



FILLER-TO-FILLER AND FILLER-TO-RUBBER INTERACTIONS IN SILICA-REINFORCED NATURAL RUBBER AS VISUALIZED BY TEM NETWORK VISUALIZATION

11th Fall Rubber Colloquium

SitiSalina Sarkaw^{a,b}, Wilma K. Dierkes^a, Jacques W.M. Noordermeer^a

^a University of Twente, Elastomer Technology & Engineering, PO Box 217, 7500AE Enschede, the Netherlands

^b Malaysian Rubber Board, RRIM Research Station, Sg. Buloh, 47000 Selangor, Malaysia
j.w.m.noordermeer@utwente.nl

Abstract

Filler-to-rubber interaction is a key parameter in the reinforcement of rubber. This paper presents an investigation into filler-to-filler and filler-to-rubber interactions in silica-reinforced Natural Rubber (NR) in the presence and absence of a silane coupling agent. Using a special network visualization technique based on Transmission Electron Microscopy (TEM), insight into the silica and rubber interaction in NR is gained. In absence of silane, vacuoles around the silica particles are formed as a result of a weak filler-to-rubber interaction, while the presence of silane leads to strong filler-to-rubber bonding, which prevents formation of vacuoles. Further, the relationship between the filler-to-rubber interaction as seen from TEM images, and bound rubber and Payne effect is discussed.

Introduction

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 car tires. However, since silica is highly polar and hydrophilic of nature, it is incompatible with apolar rubbers such as Natural Rubber (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. 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 reduced filler-filler interactions and increased filler-rubber bonds.

Transmission Electron Microscopy (TEM) was used by Julve *et al.* [4] to evaluate the microdispersion of silica in a silica tire tread compound with a high filler content. 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) in the UK to study rubber networks [5]. It involves swelling of a crosslinked vulcanizate in styrene, polymerization of the styrene, staining the rubber network and visualization using TEM.

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 [5,6] 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. Polystyrene 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 high 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 filler-to-rubber interaction in silica reinforced NR in the presence and absence of a silane coupling agent. The filler-filler interactions are monitored by measuring the Payne effect. 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. In addition, the influence of proteins contained in the rubber on the silica-NR interaction is studied by using NR with different protein contents. The relationship of the filler-to-rubber interactions as seen from the TEM images with bound rubber and Payne effect measurements is further detailed.

Experimental

Materials

Natural rubbers with various protein content were used, of which regular Natural Rubber (NR) SMR20 was taken as the reference, and compared to deproteinized natural rubber (DPNR), and skim rubber for the highest protein content. The protein contents of the rubbers used based on their nitrogen contents are 1.3, 0.4 and 12.9 wt%, respectively. The filler used in this study was highly dispersible silica: Ultrasil 7005 from Evonik Cie. 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 1.

Table 1. Compound Formulations.

Ingredients	Source	phr
Natural Rubber (varied)	Malaysian Rubber Board	100 ^{a)}
Silica Ultrasil 7005	Evonik	55
Silane TESPT	Evonik	5 ^{b)}
Zinc oxide	Sigma Aldrich	2.5
Stearic acid	Sigma Aldrich	1
Processing oil, TDAE ^{c)}	H&R Europe	8
Antioxidant, TMQ ^{d)}	Flexsys	2
Curatives:		
Sulfur	Sigma Aldrich	1.4
CBS ^{e)}	Flexsys	1.7
DPG ^{f)}	Flexsys	2.0

^{a)} For skim rubber, the formulation is adjusted to 112 phr.; ^{b)} For the compound without silane, TESPT is omitted from the formulation, ^{c)} Treated distillate aromatic extract, ^{d)} 2,2,4-trimethyl-1,2-dihydroquinoline, ^{e)} N-cyclohexyl-2-benzothiazyl sulfonamide, ^{f)} Diphenyl guanidine.

Compounding and Vulcanization

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 discharge temperature. After 24 hours, the curatives were added to the masterbatches on a two-roll mill.

Vulcanizates were prepared by curing the compounds into 2mm thick sheets for their respective t_{95} at 150°C using a Wickert laboratory press WLP 1600/5*4/3 at 100 bar. 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.

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 closed capsule was heated overnight at 68°C for the styrene to be polymerized. Only when the capsules had hardened fully, could they be subjected to microscopy. Depending on the sample, it was sometimes necessary to 'post cure' the capsules in an oven at 90° for several hours to completely harden the styrene.

Characterization Methods

Payne effects were measured prior to and after vulcanization in the RPA 2000. Before cure the sample was heated to 100°C in the RPA and subsequently subjected to a strain sweep at 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. The Payne effect after cure was measured after vulcanization in the RPA 2000 at 150°C for 10 minutes and subsequent cooling to 100°C, making use of the same strain sweep conditions.

Bound rubber content (BRC) measurements were performed on unvulcanized samples without curatives 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. In this study, total BRC refers to BRC if measured in a normal atmosphere, while chemical BRC refers to BRC measured in an ammonia environment. The physically BRC is taken as the difference between total BRC and chemical BRC.

The apparent crosslink density was determined by swelling of a vulcanized sample in toluene. A vulcanized sample of about 0.2g was cut from a sheet with a thickness of 2mm and immersed in 50 ml toluene at room temperature for 72 hours. 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 immersed in acetone for 30 minutes to remove the remaining solvent. The samples were collected and left for 24 hours at room temperature in a fume hood before the dried weight was measured. The swelling value Q , was defined as the number of grams of toluene per gram of rubber hydrocarbon. The apparent crosslink density was calculated as the reciprocal swelling value, $1/Q$.

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 Tun Abdul Razak Research Centre (TARRC), Hertford, United Kingdom. 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 and proteins on filler-filler interactions

A comparison of filler-filler interaction by means of the Payne effect in the NR-silica compounds in both the absence and presence of silane coupling agent TESPT, in the uncured state, is shown in Figure 1. The Payne effect of silica compounds with TESPT is noticeably lower than for compounds without TESPT, except for skim rubber. This indicates that the hydrophobation of the silica surface by coupling agent TESPT greatly reduces the filler-filler interaction by creating covalent bonds between rubber and fillers. The influence of non-rubber constituents in the NR, in particular proteins, on silica-silica interaction can also be seen, where the low protein DPNR

compound exhibits a higher Payne effect and the high protein skim rubber compound has the lower Payne effect.

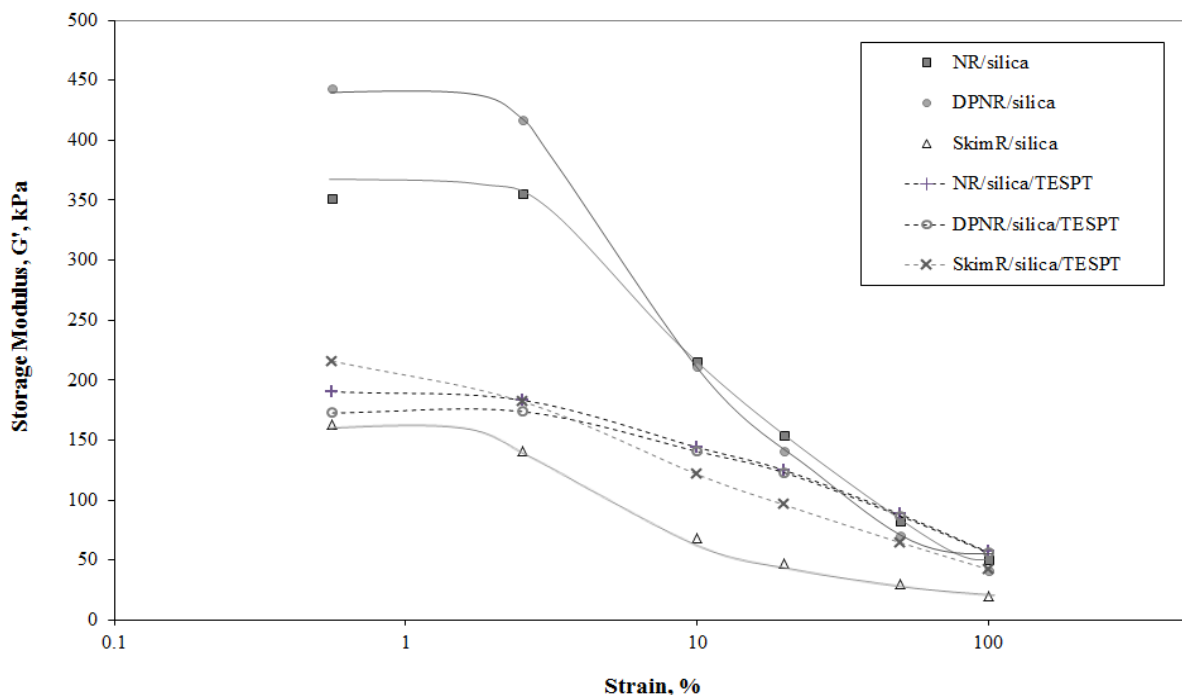


Figure 1: Payne effects of silica compounds as influenced by silane and protein contents in NR.

The proteins in NR have a similar effect as silane in hydrophobizing the silica surfaces, although not as strong, as shown in Figure 2(a). For unvulcanized samples, the Payne effect for compounds without silane decreases with increasing content of proteins in the NR. The role of the proteins is to disrupt the silica-silica network resulting in lower filler-filler interaction.

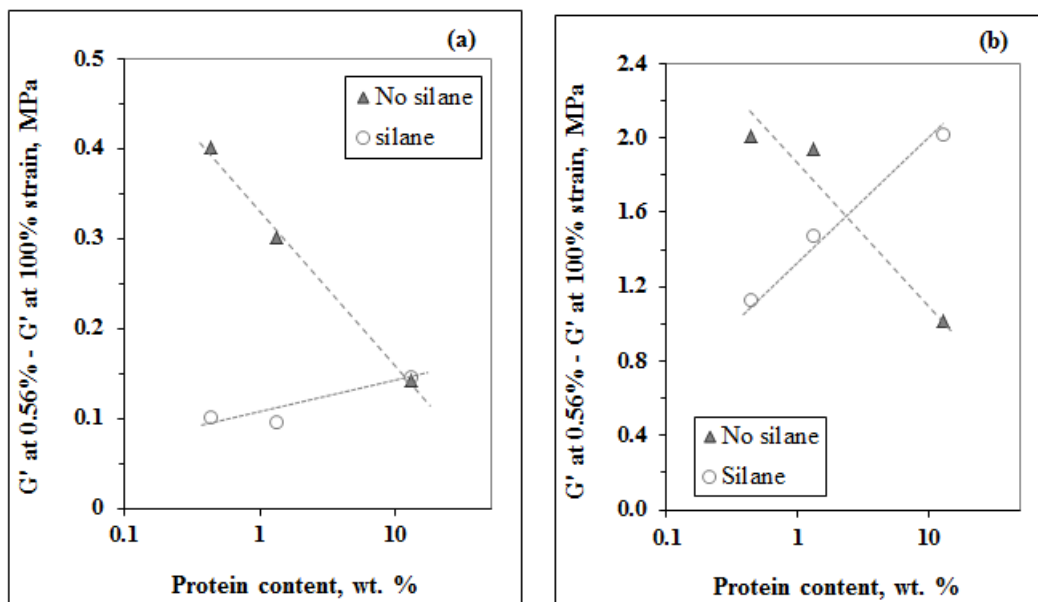


Figure 2: Comparison of Payne effect between silica-NR compounds with varying protein contents in the presence and absence of silane; (a): unvulcanized samples; (b): vulcanized samples.

This effect is not seen in the compounds with TESPT, as silica-TESPT coupling apparently is much stronger than the silica-protein interaction. Interestingly, with a lot of proteins present in the rubber, the Payne effect for the compound shows no difference whether or not silane is used.

The Payne effect measurements performed on the vulcanized compounds show opposite behavior. In Figure 2(b), the Payne effect for the vulcanized compounds with TESPT increases with increasing protein content in NR. The lower filler-filler interaction in the DPNR compound compared to NR indicates that there is more coupling between TESPT and silica with less protein present or for purified NR. The difference in the Payne effect between NR and DPNR is also seen in the compound without silane. Nonetheless, the Payne effect of the NR and DPNR compound with silane is still considerably lower than for compounds without silane. What remains puzzling is the opposite effect when silane is present in the skim rubber compound. It seems that there is a competitive effect between protein and silane in the hydrophobation of the silica surface. The high level of proteins disturbs the silane reactivity and might induce a polycondensation of the silane rather than a grafting process on the silica surface. This results in a more complex network like an interpenetrated network (IPN) and thus gives less mobility restriction on the surface of silica. This explains the higher Payne effect of the resulting skim rubber compound with silane. Another possible explanation is the denaturation of protein after vulcanization, which results in the breakage of silica-proteins interaction and consequently gives rise to a silica-silica network to reform.

Bound rubber and filler-to-rubber interactions in silica compounds

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 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. 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 chemical BRC was obtained for the silica compounds without silane after ammonia treatment.

Table 2. Comparison of Bound Rubber Contents of Silica Compounds with and without Silane.

Rubber types	Without silane		With silane	
	Physical BRC	Chemical BRC	Physical BRC	Chemical BRC
	[%]	[%]	[%]	[%]
NR	57	0	11	68
DPNR	45	0	11	76
Skim Rubber	51	0	13	80

With ammonia treatment, any loose silica-rubber interactions are destroyed and consequently no chemical BRC is obtained. Furthermore, it explains that in the silica-filled skim-rubber compound there is no chemical BRC, even though in this case the silica-silica network is disrupted by proteins, but the interaction between silica and proteins is mainly via hydrogen bonding. This finding demonstrates that the filler-filler interaction or filler morphology is one of the major factors contributing to the bound rubber formation for untreated silica filler. In addition, a lower Payne effect or less filler-filler interaction does not necessarily lead to an increase in rubber-to-filler interaction as demonstrated in the skim rubber-silica compound without silane. In this case, the protein is acting more like a surface covering agent.

TEM Network Visualization of silica-NR compounds

TEM network visualizations of silica-filled NR and silica-filled DPNR vulcanizates without silane coupling agent are depicted in Figures 3 and 4, 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 aggregates 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

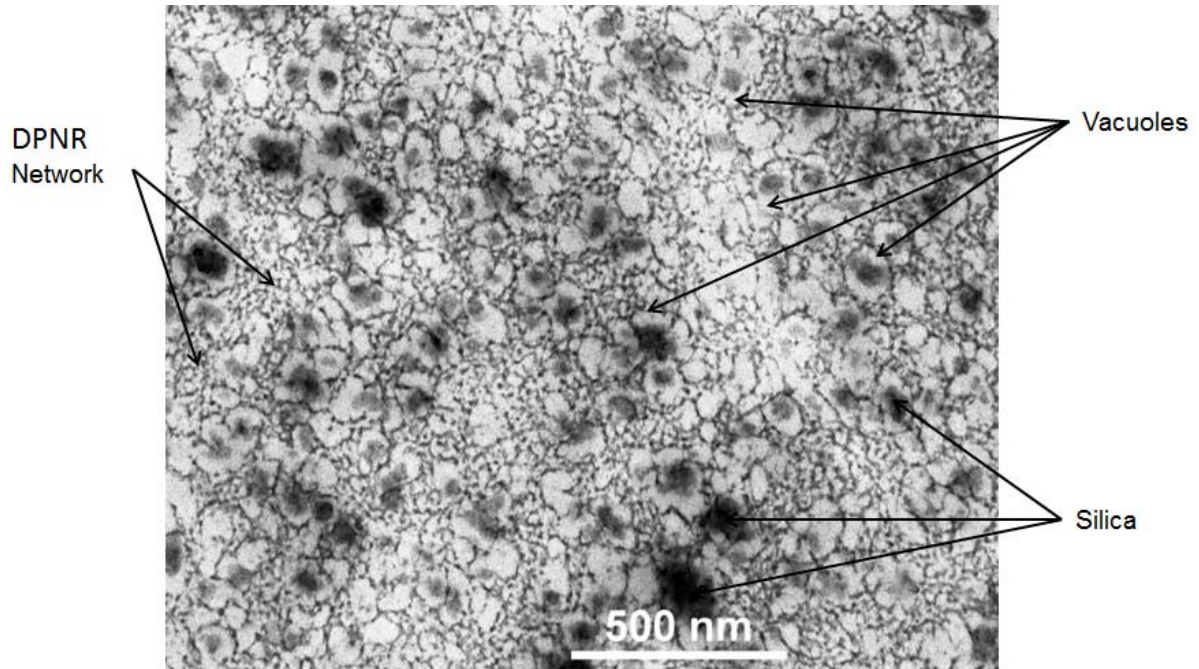


Figure 3: TEM Network Visualization of silica-filled NR vulcanizate without coupling agent.

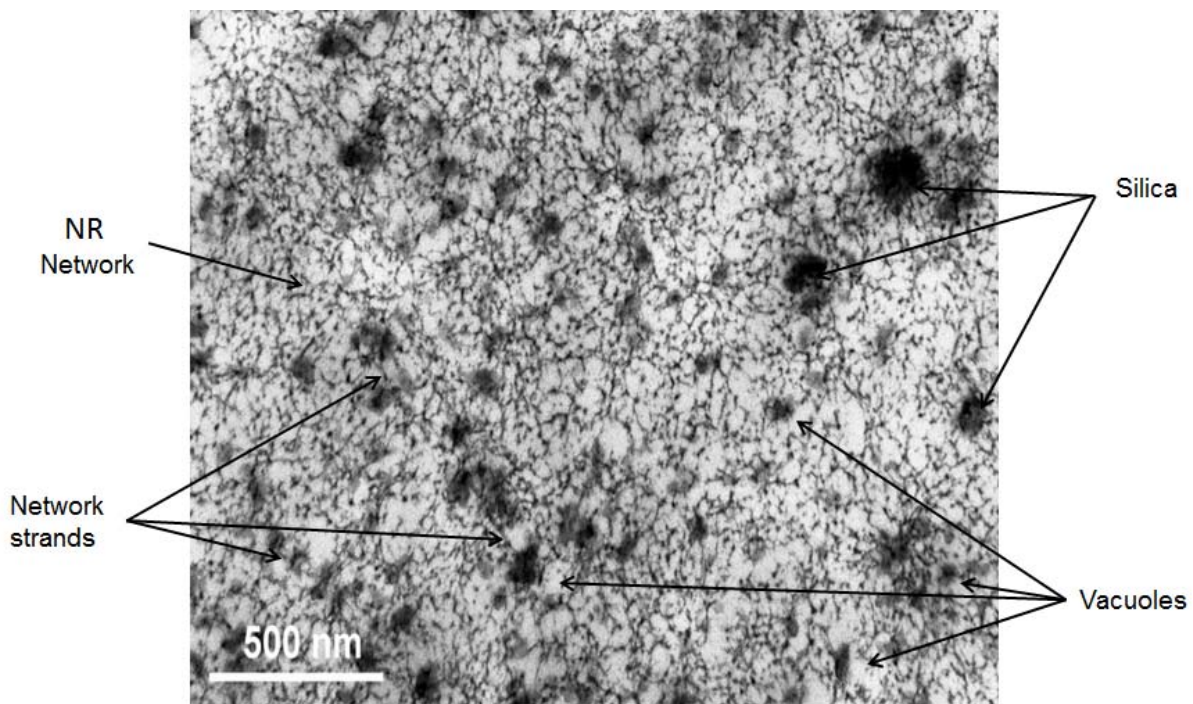


Figure 4: TEM Network Visualization of silica-filled DPNR vulcanizate without coupling agent.

surrounding the silica aggregates in the DPNR vulcanizate. The styrene polymerizes between the rubber network and the silica particles or aggregates, and this results in the polystyrene vacuoles surrounding the silica particles or aggregates. Ladouce-Stelandre *et al.* [7] have suggested that the

formation of such vacuoles is due to a weak interface between silica particles and rubber chains. 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.

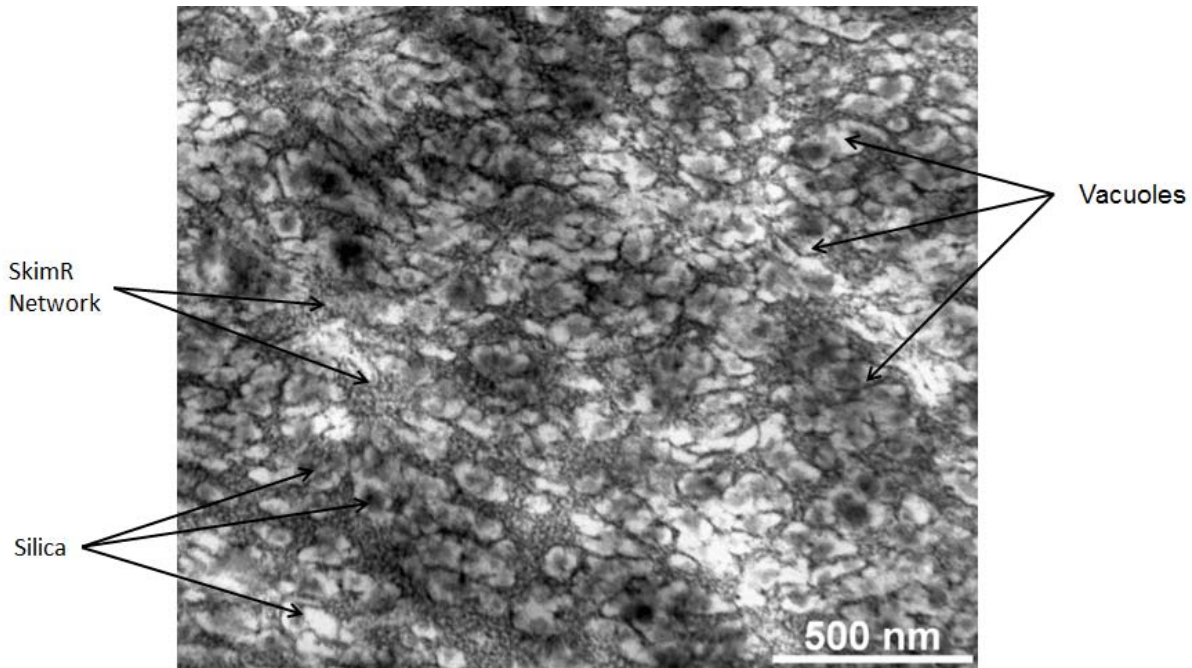


Figure 5: TEM Network Visualization of silica-filled skim rubber vulcanizate without coupling agent.

Figure 5 shows the TEM network visualization of the skim rubber-silica vulcanizate without coupling agent. The size of the silica aggregates in the skim rubber matrix is smaller as compared to those in the NR and DPNR vulcanizates without silane. This is in agreement with the earlier results of the Payne effect which demonstrated that silica-silica interactions were disrupted by the high amount of protein present in the skim rubber. However, vacuoles surrounding the silica particles and aggregates are clearly observed in the skim-rubber-silica vulcanizate. The existence of such vacuoles in the vulcanizate indicates again weak interaction between the silica and the skim rubber. This is further confirmed by no chemical BRC as obtained for skim rubber without silane.

The comparison of the TEM network visualization between NR, DPNR and skim rubber vulcanizates with TESPT coupling agent included is shown in Figures 6 - 8. Even though the micrographs are a bit less clear, it can be seen that there is strong attachment of the rubber network to the silica aggregates in all three 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 chemical 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 correlates with a higher apparent crosslink density of the vulcanizates with silane: Figure 9. TESPT is an effective silane and silica-TESPT vulcanizates produce an increase in crosslink density and decrease in the swelling capacity.

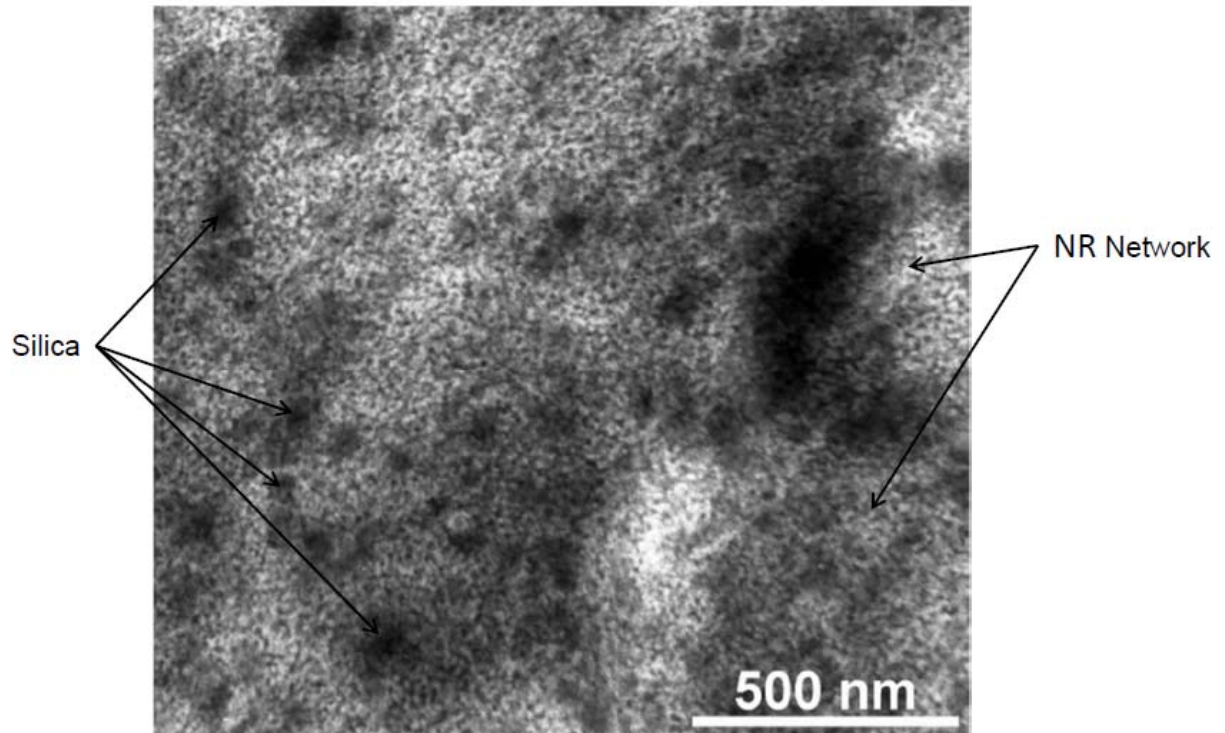


Figure 6: TEM Network Visualization of silica-filled NR vulcanizate with TESPT coupling agent.

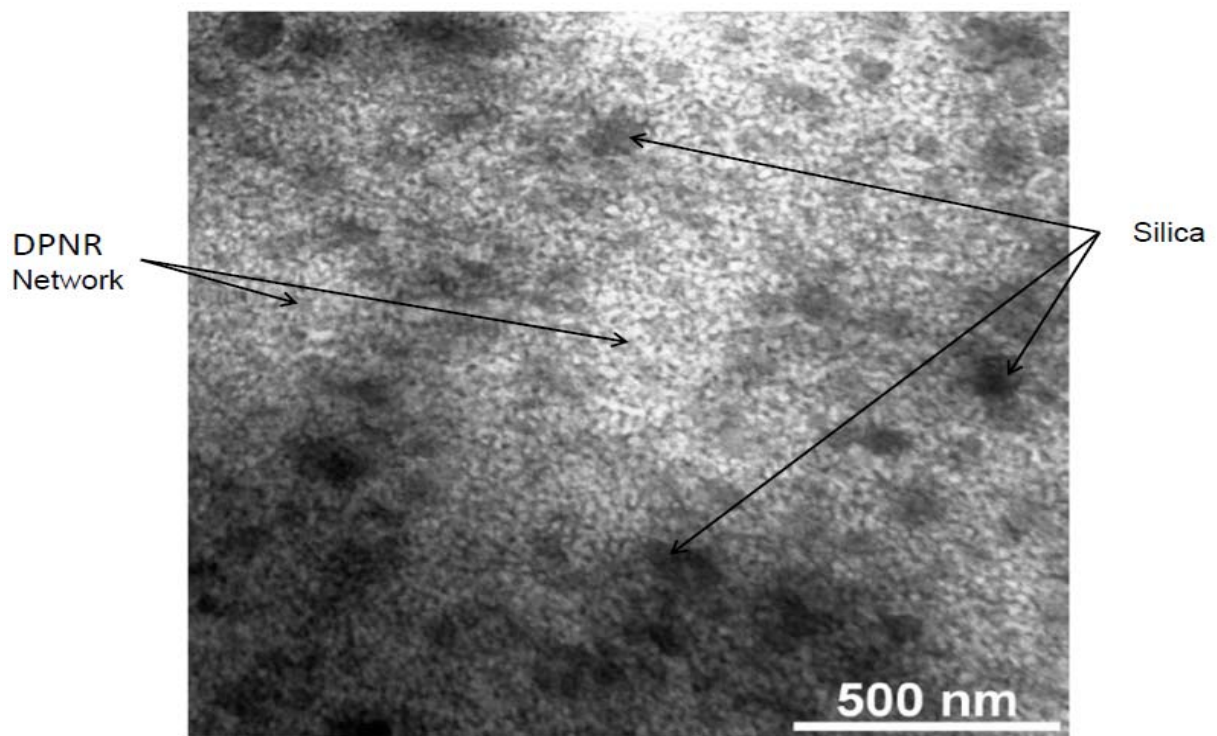


Figure 7: TEM Network Visualization of silica-filled DPNR vulcanizate with TESPT silane coupling agent.

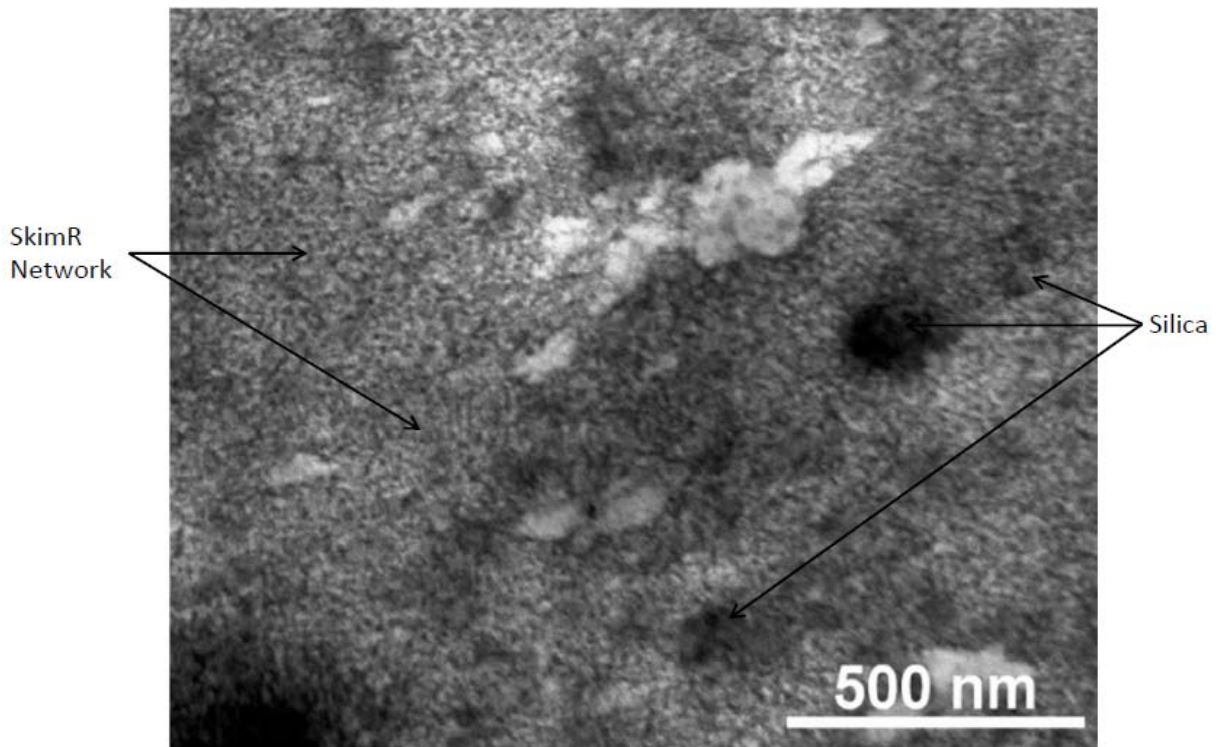


Figure 8: TEM Network Visualization of silica-filled skim rubber vulcanizate with TESPT silane coupling agent.

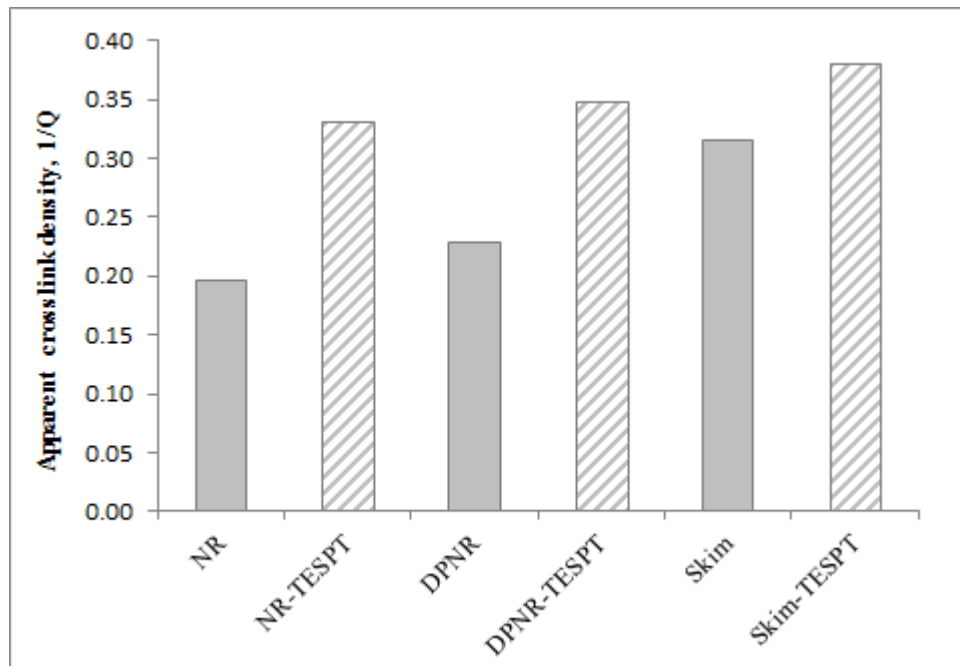


Figure 9: Apparent crosslink density of silica vulcanizates without silane and with TESPT silane coupling agent.

Conclusions

The rubber-to-filler interaction in silica vulcanizates in the absence of silane is a physical phenomenon. 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 and skim rubber-vulcanizates without silane than

in the NR-vulcanizate. The rubber-to-filler interaction of silica-filled natural rubber vulcanizates is greatly improved with the use of silane TESPT as coupling agent. 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 chemical BRC and a low Payne effect.

For NR and DPNR vulcanizates without silane, strong filler-filler interactions as observed from the higher Payne effect contribute to their physical BRC. In contrast, skim rubber vulcanizates exhibit lower Payne effects due to disruption of the silica-silica network by proteins. Even though proteins are capable to hydrophobize the silica surface and reduce the filler-filler interaction, they do not contribute to strong rubber-to-filler interactions, as the silica-protein interaction only leads to formation of physically bound rubber.

Acknowledgements

The authors would like to express appreciation to Dr. Robin T. Davies and Katherine M.E. Lawrence from the Tun Abdul Razak Research Centre (TARRC), who carried out the transmission electron microscopy work, as well as to Dr. Anna Kepas-Suwara from TARRC for help with sample preparation for the TEM Network visualization. The authors also would like to thank Noraziah M. Kassim from the Material Characterization Unit of the Malaysian Rubber Board (MRB) for the nitrogen content analysis. The financial support from MRB is greatly appreciated.

References

- [1] Meon W, Blume A, Luginsland H-D, Uhrlandt S. In: Rodgers B, editor. Rubber Compounding: Chemistry and Applications, New York: Marcel Dekker Inc., 2004. Chapter 7.
- [2] Noordermeer JW, Dierkes WK. In: White J, De SK, Naskar K, editor. Rubber Technologist's Handbook, Vol.2, Shawbury, UK: Smithers Rapra Technology, 2008; p. 59 – 96.
- [3] Payne AR, Whittaker RE, Rubber Chem. Technol. 1971; 44: 440-478.
- [4] Julve D, Menendez M, Perez J, Ramos J, Rubber Chem. Technol. 1996; 69:74-87.
- [5] Chapman AV, Natural rubber and NR-based polymers: renewable materials with unique properties, presented at 24th International H.F. Mark-Symposium, 'Advances in the Field of Elastomers & Thermoplastic Elastomers', Vienna, 15-16 November, 2007.
- [6] Cook S, Chapman AV, Tinker AJ, Oleksik L. Preferential location of silica filler in ENR/BR blends for tire tread applications, presented at Fall 172th ACS Rubber Division Meeting, Cleveland, OH, 16-18 October, 2007..
- [7] Ladouce-Stelandre L, Bomal Y, Flandin L, Labarre D, Rubber Chem. Technol. 2003; 76:145-159