**MORPHOLOGY OF SILICA REINFORCED NATURAL RUBBER:
THE EFFECT OF SILANE COUPLING AGENT**

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ABSTRACT

A good dispersion of silica in a rubber vulcanizate is important as it influences the filler-to-rubber interaction and consequently the final properties. This paper presents an investigation into the morphology of silica-reinforced Natural Rubber (NR) in presence and absence of a silane coupling agent, bis(triethoxysilylpropyl) tetrasulfide (TESPT). Micro- and nano-dispersion morphologies of silica in NR and Deproteinized Natural Rubber (DPNR) are studied by using Atomic Force Microscopy (AFM). Using a special network visualization technique based on Transmission Electron Microscopy (TEM), insight into the silica and rubber interaction in the NR and DPNR is gained. In absence of silane, vacuoles around the silica particles are formed as a result of a weak filler-polymer interaction, while the presence of silane leads to strong filler-to-rubber bonding, which prevents formation of vacuoles. Improvement of the micro-dispersion of silica in the NR and DPNR vulcanizates with the use of TESPT is observed from AFM phase imaging. The correlation between the filler-to-rubber interaction as analyzed by TEM and AFM and bound rubber contents as well as the Payne effect is discussed.

INTRODUCTION

High-dispersion silica has become the preferred alternative to carbon-black nowadays, as reinforcing filler in tire tread compounds. Its use provides considerable improvement in rolling-resistance of passenger car tires. However, since silica is highly polar and hydrophilic, it is incompatible with apolar rubbers such as NR. Hence, mixing silica and rubber is difficult. A bi-functional silane coupling agent, such as bis(triethoxysilylpropyl) tetrasulfide (TESPT) is needed to improve the filler-to-rubber interaction on the nano-scale by creating chemical links between the silica surface and the rubber chains.^{1,2}

The use of a silane like TESPT involves two main chemical reactions that need to take place at their appropriate time slots during rubber processing, namely the silica and silane reaction or silanization, and silane-rubber coupling. Since the silanization occurs *in-situ* during mixing, it also correlates to dispersion of silica in the rubber matrix. A proper silanization of silica will result in a good dispersion of silica. Dispersion of silica can be categorized into macro-dispersion and micro-dispersion. Macro-dispersion is designated as dispersion of agglomerates with sizes larger than 1 μm , while micro-dispersion refers to dispersion of aggregates of silica with a size smaller than 500 nm. The different levels of silica dispersion are schematically illustrated in Figure 1.

Atomic Force Microscopy (AFM) is one of the foremost tools to study dispersion of fillers in polymer/rubber at nano-scale. AFM is a way of visualizing a surface using the forces between atoms.³ The effect of mixing dump temperature on micro-dispersion of silica in sSBR/BR blend compounds has been studied by Reuvekamp using AFM measurements.⁴ In addition, AFM has also been used to visualize pre-vulcanization effects in the compounds: elliptical structures appear in the AFM phase image. Natchimuthu has investigated the effect of an epoxy resin on the dispersion characteristics of silica fillers in EPDM rubber using AFM.⁵ Improved silica dispersion for EPDM-silica systems with epoxy resin was reported in

terms of scanned height in the range of 0-100nm, as compared to the scanned height of a compound without resin which was found to be in the range of 0-700nm. Jeon et al. have successfully distinguished two different polymer domains in an unfilled rubber blend (natural /synthetic rubbers) using tapping mode AFM.⁶ In the phase image, the harder polymer appears as the lighter phase in the view of image contrast. Using the same AFM technique, filler morphology in filled NR and filled rubber blends was also examined by its shape as well as contrast.

In the present work, the micro- and nano-dispersion characteristics of silica in natural rubber compounds are studied using tapping mode AFM. The influence of silane coupling agent, TESPT on morphological micro-dispersion is highlighted. NR is compared with purified NR from deproteinization. In addition, silica and rubber interaction in the NR and Deproteinized NR is investigated using a special network visualization technique based on Transmission Electron Microscopy (TEM).

EXPERIMENTAL SECTION

MATERIALS

Standard Malaysian Natural Rubber (SMR20) and Deproteinized Natural Rubber (DPNR), supplied by the Malaysian Rubber Board (MRB) were used. The filler used in this study was highly dispersible silica: Ultrasil 7005 with a CTAB surface area of 164 (m²/g). Bis-(triethoxysilylpropyl) tetrasulfide (TESPT) was used as the silane coupling agent. The ingredients in the compound and their sources are listed in Table I. All ingredients were used as obtained from the respective sources.

SAMPLE PREPARATION

Compounding

All ingredients except the curatives were mixed in an internal mixer, Brabender Plasticoder 350S lab station. The mixing was done at 60 rpm rotor speed, 0.7 fill factor, 14 minutes mixing time and 150°C dump temperature. After 24 hours, the curatives were added to the masterbatches on a two-roll mill.

Vulcanization

Vulcanization curves were measured using a Rubber Process Analyzer (RPA 2000) from Alpha Technologies, under conditions of 0.833 Hz and 2.79% strain over a period of 30 minutes at a temperature of 150°C. Vulcanizates were prepared by curing the compounds for their respective t_{95} at 150°C using a Wickert laboratory press WLP 1600/5*4/3 at 100 bar.

Sample preparation for AFM

The vulcanizate samples were extracted overnight in refluxing acetone. Several samples were extracted at once in the same solvent. After extraction was complete, the vulcanizates were allowed to dry to remove residual solvent. The surface of the extracted vulcanizate samples was cryo-microtomed at -110°C using a glass knife. The sectioned samples were attached to the stub using Araldite glue.

Sample preparation for TEM Network Visualization

Samples were taken from the vulcanizates and extracted overnight using acetone to remove remaining curing additives. A strip of approx. 10mm x 5mm from the extracted vulcanizate sample was then swollen in a styrene solution containing a radical initiator (1 wt. % Benzoyl Peroxide, 2 wt. % Dibutyl Phthalate plasticizer) for 2 days. A 10mm x 2mm strip was then cut

from the swollen sample and transferred into a polymer capsule. The capsule was filled up with styrene solution and fitted with a cap. The capsule was heated overnight at 68°C for the styrene to be polymerized and harden.

SAMPLE ANALYSIS

Payne effect

The Payne effect was measured in the RPA 2000 by applying a strain sweep at 0.5 Hz and 100°C. Prior to measurement, the sample was vulcanized at 150°C for 10 minutes and subsequently cooled to 100°C. The Payne effect was calculated as the difference between the storage modulus, G' at 0.56% and G' at 100.04% strain.

Bound Rubber Content

The bound rubber content (BRC) measurements were performed on unvulcanized samples by extracting the unbound rubber with toluene at room temperature for seven days in both normal and ammonia environment. The ammonia treatment of BRC was done to obtain the chemically bound rubber as ammonia cleaves the physical linkages between rubber and silica.^{7,8} The amount of BRC (%) was calculated by:

$$BRC (\%) = \left(\frac{w_{dry} - w_{insolubles}}{w_o \times \frac{100}{w_{total, phr}}} \right) \times 100\% \quad eq.1$$

Where w_o is the initial weight of the sample, w_{dry} is the dry weight of the extracted sample, $w_{insolubles}$ is the weight of insolubles matter (mainly filler) in the sample and $w_{total, phr}$ is the total compound weight in phr. The physically BRC was taken as the difference between untreated BRC and ammonia treated BRC.

Atomic Force Microscopy (AFM)

AFM measurements were conducted using an MFP-3D Stand Alone AFM (Asylum Research, Santa Barbara, CA, USA) at Tun Abdul Razak Research Centre (TARRC), Brickendonbury, Hertford, UK. All measurements were done in non-contact tapping mode (dynamic, AC mode) at $k=2\text{N/m}$ and $f_0=70\text{ kHz}$. The AFM images were processed using Argyle Light software by Asylum Research.

Transmission Electron Microscopy (TEM)

TEM analysis of a swollen rubber sample embedded in the polymerized polystyrene matrix was done using a Philips CM12 TEM operating at 80kV at TARRC. An ultra-thin section of the sample was obtained by ultramicrotomy at room temperature using glass knives. The microtome used was PowerTome PC (RMC). The sections were collected in a water-filled trough and relaxed with xylene vapor before collecting on TEM grids. The sections were stained with osmium tetroxide vapor for one hour. Osmium tetroxide reacts with carbon-carbon double bonds and this results in the rubber network appearing darker than the polystyrene. By using this method, the regions of rubber network can be identified from the stained rubber and unstained polystyrene matrix.

RESULTS AND DISCUSSION

MICRO-DISPERSION OF SILICA-NR VULCANIZATES

Comparison of AFM images of NR-silica with DPNR-silica vulcanizates in absence of silane coupling agent for a scan size of $5 \times 5\text{ }\mu\text{m}$ are depicted in Figure 2. The left images are the height images and the right images are the phase images. In the height images, silica aggregates/agglomerates are shown in light (white) color, while rubber is shown in dark (black) color. From the phase images, the silica aggregates/agglomerates can be differentiated

based on the assumption that it has a higher stiffness compared to the rubber matrix.⁹ Thus, in phase images silica aggregates/agglomerates are shown in dark color, while rubber is shown in light color.

The structure of the silica aggregates forming agglomerates are readily distinguished from the height images of vulcanizates without silane coupling agent. For the NR vulcanizate without coupling agent, the micro-dispersion of silica aggregates of the size 500 nm and smaller is dominant, in addition to small agglomerates that are also present. The corresponding phase image confirms that the silica in the NR vulcanizate is dispersed to micro-level. In comparison, the DPNR vulcanizate without coupling agent shows poor micro-dispersion of silica as seen from the phase image where silica aggregates of 500 nm are present forming silica networking.

A comparison of AFM images of NR-silica with DPNR-silica in presence of TESPT silane coupling agent is illustrated in Figure 3. The height image shows a good micro-dispersion of silica in the NR-silica-TESPT and DPNR-silica-TESPT vulcanizates. What is striking from the phase images for the vulcanizates with TESPT is the smaller aggregates size of silica as compared to the vulcanizates without silane. This indicates that a better micro-dispersion is obtained for silica vulcanizates with the use of TESPT. The phase images further reveal that the silica aggregates in NR and DPNR vulcanizates are approximately 100 nm and smaller. In addition, there are also aggregates of the size of 200 nm randomly visible, which is more obvious in the NR vulcanizate.

NANO-DISPERSION OF SILICA-NR VULCANIZATES

The AFM images of NR-silica and DPNR-silica vulcanizates in the absence of silane at even higher magnification is illustrated in Figure 4. The size of the silica aggregates in DPNR without coupling agent is bigger than in the NR vulcanizate as seen from the height

image at 1000 x 1000 nm. The phase image of NR-silica without silane in Figure 4 shows silica aggregates of 100nm size and smaller as dispersed in the matrix. The size of the silica aggregates in the DPNR vulcanizate is almost comparable to that in NR, although they seem to be closer together.

In Figure 5, the height images show an improved nano-dispersion of silica in NR and DPNR vulcanizates with the use of TESPT as compared to without coupling agent. Clusters of a few primary particles of silica in the size of 50 nm are clearly visible in both NR and DPNR in addition to silica aggregates of approximately 100nm. However, in DPNR-silica-TESPT, the silica particles appear to be smaller indicating a somewhat better nano-dispersion. Besides, there is an intermediate region between the silica and rubber phases. A study by Nakajima and Nishi by AFM analysis on carbon black filled-NR vulcanizates showed the existence of an intermediate phase surrounding the carbon black region whose Young's modulus was stiffer than the rubbery region but softer than the filler region.¹⁰ Bielinski et al. have also shown a filler-matrix interphase from AFM images, ascribed to a bound rubber layer.¹¹ However, the filler-rubber interphase is found to be different for carbon black and silica mixes.¹² The interpretation of this intermediate region is still subject to debate as some blame it on a shadowing effect of AFM. In Figure 5, the intermediate region is clearly observed surrounding the silica aggregates in the DPNR-silica-TESPT vulcanizate, rather than only on one side. This suggests that there is a bound rubber phase covering the silica aggregates in DPNR, which demonstrates that there is more rubber-to-filler interaction in the presence of silane TESPT. This may be related to better silanization in DPNR as low amounts of protein are present in the rubber, and results in lower filler-filler interaction.

TEM images showing the dispersion of silica particles in vulcanizates with TESPT are presented in Figure 6. As shown, the use of TESPT silane coupling agent improves the nano-dispersion of silica. The TEM image reveals that the silica is mainly dispersed to primary

particles due to increased hydrophobation of the silica surface by TESPT. The average size of the primary particles of silica is about 20nm. The primary particles and aggregates of silica are homogeneously distributed in the NR and DPNR vulcanizates with TESPT.

PAYNE EFFECT OF SILICA-NR VULCANIZATES

A comparison of the Payne effect of silica-filled NR and DPNR vulcanizates is shown in Figure 7. In the absence of silane coupling agent, the Payne effects of NR and DPNR are almost comparable. This is in agreement with the results of micro-dispersion. The Payne effects of the NR and DPNR vulcanizates with silane are considerably lower than those without silane. This again correlates well with a good micro- and nano-dispersion of NR- and DPNR-silica-TESPT vulcanizates, which is confirmed by the AFM phase images in Figures 3 and 5. The lower Payne effect which results from reduced filler-filler interaction in the DPNR vulcanizate as compared to NR indicates that there is more coupling between TESPT and silica with less protein present in purified DPNR. This is also in agreement with the intermediate region surrounding the silica aggregates in DPNR-silica-TESPT aggregates, which might be ascribed to the bound rubber layer as discussed earlier.

BOUND RUBBER OF SILICA-NR VULCANIZATES

Bound rubber is the polymer portion that remains bound to the filler when an unvulcanized compound is extracted with a good solvent such as toluene. For ease of description, the bound rubber can be described according to its layer on the filler particle or aggregate, resulting in a tightly bound rubber skin and a loosely bound rubber shell. In the present study, the total BRC as measured in normal atmosphere is a combination of the tightly and the loosely bound rubber. The chemically BRC as obtained from extraction in an ammonia atmosphere is only the tightly chemically bound rubber left, as the loosely physically bound rubber is also extracted.

Figure 8 shows a comparison of BRC between silica compounds both with and without silane. Most of the BRC formed in a NR-silica-TESPT compound is chemically bound. This is obviously due to the hydrophobization of the silica surface as a result of silanization with TESPT. The increase in silica-TESPT coupling reduces the specific component of surface energy, γ_s^{sp} of silica and consequently results in more filler-to-rubber interaction. This corresponds well with the lower Payne effect of the silica compounds with TESPT. Without silane, the silica compounds still form bound rubber, as indicated by the total BRC. However, no chemically BRC was obtained for the silica compounds without silane after ammonia treatment. This indicates that silica compounds without silane have a weak interaction with rubber due to the high γ_s^{sp} of silica as reflected by a stronger filler-filler network, in the high Payne effect as shown in Figure 7.

TEM NETWORK VISUALIZATION OF SILICA-NR VULCANIZATES

Attempting to analyze the morphology of filler-to-rubber interaction in silica compounds at high loading, which in this study is 55 phr of silica, is difficult as the silica aggregates are very close together. In order to gain insight into the filler-to-rubber interaction, TEM network visualization was carried out where the vulcanizate was swollen in styrene. According to Ladouce-Stelandre *et al.*¹³ the swelling ratio of the vulcanizate swollen in styrene monomer is close to three, and the force is equally distributed in the three dimensions of the sample. Hence, it should be noted that the images of the styrene swollen compounds are not representative of the dispersion of silica in the vulcanizates, but are rather meant to look more closely into the interaction between filler and rubber.

TEM network visualizations of silica-filled NR and silica-filled DPNR vulcanizates without silane coupling agent are depicted in Figures 9 and 10, respectively. In both images, silica aggregates of around 50-100nm size can be seen as dark particles throughout the

sample. The vulcanized rubber network appears as a stained mesh structure, while polystyrene appears as unstained regions. Some silica aggregates in the NR vulcanizate are well-bonded to the NR network as seen from the network strands connecting silica particles to the NR network. In addition, there are vacuoles or voids surrounding the silica aggregates. The network visualization of the DPNR vulcanizate is markedly different from the NR vulcanizate. There are clearly vacuoles surrounding the silica aggregates in the DPNR vulcanizate. The styrene polymerizes between the rubber network and the silica particles, and this results in the polystyrene vacuoles surrounding the silica particles or aggregates. Ladouce-Stelandre *et al.*¹³ have suggested that the formation of such vacuoles is due to a weak interface between silica particles and rubber chains. Since silica exhibits a low dispersive component of surface energy, γ_s^d , the filler-to-rubber interaction is weak and not many rubber chains adsorb on its surface. Once a segment of a rubber chain is attached to the silica surface, it is possible that multiple attachment can occur due to segmental reptation of the rubber chain. There are less vacuoles present in the NR vulcanizate as compared to the DPNR vulcanizate without silane, which suggests higher filler-to-rubber interactions in the former.

A comparison of the TEM network visualization between NR and DPNR vulcanizates with TESPT coupling agent included is shown in Figures 11. It can be seen that there is strong attachment of the rubber network to the silica aggregates in both rubbers with TESPT present. Voids are scarcely visible in the TEM images. The aggregates of silica are also smaller as compared to those in vulcanizates without silane. This agrees well with the earlier data that all silica compounds with TESPT exhibited a lower Payne effect and very high chemically BRC. This also shows that these compounds have a high silanization efficiency as a result of good mixing and reaction. In addition, the rubber networks in the vulcanizates with silane appear to

be denser as compared to those without silane. This can be explained by higher crosslink density of the vulcanizates with silane due to sulfur released from TESPT.

CONCLUSIONS

The micro- and nano-dispersions of silica in Natural Rubber and Deproteinized Natural Rubber vulcanizates observed by means of tapping mode AFM give insight into filler-filler and rubber-filler interactions. In the absence of the silane coupling agent, the AFM phase image reveals that both NR and DPNR-vulcanizates have the silica dispersed to the micro level. Micro-dispersion of silica is observed in all vulcanizates with TESPT from the AFM phase images, where aggregates sizes of 500nm are dominant. The results have shown that the use of coupling agent TESPT enhances the dispersion of silica into aggregates and even into primary particles, which results in an increase of filler-to-rubber interactions. This is confirmed by the good nano-dispersion of silica in the NR-silica-TESPT and DPNR-silica-TESPT vulcanizates from the TEM- and AFM-phase images where primary particles of silica of 20-50nm are uniformly dispersed. At nano-dispersion level, tentatively a bound rubber layer is observed on primary particles of silica. The AFM analysis on micro- and nano-dispersion of silica does correlate the best with the Payne effect of the vulcanizates. In addition, a good micro-dispersion of silica in DPNR-TESPT correlates well with the lower Payne effect of the vulcanizate.

The TEM Network Visualization of the silica-vulcanizates with TESPT shows no formation of vacuoles, which demonstrates strong attachment of the rubber networks to silica aggregates. This is the result of chemical reaction between silica and TESPT, as also demonstrated by a high chemically bound rubber content and a low Payne effect. In contrast, the TEM Network Visualization of vulcanizates without silane reveals vacuoles around the silica particles and aggregates, which indicates weak filler-to-rubber interactions. This is

further supported by only physically bound rubber found in the compounds without silane. In comparison, the vacuoles are more clearly observed in DPNR-vulcanizates without silane than in the corresponding NR-vulcanizate.

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TABLE I
COMPOUND FORMULATION

Ingredients	Amounts (phr)	Source
Natural Rubber (NR or DPNR)	100	MRB
Silica Ultrasil 7005	55	Evonik
Silane, TESPT	5 ^a	Evonik
Zinc Oxide	2.5	Sigma Aldrich
Stearic acid	1	Sigma Aldrich
TDAE oil	8	Hansen & Rosenthal
TMQ	2	Flexsys
Sulfur	1.4	Sigma Aldrich
CBS	1.7	Flexsys
DPG	2	Flexsys

^a For the compound without silane, TESPT is omitted from the formulation

FIG. 1 – Schematic illustration showing the different levels of dispersion from macro, to micro and nano-dispersion of fillers.

FIG. 2 – AFM images of (a): NR-silica; and (b): DPNR-silica vulcanizates in the absence of coupling agent with scan size of 5 x 5 μm . The left is the height image and the right is the phase image.

FIG. 3 – AFM images of (a): NR-silica; and (b): DPNR-silica vulcanizates in the presence of silane coupling agent, TESPT with scan size of 5 x 5 μm. The left is the height image and the right is the phase image.

FIG. 4 – AFM images of (a): NR-silica; and (b): DPNR-silica vulcanizates in the absence of coupling agent with scan size of 1000 x 1000nm. The left is the height image and the right is the phase image.

FIG. 5 – AFM images of (a): NR-silica; and (b): DPNR-silica vulcanizates in the presence of silane coupling agent, TESPT with scan size of 1000 x 1000 nm. The left is the height image and the right is the phase image.

FIG. 6 – Comparison of TEM images of silica vulcanizates in the presence of silane coupling agent, TESPT: (a): NR and (b): DPNR.

FIG. 7 – Payne effect of silica-filled NR and DPNR vulcanizates in the absence and presence of silane coupling agent, TESPT.

FIG. 8 – Bound rubber content of NR and DPNR compounds.

FIG. 9 – TEM Network Visualization of silica-filled NR vulcanizate without coupling agent.

FIG. 10 – TEM Network Visualization of silica-filled DPNR vulcanizate without coupling agent.

FIG. 11 – TEM Network Visualization of silica-filled NR vulcanizate with TESPT silane coupling agent.

Figures Captions

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