Effect of a Silane Coupling Agent on the Morphology of Silica Reinforced Natural Rubber

Natural Rubber · Silica · Silane Coupling Agent · TEM · AFM

Filler-to-rubber interaction is a key parameter in reinforcement of rubber. 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). Improvement of the microdispersion of silica in NR with the use of TESPT is observed by Atomic Force Microscopy (AFM) imaging. Using a special network visualization technique based on Transmission Electron Microscopy (TEM), insight into the silica-to-rubber interaction in NR is gained. The presence of TESPT leads to strong-rubber bonding, which prevents formation of vacuoles.

Wirkung von Silan-Kopplungsmittel auf die Morphologie der Kieselsäure verstärkten Naturkautschuk

Naturkautschuk · Kieselsäure · Silan-Kopplungsmittel · TEM · AFM

Die Füllstoff-Kautschuk-Wechselwirkung ist ein wichtiger Parameter für die Verstärkung von Gummi. In dem vorliegenden Artikel wird die Morphologie von Kieselsäure-verstärktem Naturkautschuk (NR) mit und ohne Bis(triethoxysilylpropyl)tetrasulfid (TESPT) als Coupling Agent diskutiert. Die Analyse dieser Naturkautschuk-Vulkanisate wurde mit Hilfe einer speziellen Transmission Electron Microscopy (TEM) Technik durchgeführt, die es ermöglicht, Netzwerke sichtbar zu machen. Die Verwendung von TESPT führt zu stabilen Füllstoff-Polymer Bindungen, die die Bildung von Vakuolen verhindert. Eine Verbesserung der Mikrodispersion von Kieselsäure bei Verwendung von TESPT konnte mittels Atomic Force Microscopy (AFM) visualisiert werden.

Figures and Tables:
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In recent years, high-dispersion silica has become the preferred alternative to conventional carbon-black fillers 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. Therefore, 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 dynamic modulus of rubber increases with addition of reinforcing filler. The contributions of the fillers to the modulus of rubber can be divided into two: strain-dependent and strain-independent parts. Filler-filler interaction contributes to the strain-dependence of the modulus. The modulus decreases with increasing strain: the so-called ‘Payne effect’, which is due to a partially reversible breakdown of the filler network [3]. The strain-independent part of the modulus is a combination of filler-rubber interactions, the crosslinked rubber network contribution and a hydrodynamic effect of the filler as illustrated in Figure 1 [4-6]. Filler-filler and filler-rubber interactions are two partially competitive processes. A decrease in filler networking would lead to better filler-rubber interaction. Filler-filler interaction is commonly characterized by the Payne effect: the drop in storage modulus in a dynamic mechanical test when the strain (deformation) is increased from low (<1 %) to a high value (100 %) at constant frequency and temperature. The use of TESPT significantly reduces the Payne effect in silica-filled compounds as a result of hydrophobation of the silica surface and therefore increased filler-rubber bonds. The phenomenon of bound rubber is another evidence for filler-rubber bonds, which has been studied by many scholars [7-11]. This rubber-to-filler interaction is reflected macroscopically in the formation of bound rubber, which involves physical adsorption, chemisorption and mechanical interaction [10,12].

Transmission Electron Microscopy (TEM) was used by Julve et al. to evaluate the microdispersion of silica in a silica tire tread compound with a high filler content [13]. Reuvekamp found that a better silica microdispersion is obtained at high discharge temperature after mixing, as characterized by an increase in the amount of segregated silica particles [14]. A technique called Network Visualization using TEM is a beneficial tool to study the rubber to filler interaction in rubber compounds. This technique was first developed at the Tun Abdul Razak Research Centre (TARRC) to study rubber networks and was later used to investigate rubber-to-filler interactions [15]. The TEM Network Visualization process involves swelling of a crosslinked vulcanizate in styrene, polymerization of the styrene, staining the rubber network and visualization using TEM [16]. Using this method, the topology of a rubber network can be identified from the stained elastomer moieties and the unstained polystyrene matrix.

Chapman and coworkers used the TEM Network Visualization technique to investigate the rubber-to-filler interaction between NR and 25 mole% Epoxidized NR (ENR-25) vulcanizates filled with 20 phr silica [16,17]. Polystyrene

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1 Tab. 1: Compound Formulation

Ingredients	Source	phr
Natural Rubber (NR or DPNR)	Malaysian Rubber Board	100
Silica Ultrasil 7005	Evonik	55
Silane, TESPT	Evonik	5 a
Zinc Oxide	Sigma Aldrich	2.5
Stearic acid	Sigma Aldrich	1
Processing oil, TDAE	H & R Europe	8
Antioxidant, TMQ	Flexsys	2
Sulfur	Sigma Aldrich	1.4
CBS	Flexsys	1.7
DPG	Flexsys	2

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

void regions between the silica and rubber are clearly visible for the NR-silica vulcanizate. In contrast, the ENR-25 network is fully attached to the silica particles and no voids are seen, indicating a higher rubber-to-filler affinity for the ENR-silica vulcanizate. However, for NR there are a small number of stained network strands connecting the silica particles and the NR network which indicates that there still is a certain interaction between NR and silica.

The present paper presents an investigation into morphology of silica reinforced NR in the presence and absence of a silane coupling agent. The filler-filler interactions are monitored by measuring the Payne effect. Micro-dispersion of silica is investigated using Atomic Force microscopy. The TEM Network Visualization technique is used to look at the filler/rubber morphology and to obtain further insight into the reinforcing mechanism of silica in NR.

Experimental

Materials:

Natural rubbers (NR), SMR20, and deproteinized natural rubber (DPNR), Purepprena, were used in this study. The compound formulation used throughout this investigation is shown in Table 1. Highly dispersible silica, Ultrasil 7005 from Evonik with CTAB surface area of 164 m^2/g was used. The other compounding ingredients were used as obtained from the respective sources, as indicated in Table 1.

Sample Preparation:

The compounds were mixed in 2 steps. The first step was done using a laboratory internal mixer Brabender Plasticoder 350S lab station with 0.7 fill factor, 60 rpm rotor speed, and dump temperature of 150 ºC. After mixing for 14 minutes, the batches were sheeted out on a Schwabenthan Polymix80T 80 x 300mm two-roll mill. After 24 hours, the curatives were mixed on the two-roll mill in the second step.

Vulcanizates were prepared by curing the compounds for their respective t_{95} (time to reach 95 % of torque difference in the curemeter) at 150 ºC using a Wickert laboratory press WLP 1600/5*4/3 at 100 bar.

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.

Characterization Methods:

The Payne effect was measured in a Rubber Process Analyzer (RPA 2000, Alpha Technologies) by strain sweep at 100 ºC and 0.5 Hz. The Payne effect was calculated as the difference between the storage modulus, G' at 0.56 % and G' at 100.04 % strain. Before the Payne effect measurement, the sample was vulcanized in the RPA 2000 at 150 ºC for 10 minutes and subsequently cooled to 100 ºC.

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 environments. The ammonia treatment of BRC was done to obtain the chemically bound rubber as ammonia cleaves the physical linkages between rubber and silica [9,18]. The amount of BRC (%) was calculated by:

$$BRC\ (\%) = \frac{w_{dry} - w_{insolubles}}{w_o \times \dfrac{100}{w_{total,\,phr}}} \times 100\% \tag{1}$$

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 (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, Brickendonbury, Hertford, UK. All measurements were done in non-contact tapping mode (dynamic, AC mode) at k=2N/m and f_0=70 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 the 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

Influence of silane on filler-filler interactions

Filler-filler interaction is commonly measured by the Payne effect. A comparison of filler-filler interaction in the NR-silica compounds in both the absence and presence of silane coupling agent TESPT, is shown in Figure 1. For the compound without silane, a comparable Payne effect between NR and DPNR is observed. The Payne effect of the NR and DPNR compounds is greatly reduced with the use of silane TESPT. The DPNR-silica-TESPT compound has a lower Payne effect than the NR-silica-TESPT compound. The lower filler-filler interaction in the DPNR compound compared to NR indicates that there is more coupling between TESPT and silica with purified NR.

Micro-dispersion of silica in NR vulcanizates

The micro-dispersion of silica vulcanizates by AFM in the absence of silane is illustrated in Figure 2. 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 1x1 µm. The phase image of NR-silica without silane in Figure 2(a) 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 3, the height images show an improved micro-dispersion of silica in NR and DPNR vulcanizates with the use of TESPT as compared to without coupling agent. 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. The difference between NR and DPNR can be observed from the phase image. The distances between the silica aggregates of size 50-100nm are clearly visible in the NR-silica-TESPT vulcanizate. However, in DPNR-silica-TESPT, the distance between the aggregates looks a little smaller, indicating a somewhat better micro-dispersion. Besides, there is an intermediate region between the silica and rubber phases, suggesting the bound rubber layer [19-21].

Influence of silane on bound rubber content of silica compounds

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,

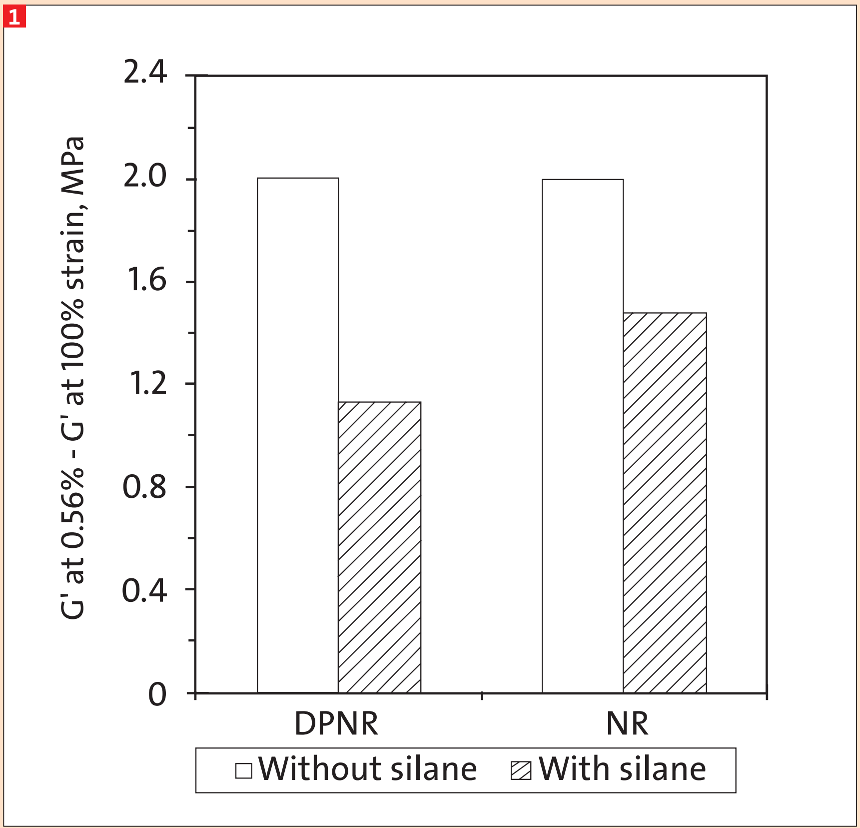

Fig. 1: Payne effect of NR and DPNR compounds in the absence and presence of silane coupling agent.

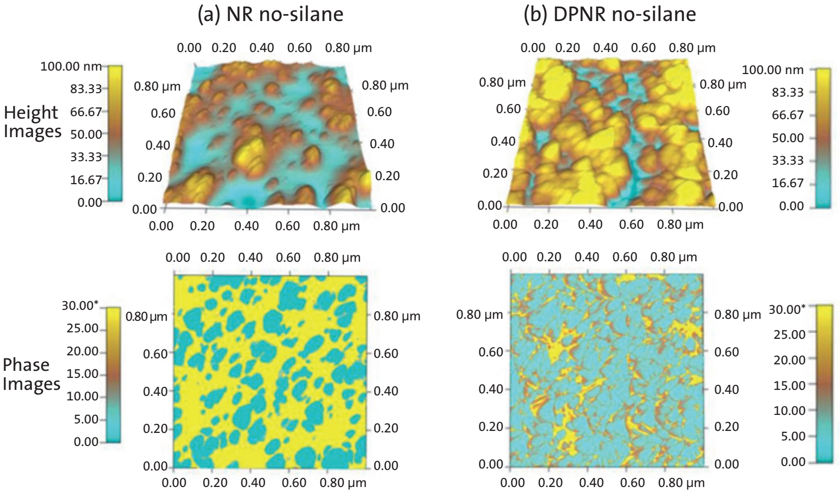

Fig. 2: Micro-dispersion of silica in NR and DPNR vulcanizates in the absence of silane coupling agent.

2 Tab. 2: Bound Rubber Contents (BRC)

Compounds	Chemically BRC (%)	Physically BRC(%)
NR-silica without silane	0	57
DPNR-silica without silane	0	45
NR-silica-TESPT	68	11
DPNR-silica-TESPT	76	11

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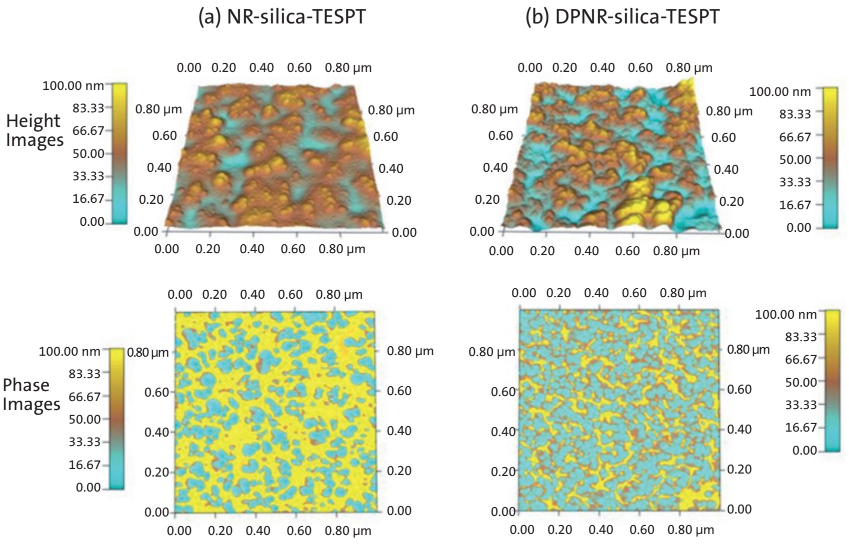

Fig. 3: Micro-dispersion of silica in NR and DPNR vulcanizates in the presence of a silane coupling agent, TESPT.

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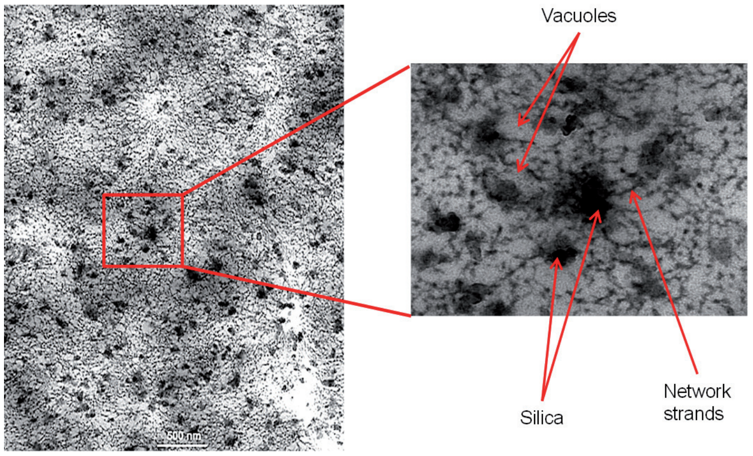

Fig. 4: TEM Network Visualization of NR vulcanizate in the absence of silane coupling agent.

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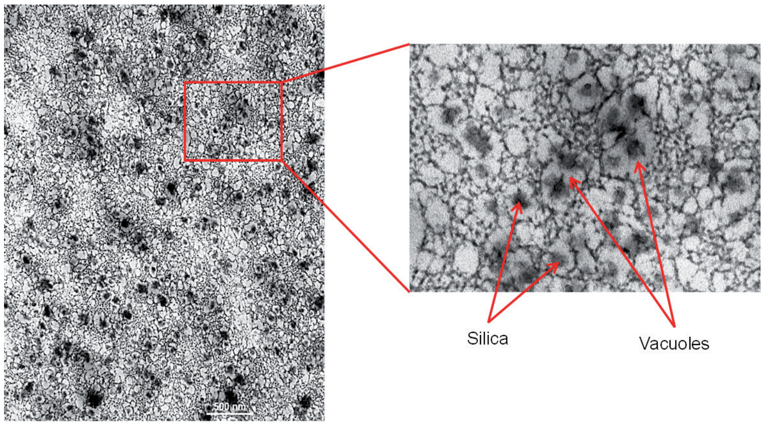

Fig. 5: TEM Network Visualization of DPNR vulcanizate in the absence of silane coupling agent.

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 tightly chemically bound rubber left, as the loosely physically bound rubber is also extracted.

Table 2 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 hydrophobation 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 which leads to a stronger filler-filler network, as reflected in the high Payne effect as shown in Figure 1.

TEM Network Visualization of silica-NR compounds

Attempting to analyze the morphology of filler-to-rubber interactions 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.

TEM network visualizations of silica-filled NR and silica-filled DPNR vulcanizates without silane coupling agent are depicted in Figures 4 and 5, respectively. In both micrographs, 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

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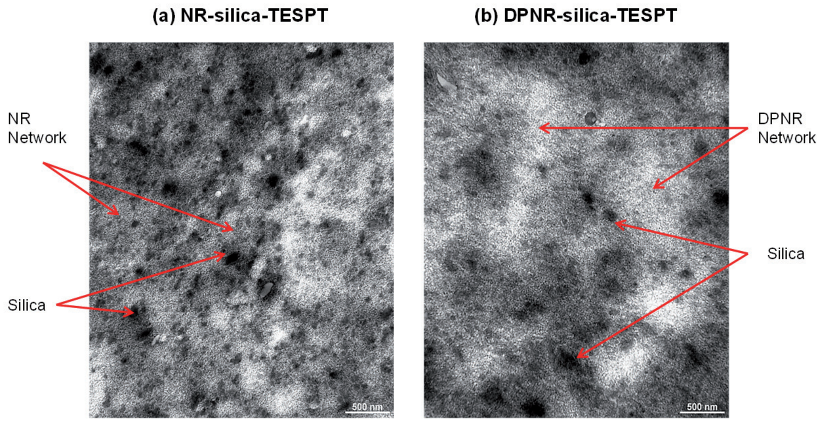

Fig. 6: TEM Network Visualization of (a) NR and (b) DPNR vulcanizates in the presence of silane coupling agent, TESPT.

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. have suggested that the formation of such vacuoles is due to a weak interface between silica particles and rubber chains [15]. Since silica exhibits a low dispersive component of surface energy, ɤsd, 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 Figure 6. 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 more dense as compared to those without silane. This relates to higher crosslink density of the vulcanizate with silane due to sulfur released from TESPT.

Conclusions

The micro-dispersion of silica and rubber-to-filler interaction in silica-filled natural rubber vulcanizates are greatly improved by the use of silane TESPT as coupling agent. 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 a 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 in the compounds without silane. In comparison, the vacuoles are more clearly observed in DPNR-vulcanizates without silane than in the NR-vulcanizate.

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