indeed shows a compatibilization effect of the PPy-modified filler in the polymer blend: a positive synergistic effect. PA-silica has the second position concerning bound rubber content; however, this value is lower (42.7%) than the individual values in the straight rubber phases (54.3% in SBR and 53.4% in EPDM): a slightly negative synergy. PTh-silica also shows higher filler-polymer interaction compared to silane-treated and untreated silica, and the bound rubber value in the blend is comparable to the value found in straight EPDM: 34.0 % and 32.5 % respectively. Similar values in the straight polymers indicate a comparable affinity of the PA-silica to both polymers; however, in the blend the morphology seems to influence the filler-polymer interaction and thus to reduce the bound rubber formation. A similar result is obtained for the silane-treated filler. Overall, it is clear that the compatibility of silica with the different polymer matrices can be improved in terms of filler-polymer interaction by a proper choice of the monomer for the coating of the filler surface.

The reinforcement parameters for all three plasma-silica filled samples, show a positive effect on dispersion compared to untreated and silane-treated silica. On the one hand, the PA- and PPy-silica filled S-SBR/EPDM blends show the best dispersion of all, as measured by the reinforcement parameter. This is in line with the improved filler-polymer interaction for these samples. On the other hand, SEU shows the highest value of reinforcement parameter, thus the lowest degree of dispersion. This is caused by the differences in compatibility with S-SBR and EPDM: The filler-filler interaction is significantly higher and the filler-polymer interaction is lower in EPDM compared to S-SBR: Figures 4.1 vs. 5.1 and 4.2 vs. 5.2. Therefore, most of the unmodified silica will eventually be dispersed in S-SBR rather than in EPDM, resulting in a grossly inhomogeneous distribution of this silica between the different phases. In global terms this picture corresponds reasonably well with Figures 4.4 for pure S-SBR and 5.4 for pure EPDM. Except that the pyrrole-coated silica performs best in the present blend case, while in pure S-SBR as well as in pure EPDM it performed worst of the three different plasma-coatings.

The PA-, PPy- and PTh-silica filled S-SBR/EPDM blends show higher moduli values compared to SEU due to an intensive polymer-filler interaction in the cured material. However, compared to the straight rubbers generally much lower values are found for all combinations.

Still, in terms of tensile strength and elongation at break there are large differences to be seen. These latter properties are often higher valued than the moduli in terms of practical performance of rubbers. In Figure 7.5 the silane-treated silica outperforms the plasma-coated samples, while on the other hand all treated silica’s performs much better than untreated. The moduli of the silane-treated silica filled blend are so high as a consequence of the chemical interaction between the polymer and the sulfur-moieties of the coupling agents[11]. Crosslinking results in a more stable network, as also confirmed by the tensile strength to be higher compared to all other samples. It also corresponds with the relative ranking of the crosslink density, which is highest for this silane-modified silica type in the S-SBR/EPDM blend. In the case of SEPTh, the lower moduli values correspond to low crosslink density values: Figure 7.6. Contrary to the silane-case, it can be the consequence of a negative contribution of the sulfur moieties present on the PTh-silica surface: They might poison the few unsaturated sites present in the EPDM structure and deactivate these for crosslinking. This is also seen in Figure 5.5, where

PTh-silica filled EPDM showed the same trend for the stress-strain properties. These latter results show, that even in the blend case the degree of crosslinking still has a strong influence on the properties obtained.

It is worth to mention at this point, that Guo using acetylene for plasma-modification of elemental sulfur and CBS vulcanizing agents also found a large improvement in tensile properties for S-SBR/EPDM blend combination[12]. Acetylene plasma-modification also performed very well in the present context. It emphasizes the important role which the degree of crosslinking plays, irrespective of whether it is boosted by polyacetylene-coating on the silica-filler or on the curatives. It is quite interesting at this point, what the combination of both in the S-SBR/EPDM blend would have given.

Still, all plasma-treated samples show an improvement in terms of dispersion and tensile properties compared to untreated silica. The different plasma-monomer treatments show different levels of improvement due to the different levels of compatibilization with the polymers in the blend, and the interaction of the polymers with active moieties on the filler surface.

A remarkable result is that the silane-treated silica shows the lowest Payne effect in all straight polymers and in this blend. For the blend, it remains a point of discussion though, how to interpret the degree of dispersion of silica in terms of Payne effect. The Payne effect has been well documented for single polymer compounds; however, whether it also applies for blends in the same manner was never investigated. The effects throughout this study such as filler-filler as well as filler-polymer interaction and dispersion are difficult to relate to the final tensile properties. This needs to be further investigated with detailed morphological studies in order to clarify this in more detail.

7.5 Conclusions

The behavior of different filler types in a blend is commonly not related to the behavior of these fillers in the straight polymers via a simple blend law. In a blend, the interaction between the different components of a compound can be very different from a single polymer.

In the 50/50 S-SBR/EPDM blend, the plasma-pyrrole coating reduces the filler-filler interaction, while plasma-acetylene and -thiophene treatment of silica leads to an increase. The balanced filler-filler interaction for the pyrrole-treated silica in both straight polymers apparently has a positive effect on the compatibility with the individual phases within this blend. Additionally, this combination shows the best filler-polymer interaction and dispersion, resulting in the best overall mechanical properties of this material within the series of plasma-coated silica's.

All plasma-treated silica filled samples show higher bound rubber contents compared to untreated and silane-treated silica, due to a better compatibilization of the fillers with the polymers. The improvements in filler-filler and filler-polymer interaction finally result in a better dispersion of all three plasma-silica filled samples compared to both other silica types: untreated and silane-modified. Still, silane-treated silica performs the best in this blend as a consequence of interaction between the individual polymers and the sulfur-moieties in the coupling agents.

These results show that the compatibility and interaction of silica with different rubbers can be controlled by tailoring the surface energy of the filler by plasma-polymerization. Different functionalities and polarities of the filler surface determine the compatibility and interaction with the elastomeric matrix, which for a proper combination may lead to improvement of the final vulcanizate properties.

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Chapter 8

Reinforcement of NBR/EPDM Blends by Plasma Polymerized Acetylene-, Pyrrole- and Thiophene-Coated Silica

The properties of blends based on NBR and EPDM, filled with plasma-acetylene, -pyrrole and -thiophene coated as well as untreated and silane-treated silica, are investigated by measurement of the Payne effect, the bound rubber content, the reinforcement parameter and the mechanical properties. The pyrrole- and silane-treated silica filled samples show a significantly reduced Payne effect for this blend compared to the rubber blends filled with acetylene- and thiophene-treated as well as unmodified silica, indicating a reduced filler-filler interaction of these silicas in NBR/EPDM. The low reinforcement parameter values for all plasma-modified silica types in the blend indicate an improved dispersion in comparison to untreated silica. The polypyrrole-silica filled samples show the best filler-polymer interaction and dispersion properties compared to the other plasma-treated and the untreated silica in the blend. Contrary to the results in the SBR/EPDM blends in the previous Chapter 7, the plasma-coatings have no positive effect on the overall crosslink density of this NBR/EPDM system. The large improvements yet obtained in the mechanical properties, especially for the polyacetylene-coated silica, are primarily the result of a compatibilization effect of the two otherwise incompatible NBR and EPDM polymers.

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M. Tiwari, W. K. Dierkes, J. W. M. Noordermeer, W. J. van Ooij, Polym. Adv. Technol., 19, 1672 (2008).

8.1 Introduction

Blends of elastomers are used in a wide variety of rubber products. The purpose of using rubber blends in the industry is to obtain the best compromise in physical properties, processability and costs, which is not commonly achievable with a single elastomer. One important component for rubber blends may be ethylene-propylene diene rubber (EPDM) due to its good heat ageing properties and improved ozone resistance compared to high diene rubbers, but it possesses poor solvent resistance. NBR has a high resistance to swelling in oils and solvents but suffers from poor ozone resistance and heat aging properties. A blend of these two polymers might allow to tailor a material which withstands ozone, heat aging, oil and solvent swelling, while maintaining good mechanical properties. Unfortunately, rubber-rubber blends often show poorer physical properties than the straight elastomers due to thermodynamic incompatibility, which results in a lack of physical and chemical interactions across the phase boundaries and poor interfacial adhesion[1-4].

From the previous studies in this thesis, the reinforcement of EPDM with plasma-treated silica clearly shows an improvement in filler dispersion and mechanical properties of the vulcanizates in comparison with untreated silica. In the case of NBR, plasma treatment of silica results in a higher bound rubber content due to stronger filler-polymer interactions. Further, plasma-treated silica-filled NBR shows significantly higher moduli and tensile strength values compared to untreated as well as silane-treated silica, considered to be the result of improved dispersion and compatibilization with NBR.

By considering the above-mentioned facts of improved compatibility of plasma-treated silica with straight NBR and EPDM, it might also be possible to improve the filler dispersion and final mechanical properties in NBR/EPDM polymer-polymer blends by the plasma surface modification technique applied onto fillers[5-10], which is the subject of this chapter.

8.2 Experimental

8.2.1 Materials

A detailed description of the materials used for the study can be found in Chapters 5 and 6.

8.2.2 Plasma polymerization of silica

The surface modification of silica by plasma polymerization using acetylene, pyrrole and thiophene monomers was discussed in Chapter 3. A detailed description of the plasma polymerization technique as well as the preparation and characterization of untreated and plasma-treated silicas was reported.

8.2.3 Preparation of rubber samples

The compound formulations used for the NBR and EPDM blends (NBR/EPDM) are given in Table 8.1. In the recipe containing the silane, the amount of sulfur was adjusted to compensate for the presence of sulfur contained in bis-(triethoxysilylpropyl) tetrasulfide (TESPT), to represent equimolar quantities in all cases.

The mixing procedure as discussed in the experimental part of Chapter 4 was applied here as well with the difference, that both polymers were introduced into the mixing chamber at the same time in the very beginning of the mixing cycle.

Table 8.1 Compound formulations of silica reinforced NBR/EPDM (50/50) blends.

Components	NEU	NEPA	NEPPy	NEPTh	NET
	phr	Phr	phr	phr	phr
NBR	50	50	50	50	50
EPDM	50	50	50	50	50
Silica	50	50	50	50	50
ZnO	2.5	2.5	2.5	2.5	2.5
Stearic acid	2.5	2.5	2.5	2.5	2.5
Silane (TESPT)	--	--	--	--	4.0
Sulfur	1.50	1.50	1.50	1.50	1.04
CBS	0.75	0.75	0.75	0.75	0.75
TMTD	0.40	0.40	0.40	0.40	0.40
ZBEC	0.75	0.75	0.75	0.75	0.75
MBTS	0.75	0.75	0.75	0.75	0.75

Sample codes: NE: *Acrylonitrile-butadiene rubber/ Ethylene-propylene-diene rubber blend;* ***U:*** *Untreated silica;* ***PA:*** *Plasma-acetylene coated silica****; PPy:*** *Plasma-pyrrole coated silica;* ***PTh:*** *Plasma-thiophene coated silica;* ***T:*** *Silanized silica*

8.2.4 Material characterization

The materials were characterized in terms of filler-filler interaction by measuring the Payne effect, and filler-polymer interaction by bound rubber measurements and TGA measurements on the bound rubber extract, as discussed in detail in the experimental part of Chapter 4. The methods to determine the cure characteristics, the apparent crosslink densities and the stress-strain properties are also explained in the same chapter.

8.3 Results

8.3.1 Filler-filler and filler-polymer interactions

The strain sweep data of filler reinforced compounds in general show a highly non-linear behavior. This strong strain-dependence of the elastic modulus is known as the Payne effect[11,12]. The decrease of the storage modulus G' with increasing strain is due to the progressive destruction of the secondary filler-filler network. It has been shown that the ΔG' obtained from the difference in G' measured at 0.56% and 100.04% strain in unvulcanized compounds can be used to quantify the Payne effect[13].

The Payne effect values of untreated, plasma-acetylene, -pyrrole, -thiophene coated and silane-modified silica-filled NBR/EPDM-blend samples are shown in Figure 8.1. In the case of plasma-treated silica filled NBR/EPDM, all samples show a reduction in Payne effect compared to the untreated silica filled sample (NEU). Plasma-pyrrole (NEPPy) treated silica shows the lowest Payne effect within this group; however, the silane-treated silica reinforced material (NET) shows an even lower Payne effect. Surprisingly, although the absolute values for all samples are different, their relative ranking is the same as seen for straight EPDM in Figure 5.1.

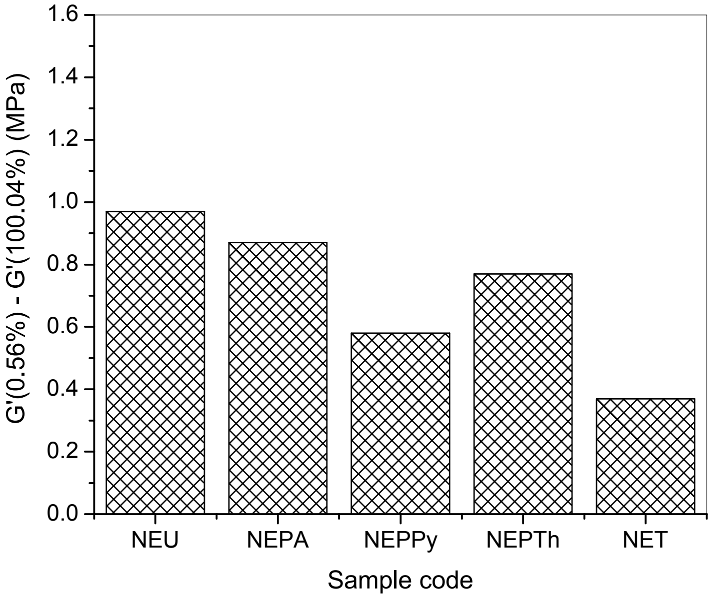

Fig. 8.1: Payne effects of untreated, plasma-polymerized acetylene-, pyrrole-, thiophene- and silane-modified silicas in the NBR/EPDM blend.

The level of rubber-silica interaction was studied by bound rubber measurements. Figure 8.2 shows the bound rubber contents of untreated, plasma-modified and silane-treated silica filled compounds. In this series, the plasma-pyrrole (NPPy) treated silica shows the highest bound rubber content. The untreated silica (NEU) and silane-treated (NET) silica show similar values for the bound rubber content, both lower than the values of the plasma-treated silica samples. The mutual ranking of the various silica-types with respect to bound rubber is totally different from those for the pure rubbers: Figures 5.2 and 6.2.

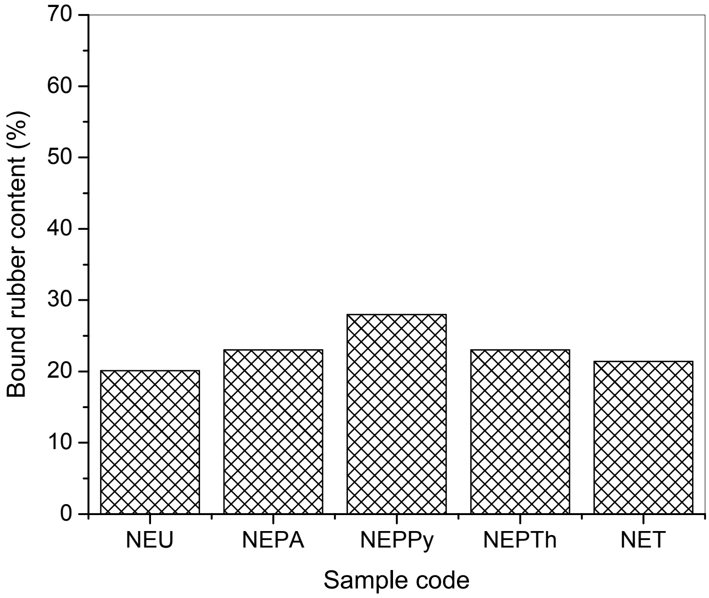

Fig. 8.2: Bound rubber content of unmodified-, plasma-polymerized acetylene-, pyrrole-, thiophene- and silane-treated silicas in a NBR/EPDM blend.

Figure 8.3 shows the results of TGA measurements performed on the dried filled rubber materials after extraction: the filler with attached bound rubber. The weight loss correlates with the bound rubber content as presented in Figure 8.2. As expected, the values follow the trend shown in Figure 8.2, thus confirming these results. Again, the PPy-silica filled sample shows the highest bound rubber content. However, the PA- and the PTh-silica filled materials differ somewhat compared to their same value seen for the bound rubber content.

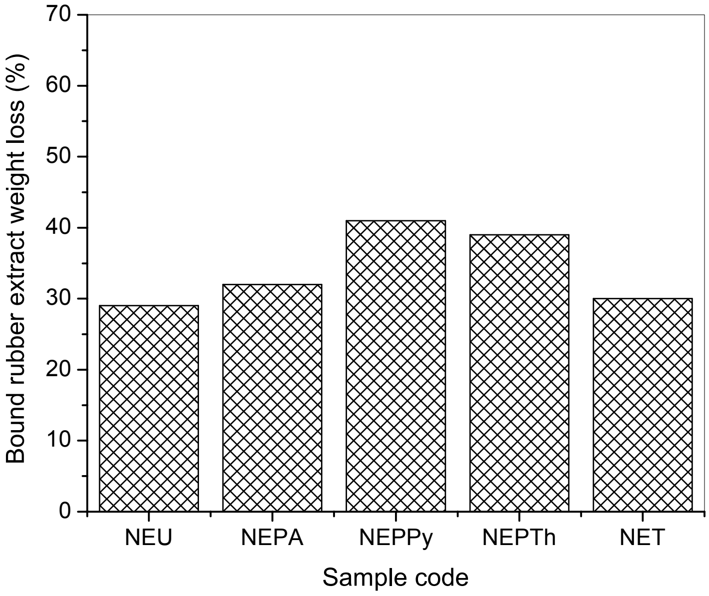

Fig. 8.3: TGA weight loss of the bound rubber extract of NBR/EPDM blends with unmodified, plasma-polymerized acetylene-, pyrrole-, thiophene- and silane-treated silicas.

8.3.2 Dispersion and reinforcing effects

Figure 8.4 shows the reinforcement parameter α_F of the different samples. A lower reinforcement parameter indicates an improved dispersion of the filler in a polymer. The samples with plasma-acetylene, -pyrrole, -thiophene and silane-treatment show lower values of the reinforcement parameter compared to the untreated silica filled material, which indicates a lower degree of agglomeration of the silica and consequently an improved dispersion in the incompatible polymer matrices. The PPy-silica filled sample of NBR/EPDM shows the lowest value. In comparison with the Payne-effects as seen in Figure 8.1, about the same ranking is observed, with the exception of the silane-modified silica which shows less of a decrease in reinforcement parameter and therefore improvement in dispersion, than might have been anticipated based on the large reduction in Payne effect.

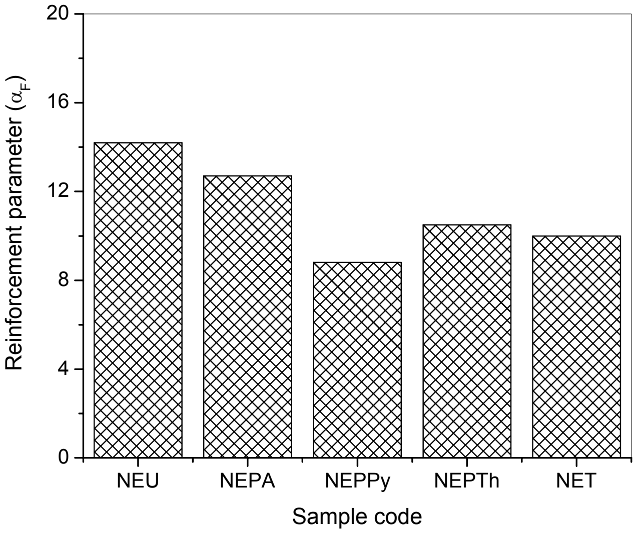

Fig. 8.4: Reinforcement parameter of the filled NBR/EPDM blends with unmodified, plasma-polymerized acetylene-, pyrrole-, thiophene-and silane-treated silicas.

8.3.3 Tensile properties and apparent cross-link density

The stress-strain curves of vulcanizates of the various silica filled NBR/EPDM vulcanizates are represented in Figure 8.5.

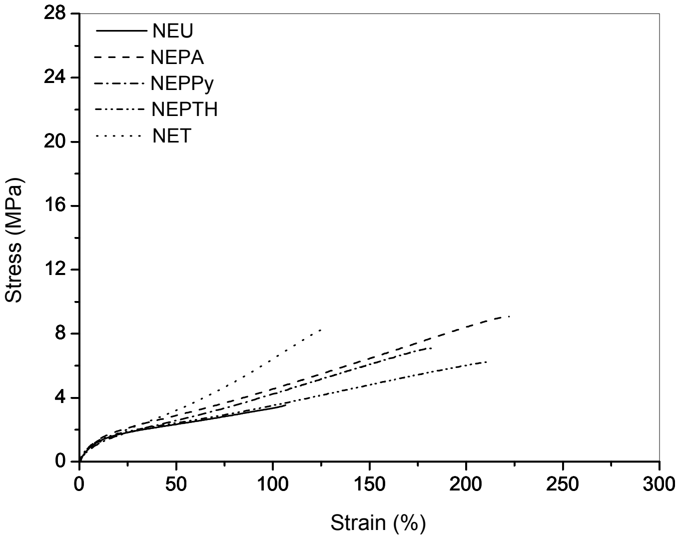

Fig. 8.5: Stress-strain curves of reinforced NBR/EPDM blends with unmodified, plasma-polymerized acetylene-, pyrrole-, thiophene-and silane-treated silicas.

Contrary to the modest effects seen in the SBR/EPDM-blend in the previous chapter, in the case of NBR/EPDM filled with PA-, PPy- and PTh-silica, a significant change in the stress-strain curves with a considerable increase in tensile strength is observed as consequence of the plasma-treatment. In the case of untreated silica, NEU, very low values of tensile strength and elongation at break are found. But, the silane-modified silica clearly shows the highest increase in moduli, like it did in pure EPDM: Figure 5.5, but the opposite in NBR: Figure 6.5. In terms of tensile strength and elongation at break, the polyacetylene coated, NEPA, and polypyrrole coated, NEPPy, silica perform the best; again similar to their behavior in pure EPDM: Figure 5.5. Overall, the results resemble most those of the pure EPDM and certainly not those of pure NBR. Again all values of the tensile strength, irrespective of the type of silica, for the NBR/EPDM blend are much lower than for the pure polymers.

The crosslink densities were measured by swelling of the filled vulcanizate samples, and the reciprocal of the swelling value represents the apparent crosslink density. The relative ranking of crosslink densities of the cured samples is shown in Figure 8.6. Surprisingly, in this particular case, comparing the relative ranking of the respective curves for NBR/EPDM, it becomes clear that there is no real correlation between the moduli at 100% and the apparent crosslink densities for the different types of silica filled NBR/EPDM blends. The small differences seen look more like pure NBR: Figure 6.6, than pure EPDM for which actually large differences in relative crosslink densities were seen: Figure 5.6.

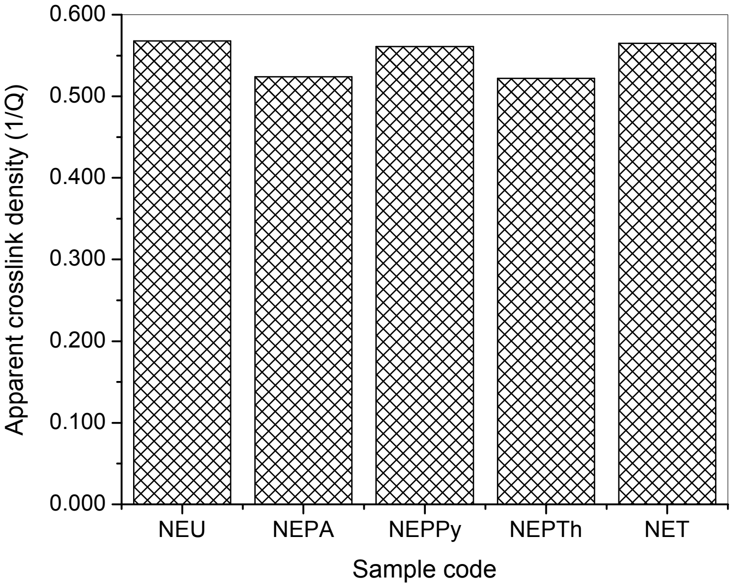

Fig. 8.6: Apparent crosslink density (1/Q) of NBR/EPDM blends with unmodified, plasma-acetylene, -pyrrole, -thiophene and silane-treated silicas.

8.4 Discussion

It is very surprising to see, that this blend system of NBR and EPDM in its various properties sometimes resembles pure EPDM and other times NBR. The shielding of the silica surface by hydrocarbons reduces the extent of hydrogen bonding, which results in a lower Payne effect. Figure 8.1 shows that the surface modification of silica by all different monomers has a positive influence on the Payne effect in the NBR/EPDM compounds. From the different monomers used for plasma-coating of silica, the polypyrrole coating is most effective in shielding the surface and improving the compatibility with the polymers. A similar trend was found in straight EPDM as shown in Figure 5.1. In contrast to this, there was no reduction of the Payne effect for PPy silica observed in straight NBR, although the PA- and PTh-coatings even increased the Payne-effect relative to unmodified silica. This leads to the conclusion that PPy-silica has the highest compatibilizing effect for EPDM compared to NBR in the blend. As in the other polymers and polymer blends, it is the silanized-silica filled sample which still shows the lowest Payne effects of all: The effective chemical modification of the polar silica surface by the silane apparently still leads to the best compatibilization of the surface for all polymers used in this study.

Figures 8.2-8.3, the bound rubber measurements, show a stronger filler-polymer interaction for all plasma-treated silica's compared to the untreated and silane-treated silica in this blend. The plasma-pyrrole treated silica filled NBR/EPDM shows by far the highest filler-polymer interaction in this series (28%), and the value is roughly the average of the values found in the straight polymers: 24% in EPDM and 34% in NBR. This indicates a balanced distribution of the silica in the two polymers, and a good dispersion as was seen already in the low Payne effect. The polypyrrole-coating compatibilizes the filler for both polymers and seems to match the surface energy of both rubbers in the NBR/EPDM blend to the same extent. In all other cases, the bound rubber content in the blend is lower than both values in the straight polymers, indicating uneven distribution and reduced interaction with the polymers. The most extreme case is found for the polyacetylene coating: in NBR, the bound rubber content is 37%, in EPDM, the content is 53%, and in the blend the bound rubber content is even reduced to 23%.

The reinforcement parameters for all plasma-treated silica filled samples show a positive effect on dispersion compared to untreated silica. This is in correlation with the Payne effect as discussed above. Again, the NEPPy shows the best result: It has the highest degree of dispersion and confirms the compatibilization effect of this surface modified filler for the elastomer blend.

The absolute values of the reinforcement parameters are significantly higher than the values in the straight polymers and the SBR/EPDM blend. Looking at the Payne effect, the same trend is observed: higher values in the NBR/EPDM blends compared to the other polymer matrices, with the exception of the straight EPDM compound. This indicates that the dispersion in this NBR/EPDM blend does not reach the level found for the straight polymers, nor for the SBR/EPDM blend. So, even though the effect here is a balanced distribution of the silica in the polymer blend, there is still a low compatibility with both polymers, which is also confirmed by the low bound rubber contents.

The final vulcanizate properties represent the combinatorial effect of dispersion, filler-polymer interaction as well as polymer entanglements and crosslink density. All plasma-treated silica-filled NBR/EPDM materials show a considerable increase in tensile strength compared to untreated silica. The NEPA-blend shows the highest value in tensile strength, followed by the blend with the silane treated filler. The PA-silica also shows the highest modulus at 100% and elongation at break compared to all other samples of silica-filled NBR/EPDM. As this is combined with low crosslink density, moderate dispersion and filler-polymer interaction based on the previous experiments, this must be the effect of compatibilization of the two polymers by the filler, reducing the weakening effect of the phase boundaries between the polymers in the blend. Against the expectations, plasma pyrrole silica does not show the best improvement in terms of tensile properties after showing the best dispersion and filler-polymer interaction level in comparison to all other samples. This might be due to the interface incompatibility of the NBR and EPDM, which in this case apparently is not reduced by the treated filler.

The two samples coated with sulfur-containing substances: polythiophene and TESPT, result in very different stress-strain curves: The addition of the silane treated silica results in high moduli, high tensile strength but low elongation at break, while the polythiophene-treatment results in low moduli, low tensile strength and high elongation at break. The silane treatment seems to be more effective in providing additional crosslink moieties, as can also been seen in the crosslink density values.

The relative ranking of the crosslink densities does not show any correlation with tensile properties, especially not with the modulus at 100% in any case. The unmodified, polypyrrole- and silane-treated silica-filled samples show similar crosslink densities; the polyacetylene- and polythiophene-treated silica-filled materials also show comparable values, but on a slightly lower level. No additional crosslinking from unsaturated or sulfur functionalities is observed for these two coatings. However, compared to the crosslink density measured in the S-SBR/EPDM blend, the density here is significantly higher: 0.55 in NBR/EPDM compared to 0.36 in S-SBR/EPDM.

Overall, the PA-silica ranks best in terms of tensile properties in the NBR/EPDM blend. Guo evaluated polyacetylene-coated sulfur and CBS vulcanization agents in this same blend, with practically no improvement over unmodified curatives[14]. The author demonstrated that this blend system could not be improved in co-curing behavior, with the exception of a polyacrylic coating on sulfur (not tested in the present context). Combining those observations with the present ones, supports the conclusion that the improvements in tensile properties observed for the polyacetylene-coated silica are mainly the result of compatibilization of the otherwise incompatible EPDM and NBR polymers by the modified silica. This in sharp contrast with the S-SBR/EPDM blend system in the previous Chapter 7, where the improved mechanical properties were mainly due to a higher overall degree of crosslinking.

8.5 Conclusions

The behavior of different filler types in a blend is not necessarily related to the performance of these fillers in the straight polymers. In a blend, the interaction between the different components can be totally different from the straight polymers.

In the NBR/EPDM blend, the plasma-pyrrole coating significantly reduces the filler-filler interaction, while plasma-acetylene and -thiophene treated silica show a smaller reduction relative to untreated silica. This indicates a balanced distribution of the pyrrole-treated silica in both polymers, and a positive effect on the compatibility within this blend. Additionally, this combination shows the best filler-polymer interaction and dispersion. But afterall, it does not result in the best overall mechanical properties of this blend.

All plasma-treated silica-filled samples show higher bound rubber values compared to untreated and silane-treated silica, due to better compatibilization of the filler with the polymers. The improvements in reduced filler-filler and increased filler-polymer interactions result finally in a better dispersion of all three plasma silica-filled samples compared to untreated and silane-treated silica. The higher moduli and tensile strength values of PA-silica filled NBR/EPDM compared to the untreated and plasma-pyrrole and -thiophene treated samples, are due to a better chemical interaction of the PA-silica with EPDM and a reduced incompatibility between the two polymer phases. Effects of crosslink density were not detected for this system.

These results show that the compatibility and interaction of silica with different rubbers can be controlled by tailoring the surface energy of the filler by plasma-polymerization.

8.6 References

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Chapter 9

Morphological Investigations of S-SBR, EPDM, NBR and their Blends, Reinforced with Untreated and Plasma-Modified Silica

Micro-morphology of rubber compounds, such as polymer and filler distribution, is one of the most important parameters affecting compound properties. Atomic Force Microscopy (AFM) is a powerful technique for analyzing phase morphology. In this study, the morphology of compounds filled with untreated, plasma acetylene-coated (PA) and silane-treated silica is investigated in S-SBR, EPDM, NBR and their 50/50 blends. The microdispersion of PA-silica shows improved dispersion in S-SBR, EPDM and NBR in comparison with untreated silica. Silane-treated silica also shows a good dispersion in all straight rubbers. PA-silica filled S-SBR/EPDM and NBR/EPDM blends show co-continuous phase morphologies with distinct interfaces compared to samples with untreated silica. The S-SBR/EPDM blend with silane-treated silica also shows a co-continuous phase morphology with sharp interfaces, but not the NBR/EPDM blend. In both blends, the filler is more concentrated in the EPDM phase, and PA-silica forms a new interlayer between the two polymer phases. The co-continuous morphology observed in the various blends does correspond with the best mechanical properties, as observed in previous chapters.

9.1 Introduction

It has long been recognized that the performance of elastomeric materials (e.g. strength, wear resistance, resilience) can be improved by loading them with particulate fillers. Particle and aggregate size, morphology, and surface characteristics as functional groups and surface free energy, are the most important characteristics of the fillers. It is well known that the reinforcing potential of fillers can only be realized if a good dispersion is achieved. In addition, a factor of great importance for the desired reinforcement of the elastomer is the interaction between the filler and the polymer. The macroscopic properties such as toughness, strength, wear, and chemical resistance of filled polymers and polymer blends are determined by interfacial and micro-phase characteristics of the ingredients. In order to determine and optimize structure-property relationships in these polymeric systems, knowledge of the microscopic morphology and physical properties is essential.

Electron microscopy is a well-known method for determining polymer morphology[1,2]. This technique provides information on nano-meter scale spatial resolution. Blend microstructures are commonly determined by Transmission Electron Microscopy (TEM) analyses. These types of analyses require cryogenic microtoming pretreatment to get thin sections for electron transmission, and etching/staining procedures to achieve sufficient contrast between phases[1,2].

Atomic Force Microscopy (AFM) is an alternative version of scanning tunneling microscopy. Both systems were developed by Binnig and co-workers and have the potential for atomic resolution[3,4]. AFM has rapidly developed into a powerful tool, which can image surface topology of both, insulating and conductive samples[5]. Since its invention in 1986, AFM has been applied extensively in polymer science and technology. During the last years, this technique was applied for visualization of phase morphologies of elastomeric blends and to study carbon black microdispersions[3,6-10]. It was also used to visualize the microstructure of carbon black and silica[11,12]. In general, AFM is a multifunctional technique suitable for (surface) characterization in terms of topography, dispersion, adhesion and other properties on scales from hundreds of microns down to nanometers. Recently, AFM has provided new opportunities for determining polymer morphology on a nanometer scale or even higher resolution[13-17]. Especially the capability for rubber blend analysis has been greatly improved by the development of dynamic AFM measurements, the so-called modulation technique, such as force modulation (FM), tapping mode and non-contact or intermittent contact mode AFM. In these methods, either the cantilever is vibrated at its resonance frequency or the vertical sample position is modulated. The tip-sample force interaction causes a change in the amplitude, the phase and the resonance frequency of the vibrating cantilever[18]. The spatial variations of the changes can be presented in height or interaction (amplitude, phase or frequency shift) images. Typically, height and interaction images are collected simultaneously.

In this study, AFM is applied for a study of the microdispersion of untreated, plasma-acetylene and organosilane-modified silica fillers in solution-styrene-butadiene rubber (S-SBR), ethylene–propylene–diene terpolymer (EPDM) rubber, acrylonitrile-butadiene rubber (NBR) and their blends.

9.2 Experimental

9.2.1 Materials

The following polymers were used in the investigation:

- Solution SBR (Buna® VSL 5025-0 HM, Lanxess GmbH) containing 25wt% styrene and 75wt% butadiene (50wt% vinyl and 25wt% cis/trans butadiene);
- EPDM (Keltan® 4703, DSM Elastomers B.V.) with an ethylidene norbornene content of 9 wt%, an ethylene content of 48 wt% and a propylene content of 43 wt%;
- NBR (Perbunan® 3446 F, Lanxess GmbH) containing 34.7 wt% acrylonitrile and 65.3 wt% butadiene.

Conventional precipitated silica (Ultrasil VN3) obtained in fluffy form from Degussa GmbH, was used as reinforcing filler in untreated as well as in surface modified form. High purity acetylene gas for the plasma polymerization was obtained from Wright Brothers, Inc. Bis-(triethoxysilylpropyl) tetrasulfide, TESPT (Si69, Degussa GmbH) was used as a standard for the modification of silica.

9.2.2 Preparation of plasma-acetylene coated silica and rubber samples

The surface modification of silica by plasma polymerization using acetylene monomer was discussed in Chapter 3. A detailed description of the plasma polymerization technique as well as the preparation and characterization of untreated and plasma-treated silica was reported. The compound formulations used for S-SBR, EPDM, NBR, S-SBR/EPDM and NBR/EPDM blends are given in Table 9.1.

The mixing procedure as discussed in the experimental part of Chapter 4 was applied here with the difference, that in the case of blends, both polymers were introduced into the mixing chamber at the same time in the very beginning of the mixing cycle.

9.2.3 Microdispersion measurements

Atomic Force Microscopy experiments were conducted using a NanoScope III multimode scanning force microscope (Digital Instruments (DI), Santa Barbara, CA, USA) in Tapping Mode with phase imaging. Standard Si Nanosensor probes were used to conduct the measurements. Unvulcanized samples for the AFM observation were prepared by razor blade cutting.

Table 9.1: Compound formulations of 50 phr silica reinforced S-SBR, EPDM, NBR, S-SBR/EPDM and NBR/EPDM (50/50) blends.

	SU	SPA	ST	EU	EPA	ET	NU	NPA	NT	SEU	SEU1	SEPA	SET	NEU	NEU1	NEPA	NET
Component	phr	phr	phr	phr	phr	phr	phr	phr	phr	phr	phr	phr	phr	phr	phr	phr	phr
S-SBR	100	100	100	--	--	--	--	--	--	50	75	50	50	--	--	--	--
EPDM	--	--	--	100	100	100	--	--	--	50	25	50	50	50	25	50	50
NBR	--	--	--	--	--	--	100	100	100	--	--	--	--	50	75	50	50
Silica	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50
ZnO	2.5	2.5	2.5	5	5	5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Stearic acid	2.5	2.5	2.5	2	2	2	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Silane	--	--	4	--	--	4	--	--	4	--	--	--	4	--	--	--	4

Sample codes: S: *Solution styrene-butadiene rubber;* ***E:*** *Ethylene-propylene-diene rubber;* ***N:*** *Acrylonitrile-butadiene rubber;* ***SE:*** *Solution styrene-butadiene rubber/Ethylene-propylene-diene rubber blend* ***NE:*** *Acrylonitrile-butadiene rubber/Ethylene-propylene-diene rubber blend;* ***U:*** *Untreated silica;* ***PA:*** *Plasma-acetylene coated silica****; T:*** *Silanized silica*

9.3 Results

The first experiment that was carried out was to study the dispersion of plasma acetylene-coated silica in straight polymers. The results are shown in paragraph 9.3.1. Additionally, the effect of plasma acetylene-coated silica in S-SBR/EPDM (50/50) and NBR/EPDM (50/50) blends are shown in paragraph 9.3.2. These results with plasma-treated silica are compared to results with untreated and silane-treated silica.

9.3.1 Dispersion of untreated, plasma-acetylene- and silane-treated silica in S-SBR, EPDM and NBR compounds

In AFM measurements, the spatial variations of the changes can be presented in height or interaction (amplitude, phase or frequency shift) images due to the variation in tip-sample force interaction. Typically, height and interaction images are collected simultaneously. AFM images (tapping mode height and phase) of untreated, plasma-acetylene-coated and silane-treated silica filled unvulcanized S-SBR are shown in Figures 9.1a–9.1c. Of the two AFM imaging modes used to visualize the microdispersion of the fillers in rubber, phase imaging was found to be the most useful. Filler aggregates are readily distinguished, having a bright contrast in the dark polymer matrix. Generally, a lighter shading can be associated with a higher stiffness of the filler particles as compared to the rubber matrix[19,20].

In Figures 9.1a-9.1c, the coated phase images (right) clearly reveal the distribution of the silica. For untreated (SU), plasma-acetylene (SPA) and silane-treated (ST) silica filled S-SBR, it is possible to differentiate between the three fillers based on the magnitude of the phase angle shift. In the sample with untreated silica, SU, silica aggregates with a broad particle size distribution are segregated within the polymer matrix. In the case of PA-silica, small aggregates and larger agglomerates are well distributed within the whole polymer matrix. The average size of the filler domains is larger in the case of PA-silica than for the untreated silica, as seen in Figures 9.1a-9.1b. The silane-treated silica-filled S-SBR shows complete coverage of silica particles with the polymer. The size of the silica aggregates is small and shows a low level of silica agglomeration compared to SU and SPA.

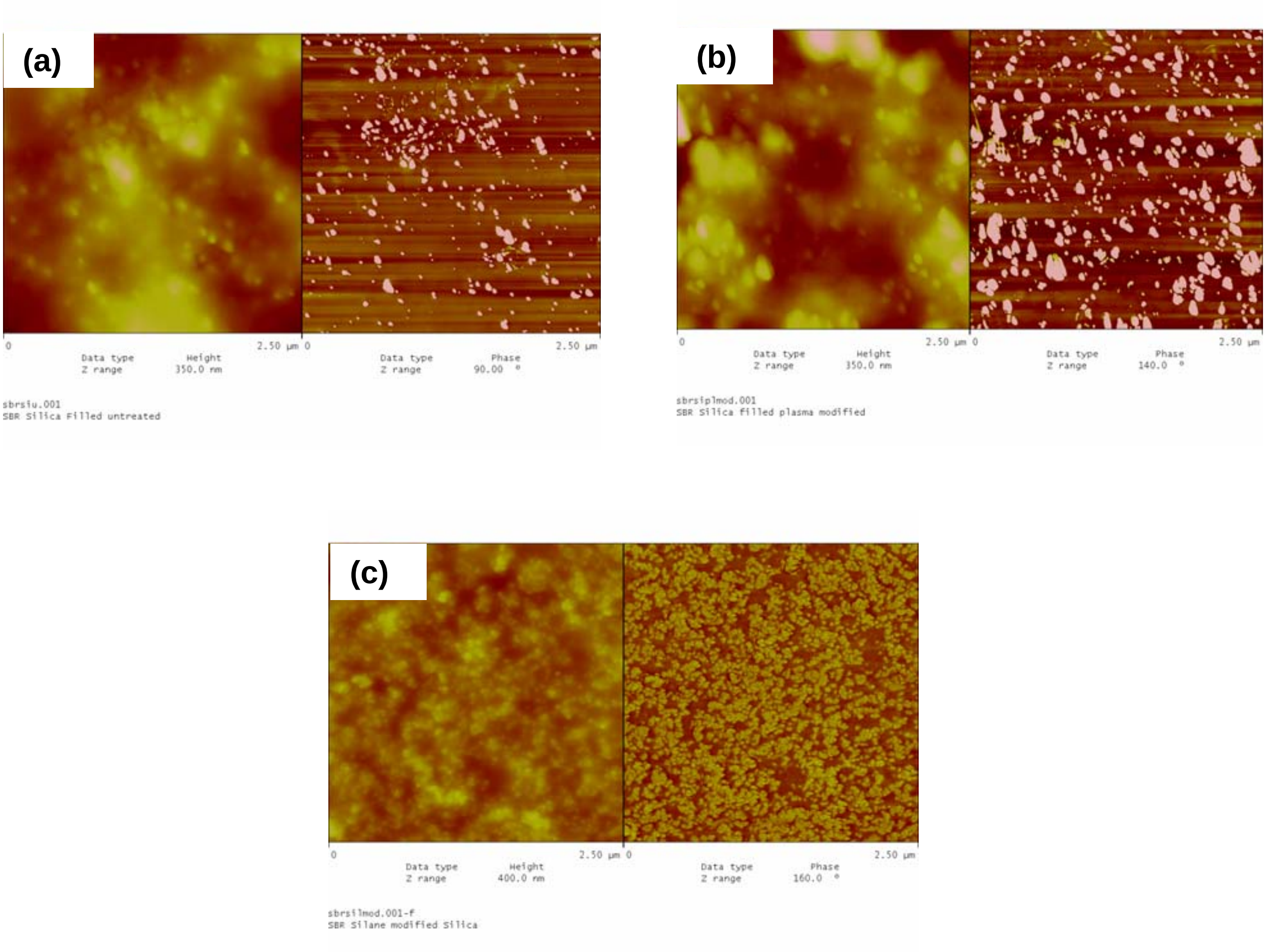

Fig. 9.1: AFM images of: a) untreated silica; b) plasma-acetylene coated silica; c) silane-treated silica reinforced S-SBR (height and phase mode, image size 2.5x2.5 µm^2).

Figures 9.2a–9.2c show the AFM images of the same series of silica samples in EPDM. Figure 9.2a shows aggregates and agglomerates of untreated silica in the polymer matrix. Again, insufficient distribution and dispersion is found for untreated silica. Plasma-acetylene silica shows a higher level of dispersion as seen in Figure 9.2b, and the aggregates are well distributed within the whole matrix. Silane-treated silica shows the lowest level of agglomeration; the average size of the aggregates is small as seen in Figure 9.2c. However, complete coverage of the filler particles with polymer, as found in S-SBR, is not seen in EPDM.

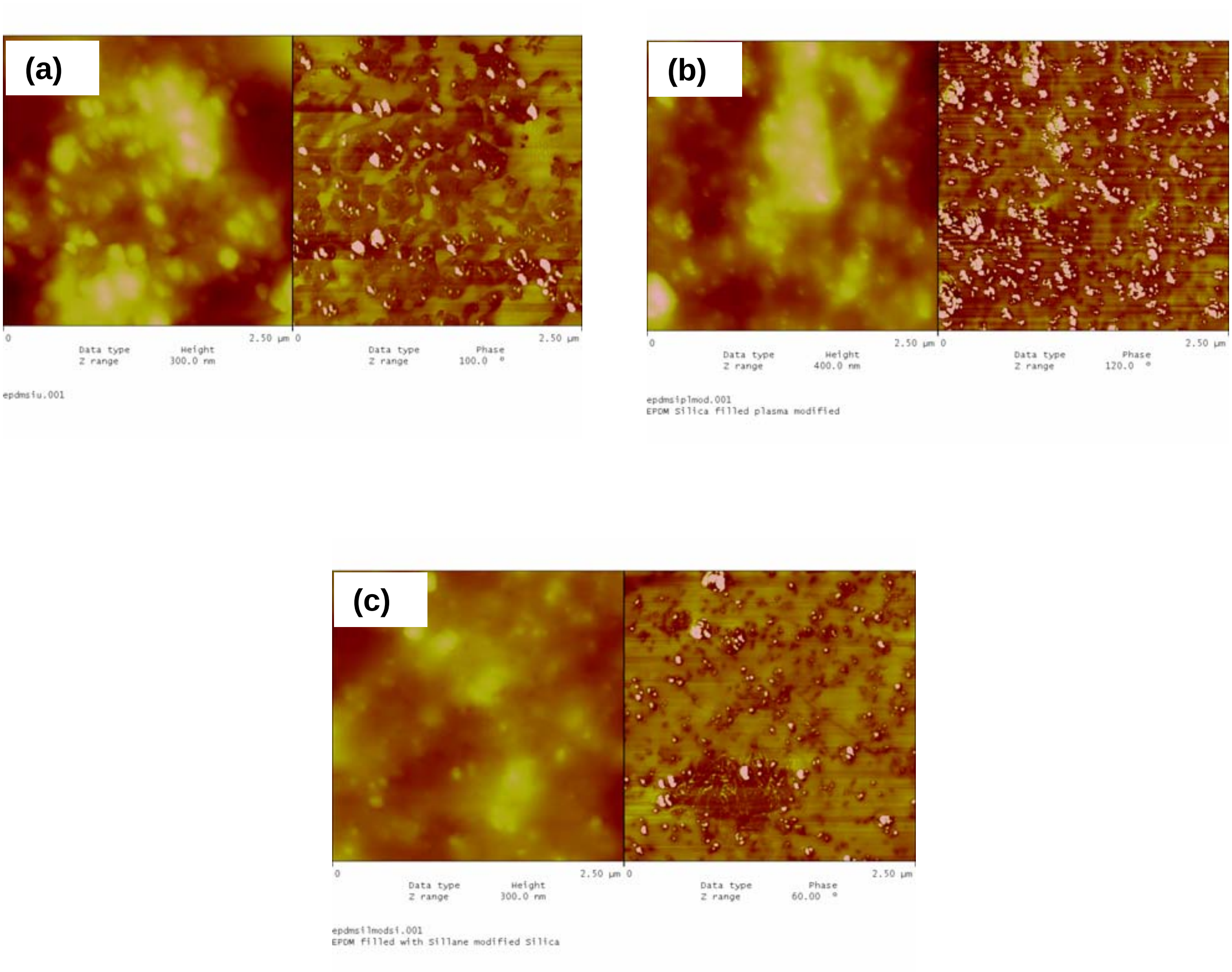

Fig. 9.2: AFM images of: a) untreated silica; b) plasma-acetylene coated silica; c) silane-treated silica reinforced EPDM (height and phase mode, image size 2.5x2.5 µm^2).

Figure 9.3a-9.3c represent the micro-dispersion of the three silica types in NBR. The picture of untreated-silica in NBR shows particles and agglomerates, which are covered with a polymer film, and their size is uniform. Silane-treated silica in NBR is dispersed to a low level and this silica does not homogenously occupy the whole polymer matrix, i.e. silica aggregates are segregated in the NBR matrix as seen in Figure 9.3c. PA-silica has a better dispersion than untreated silica. Overall the pictures look like inverted compared with S-SBR: Figures 9.1a-9.1c.

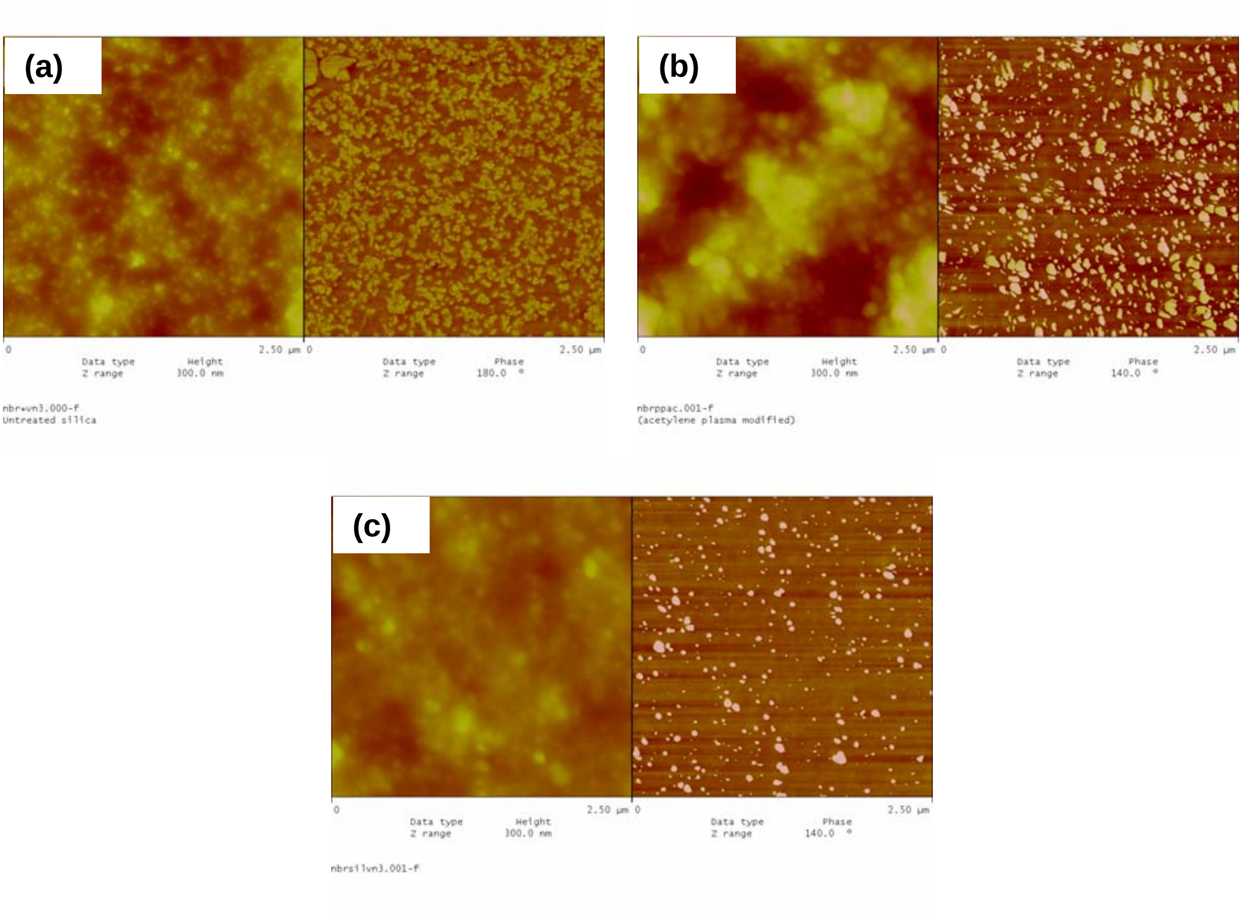

Fig. 9.3: AFM images of: a) untreated silica; b) plasma-acetylene coated silica; c) silane-treated silica reinforced NBR (height and phase mode, image size 2.5x2.5 µm^2).

9.3.2 Dispersion of different types of silica in S-SBR/EPDM and NBR/EPDM blends

Tapping height and phase images of untreated-silica filled S-SBR/EPDM (75/25); SU1 and NBR/EPDM (75/25); NU1 are shown in Figures 9.4a-9.4b. In these phase images, the filler is represented by light spherical particles in the polymer matrix. Within the polymer matrix, two different areas can be distinguished, light and dark. On the basis of ratio and contrast, it is clear that the lighter and the darker phase represent the major and minor component in the rubber matrix, respectively: the lighter phase in Fig. 9.4a is S-SBR, and the darker phase represents EPDM. In Figure 9.4b, NBR is the lighter phase, and again EPDM the darker phase.

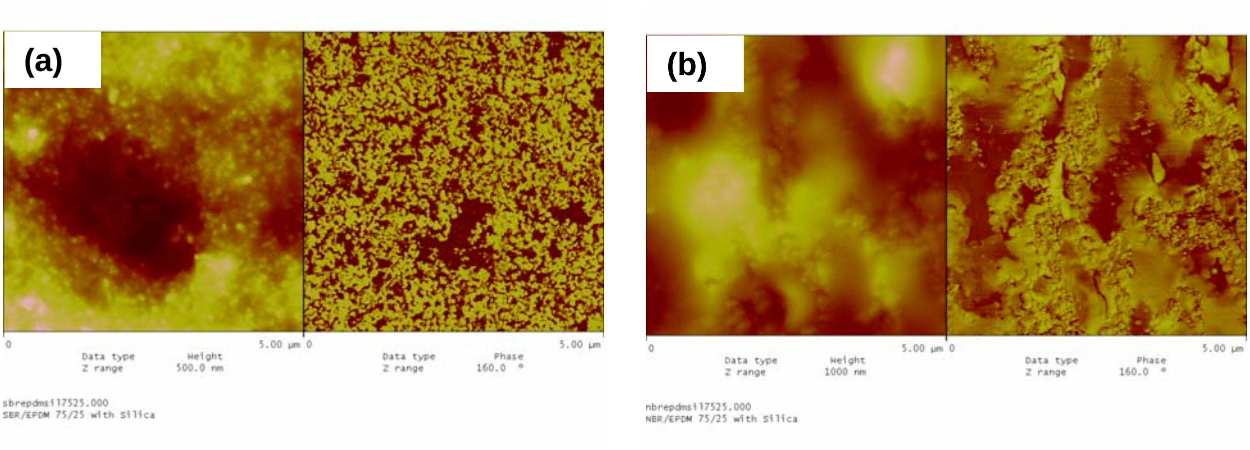

Fig. 9.4: AFM images of untreated silica reinforced a) S-SBR/EPDM (75/25); b) NBR/EPDM (75/25) (height and phase mode, image size 2.5x2.5 µm^2)

The untreated silica filled S-SBR/EPDM (50/50) compound image shows three different phases in Figure 9.5a: silica is shown as white spots, S-SBR is the lighter phase and EPDM is the darker phase. The domain sizes of the EPDM phase are rather small compared to the samples with PA-treated silica in Figure 9.5b: app. 100 nm in size. The EPDM phase in Fig. 9.5a is not continuous; and silica is most apparent in this discontinuous phase. The PA-silica filled blend shows a clearly co-continuous phase morphology as seen in Figure 9.5b. A few large aggregates of PA-silica are visible, which are preferably located at the interphase between the polymers. In Figure 9.5c, silane-treated silica-filled S-SBR/EPDM (50/50) also shows a co-continuous phase morphology. However, in contrast to the PA-silica filled blend, the two polymer phases have sharp interfaces in the case of silane-treated silica. Silane-treated silica also locates itself preferably on the interface between the polymers.

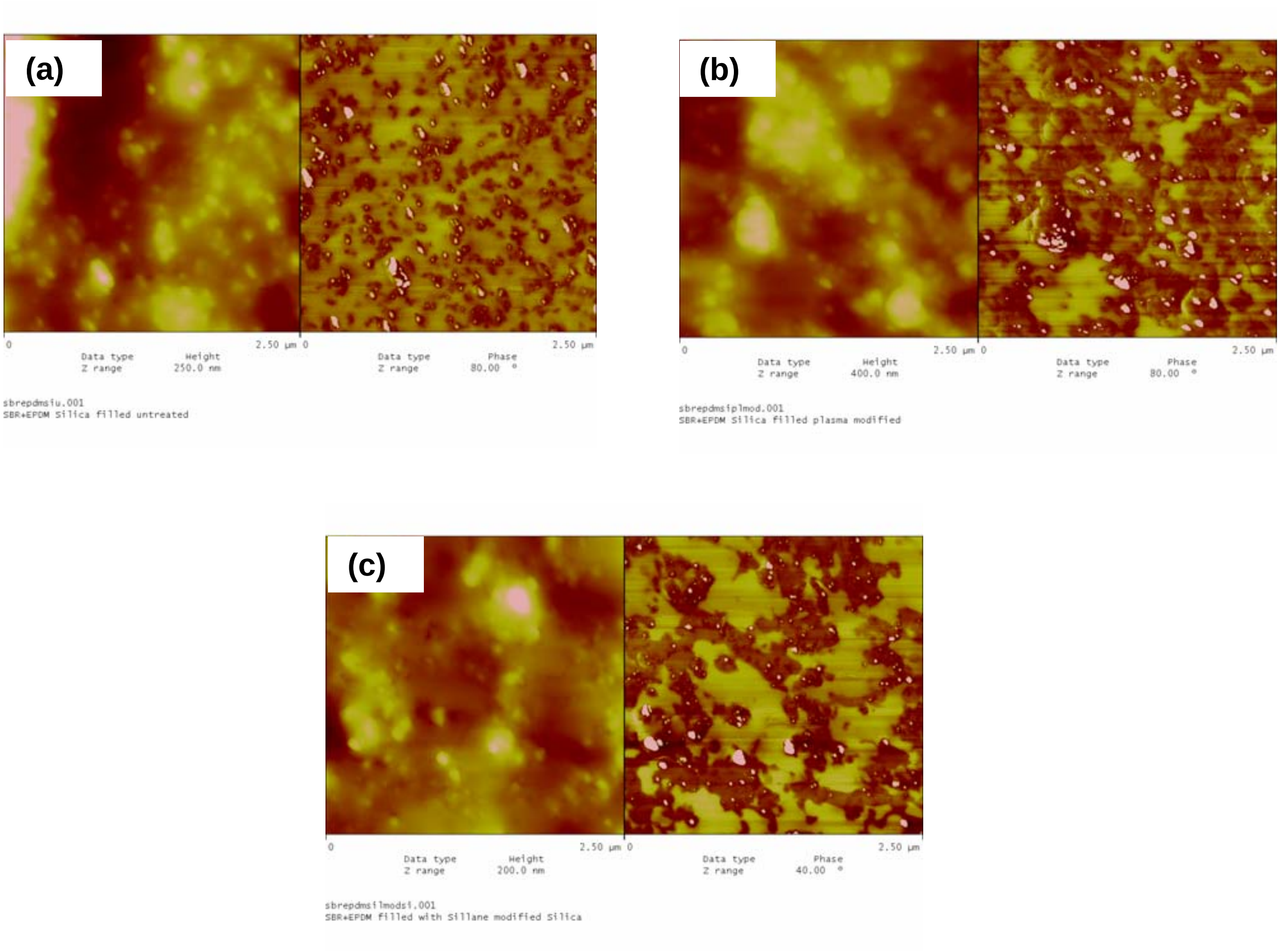

Fig. 9.5: AFM images of: a) untreated silica; b) plasma-acetylene coated silica; c) silane-treated silica reinforced S-SBR/EPDM (50/50) (height and phase mode, image size 2.5x2.5 µm^2).

Figures 9.6a-9.6c show the micro-dispersion of NBR/EPDM (50/50) blends with untreated and the two treated silica types. In Figure 9.6a, untreated silica shows a very high level of filler-filler interactions. The silica aggregates and agglomerates are grossly segregated within the NBR/EPDM matrix and located in specific areas: In the phase image, silica seems to be located in the darker phase. However, in the case of the S-SBR/EPDM blend, untreated silica was more located in the lighter phase. This shows a different affinity of untreated silica towards the polymers used for the two blends in this study. In Figure 9.6b, NBR is the discontinuous and EPDM the continuous phase. PA-silica is located in both phases, in NBR as well as in EPDM. Figure 9.6c shows a discontinuous phase morphology again. Silane-treated silica is preferably located in the NBR phase and shows a high level of agglomeration again. This is confirmed by the height image, where EPDM, the dark phase, seems to be less filled with silica and silica is more visible in the lighter NBR phase.

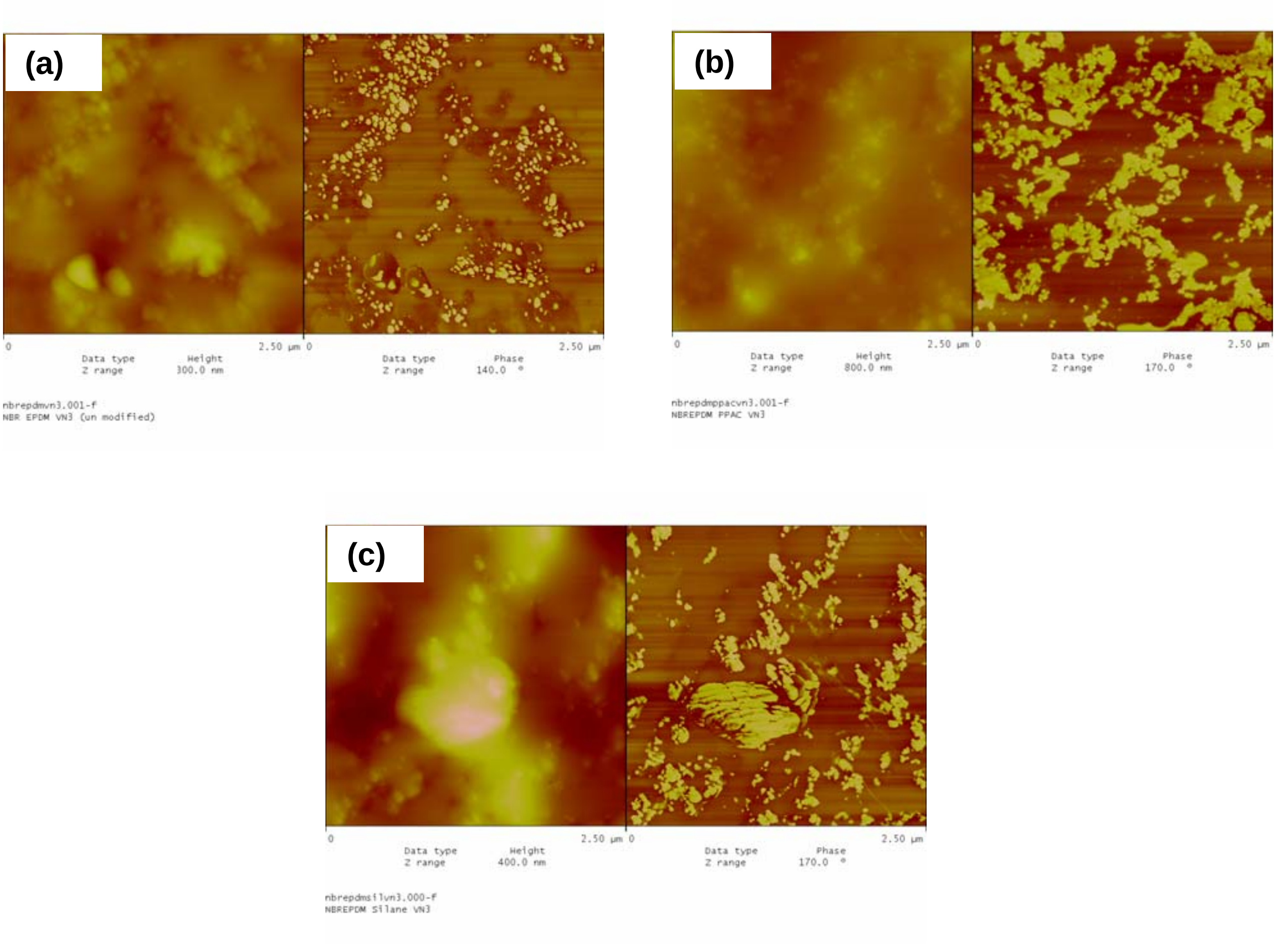

Fig. 9.6: AFM image of: a) untreated silica; b) plasma-acetylene coated silica; c) silane-treated silica reinforced NBR/EPDM (50/50) (height and phase mode, image size 2.5x2.5 µm^2).

9.4 Discussion

The interaction of silica with elastomers is very different from the interaction of carbon black with the polymers in rubber compounds: weaker interaction between filler and polymer and stronger attraction between the polar filler particles. This difference requires a higher mechanical energy input to acquire sufficient silica dispersion during compounding, and a coupling agent or other surface modification method like plasma-polymerization to increase the compatibility of the filler particles with the polymer. This is shown in Figure 9.1a, where in some areas individual particles are observed while agglomerates occur elsewhere. The latter indicates the high filler-filler interaction of silica due to its polar nature. After plasma-acetylene polymerization, the filler-filler interaction is lower and silica aggregates are better dispersed in the whole S-SBR matrix, caused by the higher compatibility of PA-silica with S-SBR due to a better match of the surface energy. This improved dispersion of PA-silica in the S-SBR matrix is also in line with the higher bound rubber content (54.3%) compared to untreated silica (42.5%) observed in Chapter 4, which represents a higher filler-polymer interaction for PA-silica. The improved morphology of PA-silica is also confirmed by the lower filler-filler interaction for PA-silica in the S-SBR-matrix as measured by the Payne effect in Chapter 4. Furthermore, PA-silica results in improved mechanical properties in comparison to untreated silica, which is again due to the improved PA-silica morphology and the increased filler-polymer interaction in the S-SBR-matrix. However, after silanization the silica aggregates are even smaller in size compared to PA-silica, and the silica aggregates are well-dispersed within the whole S-SBR matrix. This is due to a good hydrophobization of silica, which prevents further agglomeration of the filler in the rubber matrix. Again, the improved morphology of silanized silica is in agreement with a low Payne effect in comparison with untreated silica as found in Chapter 4.

The larger size of the silica aggregates and the high degree of agglomeration indicates a lower compatibility of all three silica types with EPDM compared to S-SBR, also indicated by generally higher Payne-effect values in Chapter 5. The dispersion is better for PA-silica compared to untreated silica as shown in Figures 9.2a and 9.2b and in Figure 5.4: PA-silica shows a lower reinforcement parameter. The micro-dispersion of untreated silica is on a lower level than for PA-silica, which demonstrates a higher compatibility of PA-silica with EPDM. This is due to the similarity in chemical structure of the polyacetylene coating of the PA-silica, and the EPDM rubber as such. Furthermore, the polarity of the silica is reduced by the coating, shifting it towards the polarity of EPDM. As a result, the bound rubber content is higher by about 20% compared to untreated silica in EPDM, see Chapter 5. Silane-treated silica aggregates are dispersed at micro-level due to better hydrophobation, which reduces the filler-filler interactions, also expressed by the very low Payne effect. However, there is no indication that the filler-polymer interaction is improved: the bound rubber contents are similar for untreated and PA-silica in Chapter 5. If filler morphology and final properties are correlated: The improved morphology of PA- and silanized-silica in the EPDM matrix compared to untreated silica result in an improvement in tensile properties in both cases, as shown in Figure 5.5.

As NBR is highly polar in comparison with S-SBR and EPDM, untreated-silica aggregates show better dispersion due to the better polarity match as seen in Figure 9.3a. PA-silica is well dispersed in the NBR matrix, in accordance with the low reinforcing parameter as shown in Figure 6.4. This, together with the high crosslink density, results in a significantly improved strength, as seen in Figure 6.5. The silanized silica shows a low degree of agglomeration in NBR due to an efficient coverage of the filler surface by the coupling agent, which suppresses filler-filler interaction, also shown by the low Payne effect in Figure 6.1.

The morphologies formed during phase separation in blends are very complex[21]. The morphology of a blend can be altered dramatically when fillers are added. Depending on the mutual interactions between the polymers and their individual interactions with the filler, different filler distributions are possible[21]. This is very clear from the morphology of PA-silica filled S-SBR/EPDM and NBR/EPDM blends, where both blends show co-continuous phase morphologies compared to the blends with untreated silica. The polarity of the silica is lowered by the PA-coating, making it more compatible with EPDM and less compatible with NBR. Due to this, an improved morphology is observed in Figures 9.5b and 9.6b for PA-silica filled S-SBR/EPDM and NBR/EPDM rubber blends in comparison to untreated and silane-treated silica. This is based on the improved compatibility of PA-silica with EPDM and the better match of surface energies, as stated earlier. The NBR/EPDM blend filled with silane-treated silica does not show co-continuous phase morphology, even though as expected that the filler surface had changed from hydrophilic to a more hydrophobic character due to the silane coating and consequently would compatibilize more with the EPDM phase. A correlation between the filler morphology and final properties leads to a low tensile strength for the untreated silica filled S-SBR/EPDM blend in comparison with the PA- and silane-treated silica blend. From Figures 9.5b and 9.5c can be seen, that PA- and silane-treated silica show only slight differences in morphology, which, however, do not manifest themselves much in the tensile properties: The stress-strain curves do grossly coincide, although the tensile strength was found to be higher for silane-treated silica in comparison to PA-silica: Chapter 7. The only indication for a property improvement of in this blend is the low filler-filler interaction; however, within these filled blend systems there are other factors which also influence the mechanical properties.

In the case of NBR/EPDM rubber blends, the correlation between the filler morphology and final properties is again not very clear, showing that blends behave differently from straight polymers. This can be understood by comparing the morphological behavior of different types of silica in straight NBR and EPDM. The untreated silica clearly demonstrates an improved dispersion in NBR compared to EPDM. This shows that untreated silica has a higher preference for NBR than for EPDM in a NBR/EPDM blend. Due to a better compatibility of PA-silica with both polymers, the blend shows improved dispersion. In the case of silanized silica, it might be possible that silica and silane end up in different polymer phases during mixing due to a difference in polarity: silica is much more polar than the silane. So, silica might remain unsilanized to some extent and therefore keeps its higher preference towards NBR compared to EPDM. Overall, PA-silica shows a better morphology and tensile properties in comparison with silanized silica in the NBR/EPDM blend: Chapter 8. Untreated silica ranked lowest in comparison to both other fillers, as it also did in tensile properties.

Overall, the morphological investigations show that surface modification of silica by plasma-acetylene polymerization can improve the micro-dispersion and thus the reinforcement properties in straight polymers as well as in blends. Key properties here are compatibility and surface energy of filler and polymers. The PA-silica shows a higher compatibility with EPDM compared to untreated-silica, which is also effective in the incompatible blends of S-SBR/EPDM and NBR/EPDM: PA-silica has a higher preference for the EPDM phase.

9.5 Conclusions

In this study, AFM was applied for the investigation of untreated-, plasma-coated and silane-treated silica microdispersion in unvulcanized S-

SBR, EPDM, NBR and their blends. Phase imaging AFM mode was found to be particularly useful for imaging the filler aggregates.

After plasma-acetylene polymerization, the filler-filler interaction is reduced and silica aggregates are better dispersed in the S-SBR, EPDM and NBR matrix, caused by the higher compatibility of PA-silica with the rubber matrices due to a better match of the surface energy and chemistry. Silanized-silica also shows a good dispersion in the S-SBR, EPDM and NBR matrix due to a reduction of the filler-filler interaction.

PA-silica filled S-SBR/EPDM and NBR/EPDM blends show a more co-continuous phase morphology with distinct interfaces compared to the samples with untreated-silica. Silane-treated silica also shows a co-continuous phase morphology in the S-SBR/EPDM blend with sharp interfaces, but not in the NBR/EPDM blend. Preferential location of the different types of silica in both blends was also detected with AFM. The PA-silica is mostly concentrated at the interphase between two polymer phases. The polarity of the silica is lowered by the PA-coating, making it more compatible with EPDM. Due to this, an improved morphology is found for PA-silica filled S-SBR/EPDM and NBR/EPDM rubber blends in comparison with untreated- and silane-treated silica, which is also valid for the two polymers in the blend.

9.5 References

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Chapter 10

Summary and Outlook

10.1 Motivation

The physical properties of blends of dissimilar polymers are strongly influenced by the heterogeneity of the mixture and the distribution of additives, especially of reinforcing fillers in each of the polymer phases. For filled elastomer blends, a controlled morphology, i.e. a well-defined distribution of the fillers and curatives in the individual rubber phases, is of primary importance. Generally, reinforcing fillers mainly end up in one of the two phases due to their different compatibility with the polymers, leading to over-reinforcement of one and under-reinforcement of the other phase. Interphase transfer of fillers is also observed in blends of both, high diene and saturated elastomers, explained by a different solvation of the fillers by the polymers in the mixed blends.

In recent years, the interest in silica reinforcement for elastomeric applications has grown, especially for tread compounds in tire manufacturing. However, the strong interparticle forces of silica are a drawback in obtaining a good dispersion within the polymer matrices. The surface of precipitated silica carries, on an average, 5-6 silanol groups per nm^2 and, therefore it exhibits a strong hydrophilic character. The active silanol groups on the silica surface are responsible for the formation of aggregates and agglomerates. The hydrophilic nature of the silica surface and the tendency to form hydrogen bonds cause strong filler-filler interactions which prevent easy dispersion during mixing and, as a consequence, weaken the final physical properties. Furthermore, extensive transfer of silica from an elastomer with low unsaturation (e.g. ethylene-propylene-diene rubber: EPDM) to rubbers with high unsaturation (e.g. high diene rubbers such as solution-styrene-butadiene rubber: S-SBR and acrylonitrile-butadiene rubber: NBR) was found by many researchers.

Presently, the aggregate structure of silica in elastomers, especially in hydrocarbon rubbers, can be tailored by modifying the filler surface in order to obtain the same or better reinforcing properties compared to other active fillers like carbon black. In a physical sense, variations in surface energy determine the adsorptive capacity and energy. The typical characteristic features of silica are:

1. a relatively low dispersive component of the surface energy, and
2. a very high specific or polar component of the surface energy.

The chemical modification of silica with silanes is a commonly used method to reduce the specific component of the surface energy. This modification increases the compatibility of silica with hydrocarbon elastomers, hence improves the filler dispersion, compound processability, and various vulcanizate properties. The reinforcement also markedly depends on the extent of interaction between the silica surface and the rubber matrix, which can be controlled as well by varying the characteristics of the silica surface. It is possible to improve the silica filler dispersion in polymer-polymer blends by physical surface modification techniques.

In this respect, plasma polymerization is a technique newly used for this purpose, with the advantage of preserving the bulk properties of the material while allowing to tailor the surface properties. It has been used in many applications for decades already, but has not specially been applied for surface modification of reinforcing fillers like precipitated silica. Plasma polymerization of simple monomers (i.e., hydrocarbons and silanes) produces films that are highly cross-linked, pinhole-free, thermally and chemically stable, and very adherent to the surface of a substrate. Recently, surface modification by plasma-polymerization has received considerable attention for improving the wettability of reinforcing fillers like carbon black, silica, clay, talc etc. It is a valuable alternative to existing surface modification technologies, as it is an environmentally clean process and causes less pollution than other techniques.

The objective of the present project was to modify the surface of silica powders by plasma-polymerization with acetylene, pyrrole, and thiophene monomers in order to improve the distribution in single elastomers and to control the distribution in elastomer blends by matching the surface energies of the silica fillers and the elastomers.

10.2 Summary

Silica is hydrophilic in nature and difficult to disperse in different rubbers, which are more hydrophobic than the filler, and in blends of polymers during the mixing process. Later, the poor dispersion of silica leads to a deterioration of the final vulcanizate properties. A better match of the surface energies of the silica filler and the rubber polymers is an important precondition for improvement of the final vulcanizate properties. To study and understand this phenomenon, it was necessary to find a technique, which can be used for the bulk modification of silica fillers as used in rubber reinforcement. The plasma-polymerization technique was considered as a suitable choice. Another reason to use this technique was the fact that it is an environmentally friendly and easy to handle process for tailor-made surface modification. For the surface modification of silica using this technique, different monomers were selected: acetylene, pyrrole and thiophene, chosen for the different chemical moieties in their structure, which might be active in the vulcanization process of the elastomers. Additionally, these monomers allow to modify the surface in terms of polarity and chemical structure, making it possible to match the surface energies of silica with that of the different polymers.

The plasma polymerization onto the silica surface with different monomers was done in the plasma reactor located at the University of Cincinnati, USA. Chapter 3 of this thesis describes that plasma film deposition was successfully applied onto the silica surface by using different monomers as previously mentioned. As a result, the coated silica shows a higher hydrophobicity in comparison with untreated silica. This also clearly indicates the reduction of the surface energy for plasma-treated silica fillers. An interesting fact to notice is that this surface modification does not influence the bulk properties of the filler: no major changes in morphology are noticed. This is important for sustaining the reinforcing ability of silica fillers in elastomers.

As previously stated and also discussed in Chapter 3, the matching of the surface energies of plasma-modified silica with different rubber polymers and their blends will improve the dispersion of silica, filler-polymer interaction and, as a result, the final vulcanizate properties. To investigate this phenomenon in more depth, EPDM, S-SBR and NBR were chosen for the reinforcement studies, as these elastomers vary widely in polarity and degree of unsaturation. Chapters 4, 5 and 6 are dedicated to the mixing of plasma-acetylene, -pyrrole, and -thiophene coated silica into S-SBR, EPDM and NBR respectively, and the characterization of these materials. Furthermore, these composites were compared to compounds containing untreated and silane-treated silica. It is interesting to see that all plasma-modified silica filled samples show an improved dispersion and lower degree of agglomeration in comparison to untreated as well as silane-treated silica in EPDM. However, this was not the case for S-SBR and NBR filled with plasma-coated silicas. In NBR, the plasma-coated silicas do not result in improved dispersion compared to the unmodified silica-filled elastomer; only the silane-modified silica shows an improved dispersion as measured by the Payne effect. In this highly polar elastomer, all silica samples - whether modified or not - are already far more compatible with NBR than with S-SBR and EPDM.

Filler dispersion is an important factor, but not the only one, for the final vulcanizate properties; filler-polymer interaction and crosslink density also play a major role. The improvement in tensile properties achieved with the polythiophene coated silica in S-SBR was far better than all other silica types in this polymer as found in Chapter 4: The sulfur contained in the thiophene moiety enhances the filler-polymer interaction and contributes to the degree of crosslinking. However, this was not found for the EPDM compound in Chapter 5: in this polymer, the polythiophene-silica showed the negative effect in terms of filler-polymer interaction and tensile properties, and polyacetylene-silica performed best. PA- and PPy-silica showed the best improvement in mechanical properties for NBR, considered to be the result of a compatibilization effect as discussed in Chapter 6. As a general trend it was found that plasma treatment of silica results in a higher bound rubber content due to stronger filler-polymer interactions as observed in Chapters 4, 5 and 6. Overall, the plasma-modified silica’s show an improved compatibility with the various rubbers by improving their dispersion, enhancing the filler-polymer interaction and improving mechanical properties. The investigations in these chapters have also shown that properties, which seem to be complementary, in practice do not necessarily correlate.

After understanding the behavior of plasma-modified silica in straight polymers, it was interesting to elaborate their performance in different elastomer blends as discussed in Chapters 7 and 8. Two blend systems, S-SBR/EPDM and NBR/EPDM were investigated. The results in S-SBR/EPDM and NBR/EPDM blends show that the plasma-pyrrole coating improves the filler dispersion in comparison with the plasma-acetylene and -thiophene treatment and compared to untreated silica. Both blends also show the best filler-polymer interaction with PPy-silica within the series of plasma-coated silica's. The S-SBR/EPDM blend with PPy-silica shows the best mechanical properties in comparison to the blends with the other two plasma-coated silica's, while PA-silica results in the best stress strain properties in the NBR/EPDM blend. This is due to a better interaction of PA-silica with EPDM and a reduced incompatibility between the two polymer phases. Still, silane-treated silica performs best in the S-SBR/EPDM blend as a consequence of the interaction between the polymers and the sulfur-moieties in the coupling agents. It is important to note, that the behavior of different filler types in a blend are not necessarily correlated to the behavior of these fillers in the straight polymers via a simple blend law. In a blend, the interaction between the different components of a compound can be very different from the situation in a single polymer. Generally, it can be concluded from the results of Chapters 7 and 8, that the compatibility and interaction of silica with different rubbers can be controlled by tailoring the surface energy and chemistry of the filler by plasma-polymerization. Different functionalities and polarities of the filler surface determine the compatibility and interaction with the elastomeric matrix, which for a proper combination may lead to improvement of the final vulcanizate properties.

Further, the micro-morphology of rubber compounds, such as polymer and filler distribution, is one of the most important parameters affecting the compound properties. Atomic Force Microscopy (AFM) is a powerful technique for analyzing phase morphology. In Chapter 9, the morphology of compounds filled with untreated, plasma acetylene- (PA) and silane-treated silica was investigated in the straight polymers and the blends. The microdispersion of PA-silica shows improved dispersion in S-SBR, EPDM and NBR in comparison to untreated silica. Silane-treated silica also shows a good dispersion in all straight rubbers.

The most important property pertaining to rubber blends is the homogeneity or phase morphology. Homogeneity at a fairly fine level is necessary for optimum performance, but some degree of microheterogeneity is usually desirable to preserve the individual properties of the respective polymer components. In rubber blends, "technological compatibility" is very important to obtain optimal properties for a product. In Chapter 9, the two rubber blends, S-SBR/EPDM and NBR/EPDM, comprised the combination of three different types of rubbers which are “technologically incompatible”, differing in properties such as viscosity, surface energies, and vulcanization rate. The morphology of PA-silica filled S-SBR/EPDM and NBR/EPDM blends show a more ***co-continuous phase morphology*** with distinct interfaces, compared with untreated silica. Silane-treated silica also shows co-continuous phase morphology in the S-SBR/EPDM blend with sharp interfaces, but not in the NBR/EPDM blend. The PA-silica is mostly concentrated at the interphase between two polymer phases showing improved compatibility with both polymer phases. The polarity of the silica is lowered by the PA-coating, making it more compatible with EPDM, improving the morphology of PA-silica filled S-SBR/EPDM and NBR/EPDM rubber blends compared to the morphology of these blends with untreated- and silane-treated silica, The general conclusion from Chapter 9 is that a ***co-continuous phase morphology*** in the polymer blend is a key factor determining the final vulcanizate properties.

10.3 Outlook

It is very interesting to notice that plasma film deposition of different monomers onto a silica surface results in different levels of compatibility with various elastomers and their blends. Plasma-thiophene coated silica shows the best improvement in S-SBR rubber in terms of tensile properties, but plasma-acetylene- and -pyrrole coated silica’s show the best improvement in EPDM and NBR in terms of their final vulcanizate properties. In rubber blends, plasma pyrrole- and acetylene-coated silica’s show the best improvement in tensile properties for S-SBR/EPDM and NBR/EPDM blends, respectively. To obtain the optimal effect of plasma-coated silica with different monomers in a rubber blend, it will be worthwhile to use a combination of two different plasma-coated silica’s tailored for a high compatibility with the different rubbers.

Within this study, it was difficult to elaborate the exact structure of the plasma-film deposited on the silica surface; it will be very interesting to elucidate this in future work. In this thesis, mostly final vulcanizate properties were determined in a static mode. The missing information is the dynamic performance of the vulcanizates, which is very important for certain applications, e.g. tires: the dynamic properties of the materials can be correlated with the tire performance. This is even more important, as the current silica-silane compounds, which are widely used for tire tread compounds, suffer from processability problems. Temperature stability and ageing performance of the vulcanizates were also not in the scope of this thesis, but should be investigated as an important criterion for their practical importance.

Another part of this project was focused on compatibility improvement of curing additives with different polymers, using the same plasma-polymerization technique. The role of curatives to form the cross-links between the rubber polymer chains to sustain the elasticity of rubber is very important, and research on this topic has been going on for decades. However, still often a cure mismatch occurs as an outcome of inhomogeneous distribution of curatives in the different rubber phases. It will be very useful to combine the work on plasma-treated curatives, as developed in another thesis related to the same, and silica fillers, as further improvements in material properties are expected.

Plasma-polymerization is a new technique for filler modification in rubber technology. Based on the results of this thesis, it will be very interesting to scale-up the plasma-polymerization process to pilot scale in order to be able to perform more extended tests for actual products such as tires.

Samenvatting en Vooruitblik

10.1 Motivatie

De fysische eigenschappen van mengsels van ongelijksoortige polymeren worden sterk beïnvloed door de heterogeniteit van de mengsels en de verdeling van de additieven, vooral van de versterkende vulstoffen in elk van de polymeer fasen. Voor gevulde elastomeer mengsels is een gecontroleerde morfologie, een goed gedefiniëerde verdeling van de vulstoffen en vulcanisatiemiddelen in de afzonderlijke fasen, van het grootste belang. In het algemeen komen de versterkende vulstoffen in een van de twee fasen terecht vanwege hun verschillende compatibiliteit met de polymeren, hetgeen leidt tot overmatige versterking van de ene en te weinig versterking van de andere fase. Overdracht van vulstoffen van de ene naar de andere fase is ook waargenomen in mengsels van verzadigde en onverzadigde elastomeren. Dit wordt verklaard door de verschillende oplosbaarheid van de vulstoffen in de polymeren in de mengsels.

De laatste jaren is de belangstelling voor versterking met silica voor elastomere toepassingen toegenomen, vooral voor loopvlakmengsels van banden. De sterke onderlinge binding tussen de silica deeltjes is echter een nadeel voor een goede dispersie in de polymere matrices. Het oppervlak van geprecipiteerde silica bevat gemiddeld 5-6 silanol-groepen per nm^3 en heeft daardoor een sterk hydrofiel karakter. De actieve silanol-groepen op het silica oppervlak zijn verantwoordelijk voor de vorming van aggregaten en agglomeraten. Het hydrofiele karakter van het silica oppervlak en de neiging tot vorming van waterstof-bruggen veroorzaken een sterke wisselwerking tussen de vulstof deeltjes (vulstof-vulstof interactie), die een gemakkelijke verdeling/dispersie tijdens het mengen belemmeren en bijgevolg de uiteindelijke fysische eigenschappen negatief beïnvloeden. Voorts werd door veel onderzoekers grootschalige overdracht van silica van een elastomeer met lage onverzadiging (bijvoorbeeld ethyleen-propyleen-diëen rubber: EPDM) naar rubber met een hoge onverzadiging (bijvoorbeeld hoog-diëen rubber zoals solution-styreen-butadiëen rubber: S-SBR, en acrylonitril-butadiëen rubber: NBR) gevonden.

Tegenwoordig kan de aggregaat-structuur van silica in elastomeren, in het bijzonder in koolwaterstof-gebaseerde rubbers, worden afgestemd door modificatie van het vulstofoppervlak, teneinde dezelfde of betere versterkende werking te verkrijgen dan met andere actieve vulstoffen, zoals roet. In fysische zin bepalen veranderingen in oppervlakte energie het adsorberend vermogen. De karakteristieke kenmerken van silica zijn:

1. een relatief lage dispersieve component van de oppervlakte-energie, en
2. een heel hoge specifieke of polaire component van de oppervlakte energie.

Chemische modificatie van silica met silanen is een algemeen gangbare methode om de specifieke component van de oppervlakte energie te verlagen. Deze modificatie verhoogt de compatibiliteit van silica met koolwaterstof-gebaseerde elastomeren en verbetert zodoende de verdeling van de silica, de verwerkbaarheid van het mengsel en diverse eigenschappen van het gevulcaniseerde materiaal. De versterking hangt ook duidelijk af van de mate van interactie tussen het silica oppervlak en de rubber matrix, die ook kan worden beïvloed door verandering van de karakteristieke eigenschappen van het silica oppervlak. Het is ook mogelijk om de dispersie van de silica vulstof in polymeer-polymeer mengsels te verbeteren met oppervlaktemodificatie-technieken.

In dit opzicht is plasma polymerisatie een techniek die pas sinds recent gebruikt wordt voor dit doel, met als voordeel dat de bulk eigenschappen van het materiaal behouden blijven, terwijl de oppervlakte eigenschappen aangepast kunnen worden. Deze techniek is al tientallen jaren in gebruik voor veel toepassingen, maar nog niet speciaal voor oppervlakte-modificatie van versterkende vulstoffen zoals geprecipiteerde silica. Plasma-polymerisatie van eenvoudige monomeren levert films die sterk zijn gecrosslinkt, zonder “pin-holes”, thermisch en chemisch stabiel en zeer goed hechtend aan het oppervlak van een substraat. Recentelijk heeft oppervlaktemodificatie aanzienlijke aandacht gekregen voor het verbeteren van de bevochtiging van versterkende vulstoffen zoals roet, silica, klei, talk, enz. Het is een waardevol alternatief voor bestaande oppervlaktemodificatie technologieën, aangezien het een milieutechnisch schoon proces is en minder verontreiniging veroorzaakt dan andere technieken.

Het doel van het huidige project was het modificeren van het oppervlak van silica-poeders door middel van plasma-polymerisatie met acetyleen, pyrrool en thiofeen monomeren, teneinde de verdeling in enkelvoudige elastomeren te verbeteren en de verdeling in elastomeer mengsels te sturen door het op elkaar aanpassen van de oppervlakte-energieën van de silica vulstof en de elastomeren.

10.2 Samenvatting

Silica is hydrofiel van aard en moeilijk te dispergeren in diverse rubbers, die meer hydrofoob zijn dan de vulstof, en in mengsels van polymeren. Later leidt de slechte dispersie van silica tot verminderde eigenschappen van het uiteindelijke vulcanisaat. Een betere afstemming van de oppervlakte-energieën van de silica vulstof en de rubber polymeren is een belangrijke voorwaarde voor verbetering van de uiteindelijk eigenschappen van het gevulcaniseerde materiaal. Om dit verschijnsel te kunnen bestuderen en te begrijpen was het nodig om een techniek te vinden, die gebruikt kan worden voor de bulk modificatie van silica vulstoffen, gebruikt voor versterking van rubber. De plasma polymerisatie techniek werd als geschikte keuze beoordeeld. Nog een reden om deze techniek te gebruiken was het feit, dat het een milieuvriendelijk en gemakkelijk te hanteren proces is voor “tailor-made” oppervlakte modificatie. Voor het modificeren van silica met deze techniek werden verschillende monomeren: acetyleen, pyrrool en thiofeen, gekozen vanwege de verschillende functionele groepen in hun structuur, die actief zouden kunnen zijn in het vulcanisatie proces van elastomeren. Bovendien geven deze monomeren de mogelijkheid om het oppervlak te modificeren qua polariteit en chemische structuur, waardoor het mogelijk is om de oppervlakte energieën van silica af te stemmen op die van verschillende polymeren.

Plasma polymerisatie met verschillende monomeren op het silica oppervlak werd uitgevoerd in de plasma reactor van de Universiteit van Cincinnati in Amerika. Hoofdstuk 3 van dit proefschrift beschrijft dat plasma film depositie met de voornoemde monomeren met succes werd toegepast op het silica oppervlak. Het resultaat was dat de gecoate silica een verhoogde hydrofobiciteit vertoonde ten opzichte van onbehandelde silica. Dit toont ook duidelijk de verlaagde oppervlakte-energie van de met plasma behandelde silica vulstoffen aan. Het is interessant op te merken dat deze oppervlaktemodificatie de bulk eigenschappen van de vulstof niet beïnvloedt; er werden geen grote veranderingen in morfologie waargenomen. Dit is belangrijk voor het overeind houden van de versterkende eigenschappen van silica vulstoffen in elastomeren.

Zoals al eerder genoemd en besproken in Hoofdstuk 3, zal afstemming van de oppervlakte-energieën van plasma gemodificeerde silica op die van de verschillende rubber polymeren en mengsels daarvan de interactie tussen vulstof en polymeer en dientengevolge ook de uiteindelijke eigenschappen van het gevulcaniseerde product verbeteren. Om dit verschijnsel meer in detail te onderzoeken, werden EPDM, S-SBR en NBR gekozen voor de versterkingsstudies, omdat deze elastomeren zeer sterk verschillen in polariteit en mate van onverzadiging. Hoofdstukken 4, 5 en 6 zijn gewijd aan het mengen van plasma-acetyleen, - pyrrool en – thiofeen silica in achtereenvolgens S-SBR, EPDM en NBR en aan het karakteriseren van deze materialen. Bovendien worden deze composieten vergeleken met mengsels,, die onbehandelde en met silaan behandeld silica bevatten. Het is interessant te constateren,,dat in EPDM alle met plasma-gemodificeerde silica-gevulde monsters een verbeterde dispersie en een lagere graad van agglomeratie vertonen vergeleken met onbehandelde en met silaan behandelde silica. Dit is echter niet het geval voor SBR en NBR. In NBR leiden de plasma-behandelde silica’s niet tot verbeterde dispersie in vergelijking met de niet-gemodificeerde silica-gevulde elastomeren; alleen de silaan-gemodificeerde silica vertoont een betere dispersie, zoals gemeten met het Payne effect. In dit hoog polaire elastomeer zijn alle silica monsters, gemodificeerd of niet, al veel meer compatibel met NBR dan met SBR en EPDM.

Dispersie van de vulstof is een belangrijke, maar niet de enige factor voor de uiteindelijke vulcanisaat eigenschappen; vulstof-polymeer interactie en vernettingsgraad spelen ook een grote rol. De verbetering van trekeigenschappen van SBR, die bereikt worden met de poly-thiofeen gecoate silica, is veel groter dan met alle andere silica types, zoals beschreven in Hoofdstuk 4. De zwavel aanwezig in de functionele thiofeen-groep verhoogt de vulstof-polymeer interactie en draagt bij aan de vernettingsgraad. Dit wordt echter niet gevonden voor het EPDM mengsel in Hoofdstuk 5; in dit polymeer vertoont de poly-thiofeen-silica een negatieve invloed qua vulstof-polymeer interactie en trekeigenschappen, terwijl poly-acetyleen-silica het beste voldoet. In NBR geven plasma-acetyleen- en plasma-pyrrool-silica de grootste verbetering in mechanische eigenschappen, hetgeen beschouwd wordt als het resultaat van een compatibiliteitseffect, zoals besproken in Hoofdstuk 6. Als algemene trend wordt vastgesteld, dat plasma-behandeling van silica resulteert in een hoog bound rubber gehalte ten gevolge van sterke vulstof-polymeer interactie, zoals waargenomen in Hoofdstukken 4, 5 en 6. Over het geheel genomen vertonen de plasma-gemodificeerde silica's een verbeterde compatibiliteit met de verschillende rubbers door verbetering van hun dispersie, verhoging van de vulstof-polymeer interactie en verbetering van de mechanische eigenschappen. De onderzoeken in deze hoofdstukken tonen ook aan, dat eigenschappen, die complementair lijken te zijn, in de praktijk niet noodzakelijkerwijs correleren.

Na het begrijpen van het gedrag van plasma-gemodificeerde silica in enkelvoudige polymeren was het interessant om hun gedrag in verschillende elastomeer blends uit te werken, zoals verwoord in Hoofdstukken 7 en 8. Er worden twee systemen, SBR/EPDM en NBR/EPDM, onderzocht. De resultaten in SBR/EPDM en NBR/EPDM laten zien de plasma-pyrrool coating de vulstof dispersie verbetert in vergelijking met plasma-acetyleen en plasma – thiofeen behandeling, respectievelijk vergeleken met onbehandelde silica. Beide blends vertonen binnen de serie plasma-gecoate silica's de beste vulstof-polymeer interactie met plasma-pyrrool-silica. Het SBR/EPDM mengsel met plasma-pyrrool-silica vertoont de beste mechanische eigenschappen in vergelijking met de blends met de andere twee plasma-gecoate silica's, terwijl plasma-acetyleen-silica leidt tot de beste kracht-rek eigenschappen in NBR/EPDM. Dit is het gevolg van een betere interactie van de plasma-acetyleen-silica met EPDM en een verminderde incompatibiliteit tussen de twee polymeer fasen. Toch voldoet silaan-behandelde silica het beste in het SBR/EPDM mengsel als gevolg van de interactie tussen de polymeren en de zwavel van de coupling agent. Het is belangrijk op te merken dat het gedrag van de verschillende vulstof-soorten in een mengsel niet noodzakelijkerwijs verband houdt met het gedrag van deze vulstoffen in de enkelvoudige polymeren via een eenvoudige mengregel. In een blend kan de interactie tussen de verschillende componenten van een compound erg verschillen van de situatie in een enkel polymeer. In het algemeen kan uit de resultaten van

Hoofdstuk 7 en 8 worden geconcludeerd dat de compatibiliteit en interactie van silica met verschillende rubbers kan worden gestuurd door het afstemmen van de oppervlakte energie en chemie van de vulstof door plasma-polymerisatie. Verschillende functionaliteiten en polariteiten van het vulstof oppervlak bepalen de compatibiliteit en interacties met de elastomeer matrix, die bij een geschikte combinatie kan leiden tot verbetering van de uiteindelijke vulcanisaat eigenschappen.

Voorts is de micro-morfologie van rubber compounds, zoals polymeer- en vulstof-verdeling, een van de meest belangrijke parameters die de compound eigenschappen bepalen. Atomic Force Microscopy (AFM) is een krachtige techniek voor het analyseren van de fase morfologie. In Hoofdstuk 9 wordt de morfologie onderzocht van afzonderlijke polymeren en mengsels gevuld met onbehandelde, plasma acetyleen- (PA) en silaan-behandelde silica. De micro-dispersie van plasma-acetyleen-silica vertoont verbetering in SBR, EPDM en NBR in vergelijking met onbehandeld silica. Met silaan behandelde silica levert ook een goede dispersie in alle enkelvoudige rubbers.

De belangrijkste eigenschap van rubber blends is de homogeniteit of fase-morfologie. Homogeniteit op microscopisch kleine schaal is nodig voor een optimaal resultaat, maar enige mate van micro-heterogeniteit is gewoonlijk gewenst om de diverse eigenschappen van de afzonderlijke polymeer componenten te behouden. Bij rubber mengsel is “technologische compatibiliteit” zeer belangrijk om optimale eigenschappen van een product te bereiken. De twee rubber mengsels SBR/EPDM en NBR/EPDM uit Hoofdstuk 9 bestonden uit de combinatie van 3 verschillende typen rubber, die “technologisch incompatibel” zijn, verschillend in eigenschappen zoals viscositeit, oppervlakte energie en vulcanisatiesnelheid. De morfologie van met plasma-acetyleen-silica gevulde SBR/EPDM en NBR/EPDM mensels vertoont een meer **co-continue fase morfologie** met duidelijke grensvlakken, vergeleken met onbehandelde silica. Met silaan behandelde silica laat ook een co-continue fase morfologie met scherpe grensvlakken zien in SBR/EPDM, maar niet in het NBR/EPDM mensel. De plasma-acetyleen-silica is het meest geconcentreerd aan het grensvlak tussen de twee polymeer fasen, hetgeen een verbeterde compatibiliteit met beide fasen aantoont. De polariteit van silica wordt verlaagd door de plasma-acetyleen-coating, waardoor deze meer compatibel wordt met EPDM, en aldus de morfologie van de plasma-acetyleen-silica gevulde SBR/EPDM en NBR/EPDM blends verbetert ten opzichte van de morfologie van deze mengsels met onbehandelde en met silaan behandelde silica. De algemene conclusie van Hoofdstuk 9 is dat een **co-continue fase morfologie** in het polymeer mengsel een sleutel-factor is, die de uiteindelijke vulcanisaat eigenschappen bepaalt.

10.3 Vooruitblik

Het is heel interessant op te merken dat plasma film depositie van verschillende monomeren leidt tot verschillende niveau's van compatibiliteit met verschillende elastomeren. Plasma-thiofeen gecoate silica geeft de beste verbetering in SBR rubber qua trek-eigenschappen, maar plasma-acetyleen en –pyrrool gecoate silica's laten de meeste verbetering in kracht-rek eigenschappen zien in achtereenvolgens de SBR/EPDM en NBR/EPDM mengsels. Om het optimale effect van plasma-gecoate silica met verschillende monomeren in een rubber mengsel te verkrijgen, zal het de moeite lonen om een combinatie van twee verschillende plasma-gecoate silica's te gebruiken, elk aangepast ten behoeve van een hoge compatibiliteit met de verschillende rubbers.

Binnen het huidige onderzoek was het moeilijk de precieze structuur van de plasma-film in detail te bepalen; het zal zeer interessant zijn die in toekomstig werk op te helderen. In dit proefschrift werden de vulcanisaat eigenschappen meestal bepaald op een statische manier. De ontbrekende informatie is het dynamische gedrag van het vulcanisaat, wat erg belangrijk is voor bepaalde toepassingen, bijvoorbeeld banden. De dynamische eigenschappen van het materiaal kunnen worden gerelateerd aan de prestaties van een autoband. Dit is zelfs nog belangrijker aangezien de gebruikelijke silica-silaan mengsels, die reeds wijd en zijd worden gebruikt voor loopvlakmengsels, last hebben van verwerkbaarheidsproblemen. Hittebestendigheid en verouderingsgedrag van de vulcanisaten lagen ook buiten het bestek van dit proefschrift, maar zouden onderzocht moeten worden als belangrijke criteria voor hun praktische belang.

Een ander deel van het huidige project, maar buiten het bestek van dit proefschrift, was gericht op verbetering van de compatibiliteit van de vulcanisatie-middelen met verschillende polymeren met–dezelfde plasma-polymerisatie techniek. De rol van vulcanisatie middelen om de crosslinks te vormen teneinde de elasticiteit van de rubber te versterken is erg belangrijk en onderzoek op dit gebeid is al tientallen jaren gaande. Toch treedt er echter vaak een mis-aanpassing van de vulcanisatie op als resultaat van een ongelijkmatige verdeling van vulcanisatie middelen in de verschillende rubber fasen. Het zal erg nuttig zijn om het werk aan plasma behandelde vulcanisatie middelen, zoals beschreven in het andere proefschrift dat hieraan is gewijd, te combineren met dat aan silica vulstoffen, aangezien verdere verbeteringen in materiaal eigenschappen te verwachten zijn.

Plasma polymerisatie is een nieuwe techniek voor het modificeren van vulmiddelen in de rubber technologie. Gebaseerd op de resultaten van dit proefschrift zal het heel interessant zijn om het plasma-polymerisatie proces op te schalen naar pilot schaal, om in staat te zijn om meer uitvoerige testen uit te voeren voor werkelijke producten, zoals autobanden.

Symbols and Abbreviations

Symbol	Description
NR	Natural rubber
EPDM	Ethylene propylene diene terpolymer
BR	Butadiene rubber
S-SBR	Solution-styrene butadiene rubber
NBR	Acrylonitrile-butadiene rubber
CR	Chloroprene rubber
AFM	Atomic force microscopy
ΔG_m	Gibb's free energy of mixing
ΔH_m	Enthalpy of mixing
ΔS_m	Entropy of mixing
Φ	Composition
T	Temperature
P	Pressure
ΔV_m	Volume change
φ_i	Volume fraction of the component
r_i	Number of polymer segements
R	Gas constant
χ	Flory-Huggins binary interaction parameter
χ_{cr}	Flory-Huggins binary interaction parameter at the critical point
UCST	Upper critical solution temperature
LCST	Lower critical solution temperature
δ	Solubility parameter
V_1	Average molar volume of the two liquids
K	Constant
δ_1	Solubility parameters of component 1
δ_2	Solubility parameters of component 2
ϕ_1	Volume fraction of component 1
ϕ_2	Volume fraction of component 2
δ_d	Contribution from dispersive interactions
δ_p	Contribution from polarity
δ_h	Contribution from hydrogen bonding

δ_t	Total solubility parameter
PVC	Polyvinyl chloride
PMMA	Polymethyl methacrylate
PVDF	Polyvinylidene fluoride
PS	Polystyrene
PVME	Polyvinyl methyl ether
EVA	Ethylene vinyl acetate
SAN	Styrene acrylonitrile copolymer
PCL	Polycaprolactone
T_g	Glass transition temperature
M_c	Critical molecular weight
$\Delta\delta$	Difference of the solubility parameters of the components
AR	Aspect ratio
A	Surface area
γ_s	Surface energy of the solid
$W_{cleavage}$	Energy necessary to reversibly cleave a unit plane parallel to the surface
γ_s^d	Dispersive component of the surface free energy
γ_s^{sp}	Specific part of the surface energy
W_a^d	Dispersive component of the adhesive energy
W_a^p	Polar component of the adhesive energy
W_a	Total adhesive energy
W_a^h	Adhesive energy due to hydrogen bonding
W_a^{ab}	Adhesive energy due to acid-base interactions
ΔW	Total change in adhesive energy
γ_f^d	Dispersive component of the surface energy of the filler
γ_f^p	Polar component of the surface energy of the filler
γ_p^d	Dispersive component of the surface energy of the polymer
γ_p^p	Polar component of the surface energy of the polymer
W_f^h	Hydrogen bonding work of the filler
W_p^h	Hydrogen bonding work of the polymer
W_{fp}^h	Hydrogen bonding work of the filler-polymer interaction
W_f^{ab}	Work from acid-base interactions between filler surface

W_p^{ab}	Work from acid-base interactions between polymer surface
W_{fp}^{ab}	Work from acid-base interactions between filler and polymer surface
W_{ff}	Adhesion energy between the fillers
W_{pp}	Adhesion energy between the polymers
ϕ	Volumetric concentration
η_0	Viscosity of the pure liquid
η	Viscosity of the suspension
f	Form factor
ϕ_{eff}	Effective filler volume
σ	Stress of the rubber
E	Modulus of the rubber
NMR	Nuclear magnetic resonance
G'	Shear storage modulus
G''	Shear loss modulus
tan δ	Loss factor
nm	nanometer
TESPT	Bis-(3-triethoxysilylpropyl)tetrasulfane
i, j, k	Difference in the size of species
M*	Monofunctional reactive species
M	Neutral species
M	Bi-functional activated species
R_{total}	Total reaction rate
N	Electron density
E	Electron energy
LPP	Low pressure plasma
APP	Atmospheric pressure plasma
CBS	N-cyclohexyl-2-benzothiazolesulfenamide
CTAB	Cetyltrimethyl ammonium bromide
C_2H_2	Acetylene
C_4H_5N	Pyrrole
C_4H_5S	Thiophene
TGA	Thermo-gravimetric analysis
TOF-SIMS	Time-of-flight secondary ion mass spectrometry
SEM	Scanning electron microscopy
EDX	Energy dispersive X-ray
RF	Radiofrequency

Pa	Pascal
W	Watt
U	Untreated silica
PA	Plasma-polymerized acetylene-coated silica
PPy	Plasma-polymerized pyrrole-coated silica
PTh	Plasma-polymerized thiophene-coated silica
T	Silane-treated silica
a.m.u	atomic mass unit
Å	Angstrom
t_{90}	Time to 90% state-of-cure
S	Sulfur
DPG	N,N'-Diphenylguanidine
RPA2000	Rubber process analyzer2000
α_F	The reinforcement parameter
S'_{max}	Maximum torque of filled rubber
S'_{min}	Minimum torque of filled rubber
S'^{0}_{max}	Maximum torque of gum rubber
S'^{0}_{min}	Minimum torque of gum rubber
m_F	Mass fraction of filler
m_P	Mass fraction of polymer
Q	Swelling value
1/Q	Apparent crosslink density
HV-BR	High-vinyl polybutadiene rubber
IIR	Isoprene-isobutylene rubber
ZnO	Zinc oxide
TMTD	Tetramethylthiuram disulfide
ZBEC	Zinc dibenzyldithiocarbamate
MBTS	2, 2´-dithiobenzothiazole
phr	Parts per hundred of rubber

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2. H. H. Le, M. Tiwari, S. Ilisch, H.-J. Radusch
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Poster presentations

1. M. Tiwari, H. H. Le, S. Ilisch, H.-J. Radusch
   Characterization of the effect of molecular structure on carbon black dispersion in rubber compounds using the online measured electrical conductivity
   Poster presented at Polymerwerkstoffe 2004, Halle/Saale, Germany, September (2004)
2. M. Tiwari, H. H. Le, S. Ilisch, H.-J. Radusch
   Manufacturing an elastic and electrically conductive polymer on the basis of the filled thermoplastic elastomers
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3. H. H. Le, M. Tiwari, S. Ilisch, H.-J. Radusch
   Monitoring the mixing process of the nonconductive CB filled rubber compounds using the method of the online measured electrical conductivity
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4. H. H. Le, M. Tiwari, S. Ilisch, H.-J. Radusch
   Manufacturing of elastic and electrically conductive polymers on the basis of filled thermoplastic elastomers
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   Elastomeric and electrically conductive materials on the basis of thermoplastic elastomers and their controlled manufacturing
   Poster presented at 12. Problemseminar Polymermischungen, Bad Lauchstaedt, Germany, March (2007)
6. M. Tiwari, W. K. Dierkes, W. J. van Ooij and J. W. M. Noordermeer
   Surface modification of reinforced silica by plasma polymerization: Preparation and characterization
   Poster presented at Dutch Polymer Days, Lunteren, The Netherlands, February (2007)

Curriculum vitae

Mukund Tiwari was born on 5th of August, 1978 in Farrukhabad, Uttar Pradesh, India. He did his entire primary and secondary education in the capital of India, New Delhi. He obtained his Bachelor of Chemical Engineering in May 2002 from Punjab Technical University, Jalandhar (Punjab), India. He obtained his Master in Applied Polymer Science in January 2005 from Martin-Lüther-Universität Halle-Wittenberg (MLU), Halle (Saale), Germany. The title of his Master thesis was "Analysis of in-situ deformation of ethylene octene copolymers by using Fourier Transform Infra Red (FTIR) spectroscopy" under the supervision of Prof. Dr. -Ing. H.-J. Radusch.

In February 2005, he started his Ph.D under the supervision of Prof. Dr. Ir. J. W. M. Noordermeer at the University of Twente, The Netherlands. The topic of his research was “Plasma Coating of Silica: A key to improved dispersion and properties of reinforced elastomer blends”. The research was funded by Dutch Technology Foundation (STW). The results of this research are described in this thesis. From July 2008 till March 2010, the author was working at Technical Fibers Application institute BV, Arnhem, the Netherlands as an Application Research Engineer (Elastomer Reinforcment). From April 2010, the author has started working at Teijin Aramid BV, Arnhem, The Netherlands as R&D scientist in the end use development department (QRE).

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In July 2008, I started to work for Technical Fibers Application institute BV. From April 2010, TFA becomes full part of Teijin Aramid BV. From July 2008 and till now, I have enjoyed working in the organization. I take this opportunity to thank all of my colleagues for their great help and support. Michel, Egbert, Antons, Alex and Ed: thank you for your help and support. Dear Frits, thank you very much for your great help at personal and professional level. I would like to thank you for the dutch translation of summary and outlook part of my thesis. Fadi: thank you for being generous all the time. Robert and Toni: thank you very much for your great support during the work. Dear Marinus, thank you very much for your understanding and support in respect to the finalization of my thesis.

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Mukund