J. Rubb. Res., **19(1)**, 28–42

Compatibilisation of Silica-filled Natural Rubber Compounds by Functionalised Low Molecular Weight Polymer

P. SARAMOLEE*, K. SAHAKARO*#, N. LOPATTANANON*,
W.K. DIERKES** AND J.W.M. NOORDERMEER**

In silica-filled natural rubber, it is essential to use coupling agents or compatibilisers to enhance filler-rubber interactions, reduce silica network formation and hence to obtain good reinforcement. This work investigates the effect of epoxidised low molecular weight natural rubber (ELMWNR) in silica-filled NR compounds on processing, mechanical, dynamic-mechanical and morphological properties. ELMWNRs with 12 and 28 mol% epoxide groups having a molecular weight in the range of 50,000-60,000 g/mol were added into the compounds as compatibilisers at varying loadings from 0-15 phr. The reference compound containing bis-(triethoxysilylpropyl) tetrasulfide (TESPT) as coupling agent was also prepared for comparison. The addition of 10 phr ELMWNR-28 in the silica-filled NR compounds not only decreases mixing torque, compound viscosity and Payne effect to the levels close to those of the compound with TESPT, but also increases bound rubber content and filler dispersion resulting in improvement of mechanical properties. However, the TESPT-silica system still provides better mechanical and dynamic mechanical properties compared to the alternative ELMWNR-silica systems. Overall, ELMWNR can be an alternative as natural-based compatibiliser with no ethanol emission like in the case with TESPT.

Keywords: Natural rubber; epoxidised rubber; silica; silane; compatibiliser

Silica is widely used as non-black reinforcing filler for rubber products, but mixing of the silica with non-polar rubbers is not an easy matter. The highly polar and hydrophilic surface of silica makes it difficult to disperse in non-polar rubbers like natural rubber, butadiene rubber and styrene-butadiene rubber which are mostly used in tyre compounds. Also the silica surface adsorbs curatives resulting in a delayed vulcanisation reaction and reduction of the crosslink density. High filler-filler interactions and poor filler-rubber interactions are the important issues that affect the processing, cure characteristic,

---

*Department of Rubber Technology and Polymer Science, Faculty of Science and Technology, Prince of Songkla University, Pattani 94000, Thailand.

**Department of Elastomer Technology and Engineering, Faculty of Engineering Technology, University of Twente, 7522AE Enschede, the Netherlands.

Corresponding author (e-mail: kannika.sah@psu.ac.th)

mechanical and dynamic properties of the silica-filled rubber compounds. In general, silane coupling agents are used to chemically bond the polymer to silica, thus improving filler dispersion and increasing the level of reinforcement. However, the use of silane bears some disadvantages such as high cost, toxicity, risk of precuring or scorch during the mixing stage and emission of ethanol during mixing[1]. There were new pathways developed to avoid or reduce the use of the silane coupling agent by compatibilisation with polar rubbers such as polychloroprene rubber (CR)[2], acrylonitrile butadiene rubber (NBR)[3,4], acrylonitrile styrene butadiene rubber (AN-SBR)[5], carboxylated nitrile rubber (XNBR)[6] and maleated natural rubber (MNR)[7]. These rubbers are used to improve the interfacial bonding between the silica and the polymers, which depends on types and content of the functional groups, molecular weight of the functional additives, the miscibility between the polymer and the compatibiliser, and the processing conditions[8].

Epoxidised natural rubber (ENR) can be easily prepared by reacting natural rubber (NR) with a peroxyacid. Due to the oxirane ring in the ENR structure, it can react with silica during the heating and mixing process[9,10,11]. Varkey *et al.*[12] indicated that a small proportion of ENR could be used as an interface modifier for NR-silica systems and as a reinforcement modifier for silica-filled nitrile rubber (NBR). Incorporation of an optimum concentration of about 15 wt% of ENR with 50 mol% epoxide on total rubber in a silica-filled NBR compound was found to improve bound rubber, mechanical and dynamic mechanical properties[13,14]. Kantala *et al.*[15] comparatively studied polar rubbers, CR and ENR as compatibilisers in silica-filled NR/NBR blends. They found that the addition of ENR gave higher compound viscosities and tensile modulus than the use of CR due to the better compatibility effect of ENR in the system. Moreover, ENR was reported to have the ability to increase the wet skid resistance of tyre treads made thereof[16,17].

Epoxidised low molecular weight natural rubber (ELMWNR) constitutes a new family of polymers, chemically modified NR. It is a highly viscous rubber with a lower molecular weight, compared to virgin NR. In the present work, ELMWNRs with different loading and content of epoxide groups are applied to improve the filler dispersion and filler-rubber interaction in silica-filled NR compounds. The ELMWNRs with the epoxide groups are expected not only to interact well with the silica but also to act as plasticiser. The properties of ELMWNR compatiblised silica-filled compounds and vulcanisates were investigated in comparison with a reference compound containing an optimal amount of TESPT.

EXPERIMENTAL

Materials

Natural rubber ribbed smoked sheet 3 (RSS3), locally produced in Pattani, Thailand, was used in this study. Epoxidised low molecular weight natural rubbers (ELMWNRs) having 12 and 28 mol% epoxide, denoted as ELMWNR-12 and ELMWNR-28 were in-house prepared and characterised as detailed in a previous report[18]. The compounding ingredients were highly dispersible silica (Zeosil® 1165MP, Solvay, France), bis-(triethoxysilyl) propyl tetrasulphide (TESPT) (Evonik, Germany), treated distillate aromatic extract (TDAE) oil (H&R, Germany), polymerised 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ), diphenylguanidine (DPG) and N-cyclohexyl-2-benzothiazole-sulphenamide (CBS) (all from Flexsys, Belgium). Zinc oxide (ZnO), stearic acid and sulphur were commercial grades for the rubber industry.

Compound Preparation

The formulations of silica-filled compounds are given in *Table 1*, and the mixing procedures are described in *Scheme 1*. The ELMWNR loading was varied from 0 to 15 phr and a compound with TESPT at 9.0 wt% relative to the silica was prepared for comparison purposes. The compounds were prepared by a two-step mixing procedure[19]: the masterbatches were first mixed in an internal mixer with a mixing chamber volume of 370 cm^3 (Brabender Plasticorder 350S) whereby the polymer and all chemicals except curatives were mixed at a mixer temperature setting, rotor speed and fill factor of 100ºC, 60 rpm and 70%, respectively. The batches were discharged at a total mixing time of 15 minutes. The second step was to prepare the final compounds by mixing the curatives with the masterbatches on a two-roll mill for 5 minutes.

Testing of Compound Properties

Mooney viscosities of the compounds (ML (1+4)100ºC) were determined by using a Mooney viscometer (MV2000 VS, Alpha Technologies Akron, OH) with a large rotor. The compounds were warmed for 1 min, prior to testing for 4 min at 100ºC, according to *ASTM D1646*.

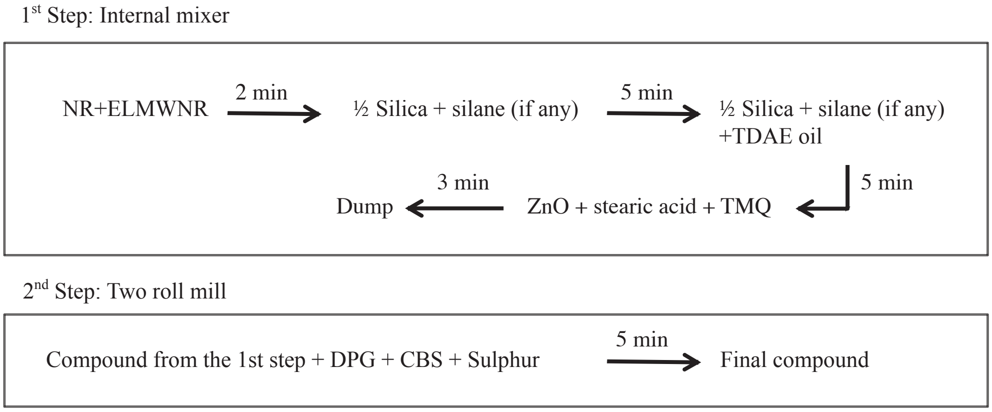
The Payne effect or filler-filler interaction of the uncured compounds was measured under shear deformation using a rubber process analyser (RPA2000, Alpha Technologies Akron, OH) which is a dynamic mechanical rheological tester. The strain was varied from 0.56 to 100% at 0.50 Hz and 100ºC.

Bound rubber content (R_B) was used to indicate the level of filler-rubber interaction which is a crucial parameter for reinforcement. The uncured compounds were cut into small pieces, then placed in a 300 mesh-steel cage and immersed in 25 mL of toluene at room temperature. After 72 h, the steel cage with the swollen sample was removed from the toluene,

TABLE 1. SILICA-FILLED COMPOUND FORMULATIONS

Ingredients	Amount [parts per 100 parts of rubber, phr]	
NR (RSS3)	100.0	100.0-85.0
ELMWNRs*	-	0-15.0
Silica (Zeosil 1165MP)	55.0	55.0
Silane (TESPT)**	4.4	-
Process oil (TDAE)	5.0	5.0
Zinc oxide	3.0	3.0
Stearic acid	1.0	1.0
TMQ	1.0	1.0
DPG***	1.1	1.1
CBS	1.2	1.2
Sulphur	1.5	1.5

* ELMWNRs with 12 and 28 mol% epoxide were used.
** Amount of TESPT (phr) = 0.00053 × Q × CTAB
*** Amount of DPG (phr) = 0.00012 × Q × CTAB
where Q is the silica content (phr) and CTAB is the specific surface area of the silica (m^2/g)[20].



Scheme 1. Mixing procedures applied for compound preparation.

dried at 105ºC for 24 h, and immersed again in toluene for 72 h either with or without an ammonia atmosphere. The toluene was renewed every 24 hours. Finally, the samples were taken out from the toluene, dried at 105ºC for 24 h and weighed. The total bound rubbers are separated into physical and chemical interactions, in which the chemically bound rubber content could be determined after the ammonia treatment, as the polar strength of the ammonium ion can cleave weak physical interactions between silica and rubber. The bound rubber content (R_B) was calculated according to the following equation[21]:

$$R_B = \frac{W_{fg} - W[m_f/(m_f + m_p)]}{W[m_p/(m_f + m_p)]} \times 100 \qquad \dots 1$$

Where W_{fg} is the weight of silica and gel (*i.e.* bound rubber), W is the weight of the rubber compound, and m_f and m_p are the weights of filler and polymer in the compound, respectively.

The cure characteristics were determined using the RPA2000 at 150ºC according to *ASTM D2084*. The samples were tested at a frequency of 0.833 Hz and 2.79% strain for 30 minutes.

Determination of Vulcanisate Properties

The test specimens were press-vulcanised in an electrically heated hydraulic press (Wickert laboratory press WLP1600) at 150ºC to their respective optimum cure times (t_{90}) as predetermined from the cure characteristics. Tensile properties (*i.e.* modulus, tensile strength and elongation at break) of the vulcanisates were measured with a Zwick tensile tester (model BZ 1.0/TH1S) at a crosshead speed of 500 mm/min using a dumbbell test specimen (die type C) according to *ASTM D 412*.

The loss tangent (tan δ) at 0ºC and 60ºC was characterised with a Metravib Viscoanalyzer VA2000, in tension mode with a temperature range from -90 to 80ºC at 0.01% strain, a frequency of 10 Hz and a heating rate of 2ºC/min.

Morphological features were analysed by using atomic force microscopy (AFM) at room temperature in the tapping mode. The samples were prepared by cutting with a 45º glass knife in cryogenic condition at approximately -100ºC in order to have an ultrasmooth surface before examining with

AFM (Nanosurf easyScan 2 AFM, Liestal, Switzerland) for surface topography and phase images.

RESULTS AND DISCUSSION

Properties of Unvulcanised Compounds

The processing behaviour of the silica-filled NR compounds can initially be determined by monitoring the mixing torques in the internal mixer which determines the mixing energy consumed by each compound. *Figure 1(a)* shows strong variations of the mixing torques of the compounds containing different compatibiliser systems with time. During the mastication step, starting torque for the NR is higher than for the mix of NR and ELMWNR, due to the plasticisation effect in the presence of small polymer molecules. After the mastication step, silica was added in two portions, and the mixing torque increased sharply when silica was added, as marked as positions A and B in the figure. The reference compound without any compatibiliser shows the highest mixing torque. The use of ELMWNRs clearly decreases the mixing torque.

In the second half of the silica incorporation, the mixing torques are separated into two groups in which the compounds with ELMWNR-28 and TESPT show very similar mixing torques on a lower range. The compound with ELMWNR-12, showed a higher torque in the second silica addition step, finally displayed more or less the same level of torque at the end of mixing compared to the one containing ELMWNR-28. The low molecular weight rubber molecules act as internal plasticisers in the rubber compounds and so improve the mobility of both rubber chains and filler. The presence of epoxide functional groups in ELMWNRs also introduces interactions with the silanol groups on the silica surface, leading to a decrease of filler-filler interactions and improved silica dispersion in the NR matrix. The decrease of silica agglomerates reduces the compound viscosity and thus the mixing torque. It is seen that the use of 10 phr ELMWNR with 28 mol% epoxide effectively decreases the mixing torque to a similar level as that of the compound with the TESPT silane coupling agent.

Figure 1(b) shows the Mooney viscosities of silica-filled NR compounds containing various amounts of ELMWNRs, compared to those of the reference compounds with TESPT and without any compatibiliser. TESPT is well known for its ability to enhance the bonding between the silica surface and rubber, and also to modify the silica surface for better compatibility with hydrocarbon rubbers leading to a reduction of compound viscosity and the enhancement of vulcanisate properties. The addition of ELMWNRs reduces Mooney viscosities of the silica-filled compounds. The use of 5 phr of ELMWNRs already reduces the Mooney viscosity substantially compared to the non-compatibilised system, and the Mooney viscosity is further decreased with increasing amount of ELMWNR. The use of a sufficient amount of ELMWNR-28, *i.e.* ≥ 7.5 phr in silica-filled compounds can decrease the Mooney viscosity to match the level of the compound with the optimal amount of TESPT. The reduction of compound viscosities can be described by three contributions: (1) The plasticising effect of the ELMWNRs as the incorporation of smaller polymer molecules increases the mobility of both rubber chains and filler (2) The interactions between epoxide groups and silanol groups on the silica surface via hydrogen bonds and/or chemical bonds formed after epoxide ring opening[22] and (3) The carbonyl groups at the chain ends[23] of the ELMWNRs also possibly interact with the silanol groups on the silica surface, resulting

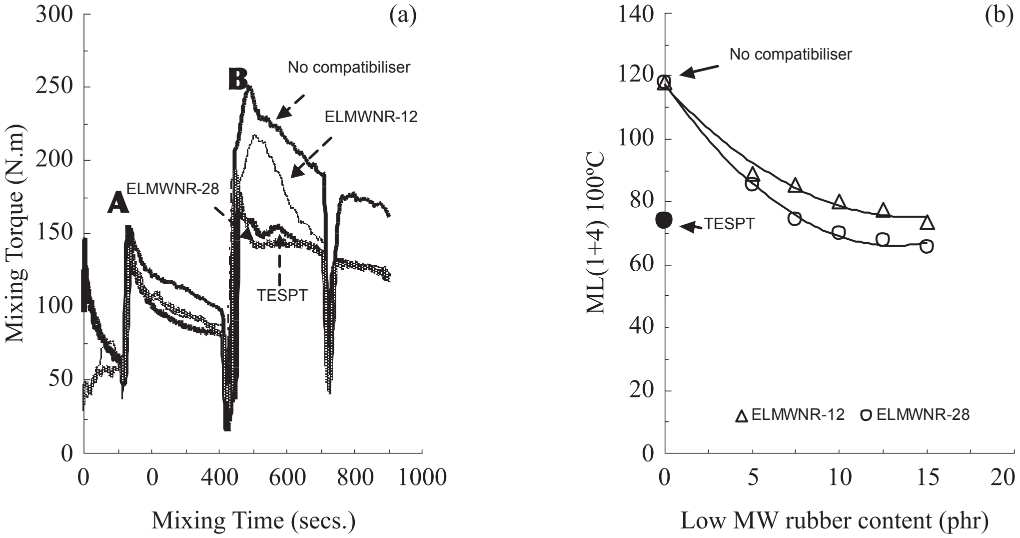


Figure 1. Typical mixing torque of silica-filled NR compounds containing 10 phr of ELMWNR (a) and Mooney viscosity at various amounts of ELMWNRs (b) compared to the compounds with and without TESPT.

in a better dispersion of silica in the NR matrix and preventing remaining filler-filler interactions[11].

In filled rubber compounds, the storage shear modulus (G') is dependent on the rubber network, the hydrodynamic effect of filler, the filler-rubber and filler-filler interactions. The first three contributions are strain independent, whereas the filler-filler interaction is strain dependent. At high strain, the breakdown of filler network causes a substantially decrease of G'. Therefore, differences between the low strain modulus (G' at 0.56 % strain) and high strain modulus (G' at 100 % strain), can be related to filler-filler interactions, the Payne effect[24]. A higher Payne effect implies higher filler-filler interaction. *Figure 2* shows the Payne effect of the silica-filled uncured compounds at various amounts of ELMWNRs. The Payne effect of the silica-filled compound without compatibiliser is the highest due to the strong filler-filler interaction caused by hydrogen bonds between the hydroxyl groups on the silica surface. The use of ELMWNR substantially decreases the Payne effect of the silica-filled NR compound compared to the one without any compatibiliser and the addition of 10-15 phr of ELMWNR-28 decreases the Payne effect to almost the same level as the reference compound with TESPT. This result indicates that the incorporation of ELMWNR weakens the filler-filler interactions, which can be attributed to the three contributions as explained above for the reduction in Mooney viscosity.

Figure 3 shows the bound rubber contents (BdR) of silica-filled NR compounds containing 10 phr of ELMWNRs compared to the compounds with and without TESPT. The compounds containing ELMWNR clearly show a higher BdR content compared to the non-compatibilised one, confirming the enhanced filler-rubber interactions by the epoxide groups. However, the compounds

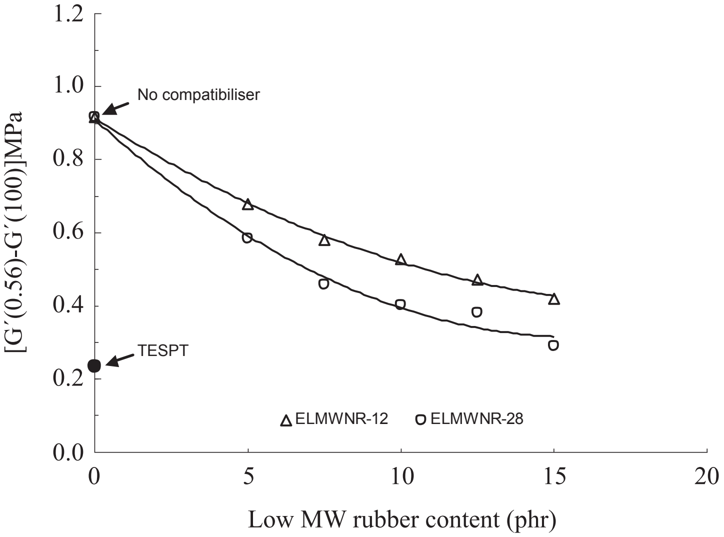


Figure 2. Payne effect of silica-filled NR compounds at various amounts of ELMWNRs compared to the reference compound with TESPT.

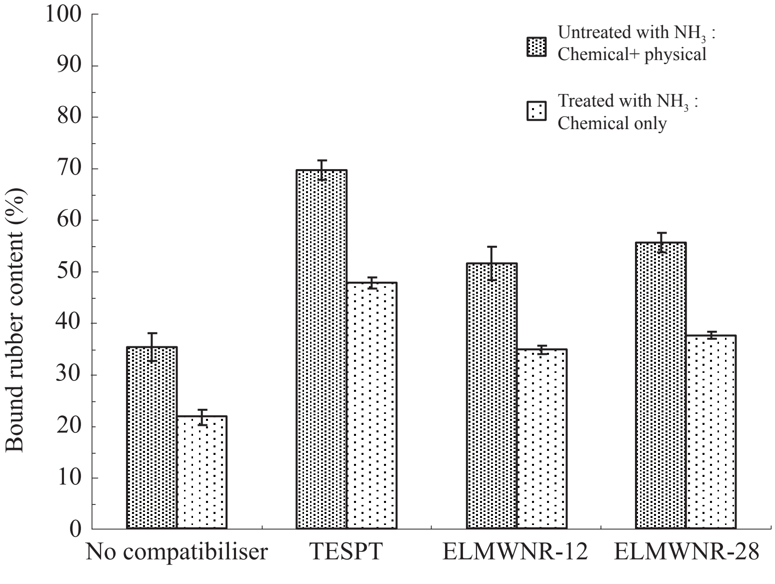


Figure 3. Bound rubber contents of silica-filled NR compounds containing 10 phr of ELMWNRs compared to the compounds with and without TESPT.

with ELMWNRs still show lower BdR contents compared to the use of TESPT. This lower bound rubber may be attributed to the lower molecular weight of the chemically bound ELMWNR versus the chemically bound NR *via* TESPT. The lubrication effect of ELMWNR causes an increase of chain mobility. The filler-rubber interactions in the ELMWNR-system involve hydrogen bonds between the epoxide groups and the silanol groups of the silica, and also a possible chemical bond in the presence of the ring-opened epoxide groups, whereas the silica-TESPT system has strong chemical bonds between silica and silane as well as some premature crosslinks[19]. The results in *Figure 3* demonstrate that as far as the chemical BdR is concerned, the effect of TESPT is better than for ELMWNR. The highest total and chemically bound rubber content of the silica-TESPT filled compound can also be affected by the tetrasulphide group of TESPT that can split under heat to react with the rubber chains to form covalent bonds, meant to happen later only during the vulcanisation process. Due to the high temperature during mixing, this can happen already in these NR compounds during the mixing step[25]. The presence of TESPT therefore enhances network formation and imparts a strong filler-rubber interaction.

The curing characteristics of the filled NR compounds in terms of scorch time (T_{c10}), 90% cure time (T_{90}) and torque difference are shown in *Figure 4*. The use of ELMWNRs delays both the scorch and optimum cure times, compared to the compound without any compatibiliser (*Figure 4(a)*). This can be attributed to the presence of polar functional groups on both the silica surface and the rubber chains which can adsorb or interact with the alkaline accelerators causing longer scorch and cure times. However, when the amount of ELMWNR-28 content is higher than 10 phr, the cure times tend to decrease, indicating that after having sufficient epoxide-silanol interactions and covering of the silanol groups by the ELMWNR molecules, the polar groups have no further interference with the curing reaction. On the contrary, the presence of smaller rubber molecules and overall less reactive double bond sites in the system decreases the cure times. The optimum cure time of the compound with TESPT is shorter than for the compounds without compatibiliser and with ELMWNRs, respectively. The shortest cure time of the silica-TESPT compound is due to the fact that the silica surface is more effectively covered by the silane, and so curative adsorption by the silanol groups is suppressed. The cure torque difference, *i.e*. the difference between maximum torque (M_H) and minimum torque (M_L), decreases with increasing ELMWNR loading, as shown in *Figure 4(b)*, due to the presence of shorter rubber chains in the originally high molecular weight matrix leading to an increase of loose or dangling chain ends, and thus lower stiffness.

Tensile and Dynamic Mechanical Properties of Rubber Vulcanisates

The effects of ELMWNR on tensile strength, reinforcement index (M300/M100) and elongation at break of the silica-filled NR vulcanisates is displayed in *Figure 5*. The reinforcement index is an indirect indication for filler-rubber interaction. It was calculated by dividing the value of modulus at 300% elongation (M300) by that of modulus at 100% elongation (M100). The higher reinforcement index implies a better filler-rubber interaction. The reinforcement index and tensile strength of the vulcanisate with TESPT are higher than those of the vulcanisates with ELMWNRs and without compatibiliser, respectively. The efficient use of TESPT enhances the reinforcement of the silica in NR through the silanisation reaction of the silanol groups of silica with the ethoxy

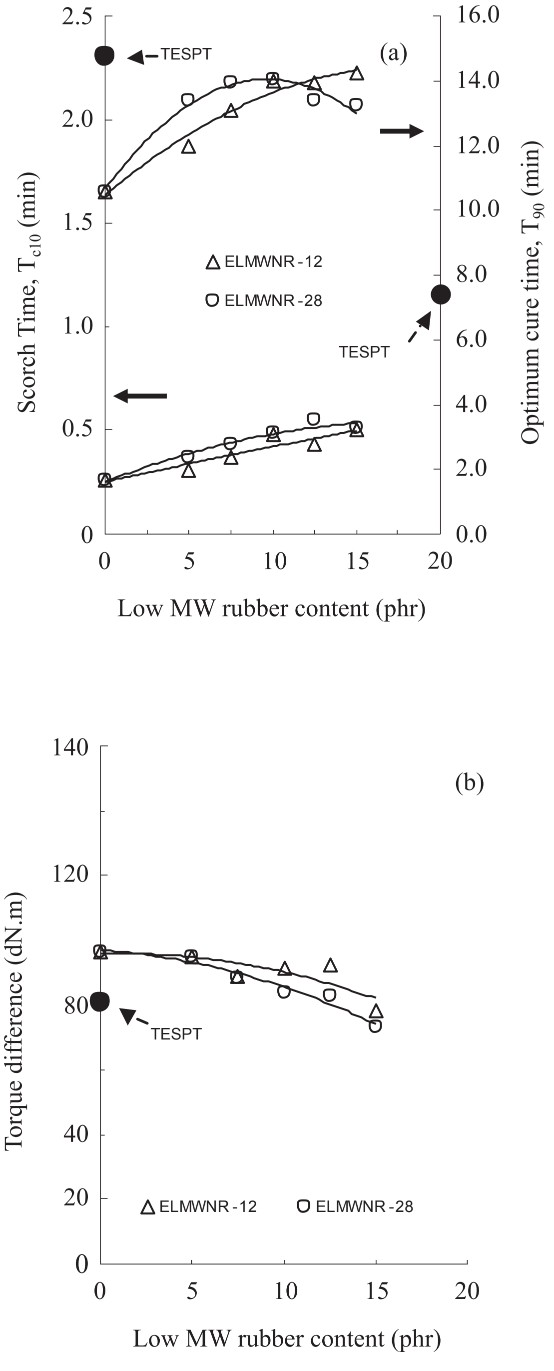


Figure 4. (a) Scorch and cure times and (b) Torque difference of silica-filled NR compounds at various amounts of ELMWNRs compared to the reference compound with TESPT.

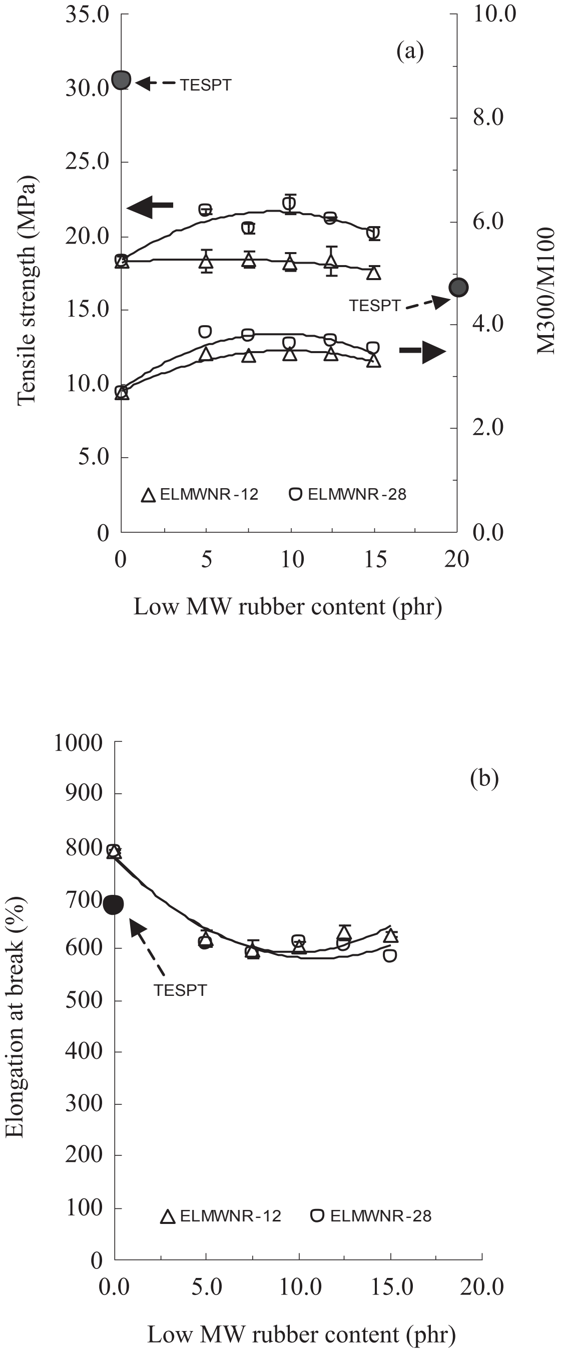


Figure 5. (a) Tensile strength, reinforcement index and (b) Elongation at break of silica-filled NR vulcanisates at various amounts of ELMWNRs compared to the reference compound with TESPT.

groups of the silane during mixing, and by the formation of crosslinks with the rubber molecule during vulcanisation. It has been proven that because of the availability of sulphur in the compound, TESPT can act as a sulphur donor and increase the crosslink density of the vulcanisates[26]. When compared to the non-compatibilised vulcanisate, the reinforcement index and tensile strength of the ones with ELMWNR-28 as compatibiliser are improved and an optimal tensile strength is observed when 10 phr of ELMWNR-28 was used. The increase of tensile stress is due to improved silica dispersion, decreasing filler-filler interaction and increasing filler-rubber interaction as previously discussed for the results observed for the uncured compounds (*Figures 1-3*). However, the use of ELMWNR-28 at high loadings (>15 phr) decreases the reinforcing index and tensile strength caused by incompatibility between the less polar NR matrix and more polar ELMWNR compatibiliser. The incorporation of ELMWNR-12 shows a slight improvement in reinforcement index, but has no effect on tensile strength. The increased interaction between the rubber and silica in the presence of ELMWNR decreases the elongation at break of the silica-filled vulcanisates as shown in *Figure 5(b)*.

Dynamic mechanical analysis is an important technique used to study the molecular motions in polymers. For tyre compound studies at laboratory scale, the loss tangent or tan δ values at 0ºC and 60ºC are commonly used as indications for wet grip and rolling resistance of tyre-tread compounds, respectively. *Figure 6* shows a comparison of the tan δ values at 0ºC and 60ºC of silica-filled vulcanisates containing 10 phr of ELMWNR, and the compounds with and without TESPT. The use of ELMWNR with 12 mol% epoxide in the silica-filled compound shows only a small effect on tan δ at 0ºC and 60ºC, but the addition of ELMWNR with 28 mol% epoxide increases tan δ significantly at both 60º and particularly 0ºC. The higher glass transition temperature (T_g) of ELMWNR-28 with a higher epoxide content has an effect on tan δ at 0ºC and the presence of shorter rubber chains or dangling chain ends in the original high molecular weight matrix enhances the chain mobility that has an effect on tan δ at 60ºC. The highest tan δ at 0ºC of the vulcanisate with ELMWNR-28 indicates a better wet grip of a tyre tread made thereof when compared to the other compounds. However, for low rolling resistance tyre tread applications, the vulcanisate needs to have a low tan δ at 60ºC.

The results show that the use of ELMWNR with high epoxide content as compatibiliser in a silica-filled compound gives a slightly higher tan δ at 60ºC compared to the TESPT-silica system and so a small negative effect on tyre rolling resistance. The TESPT-silica system that has the lowest tan δ at 60ºC implies the lowest rolling resistance among all the vulcanisates as a result of the increased filler-rubber interactions and enhanced rubber network formation by the sulphur in the TESPT. The dynamic mechanical properties of the silica-filled NR compounds in the presence of epoxidised rubber are in agreement with the work reported by Sengloyluan *et al.*[14] for high molecular weight epoxidised natural rubber.

Morphological Properties

Analysis of filler dispersion in highly filled-NR compounds is difficult. The present work employed the AFM tapping mode technique to characterise filler distribution and dispersion in the rubber matrix. The height (topography) and phase images were acquired for a scan size of 50 × 50 μm^2. *Figure 7* shows a comparison of AFM images of silica-filled NR vulcanisates without any compatibiliser against the use of 10 phr of ELMWNR-28 and TESPT as compatibilisers. The morphological

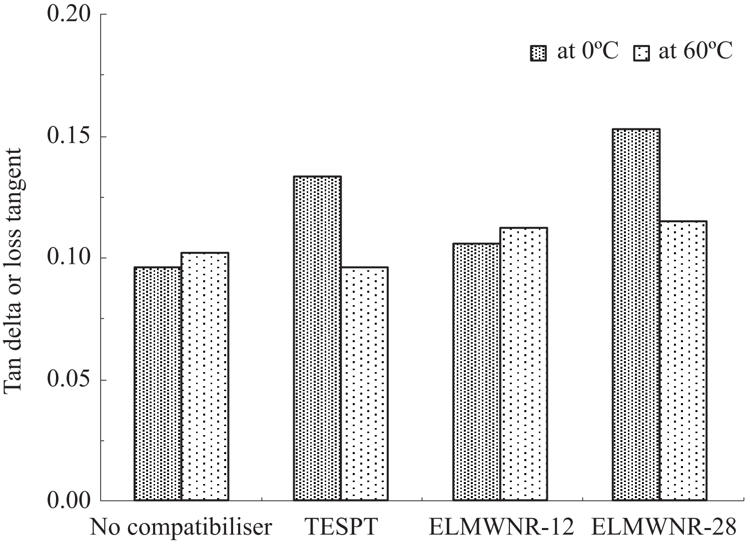
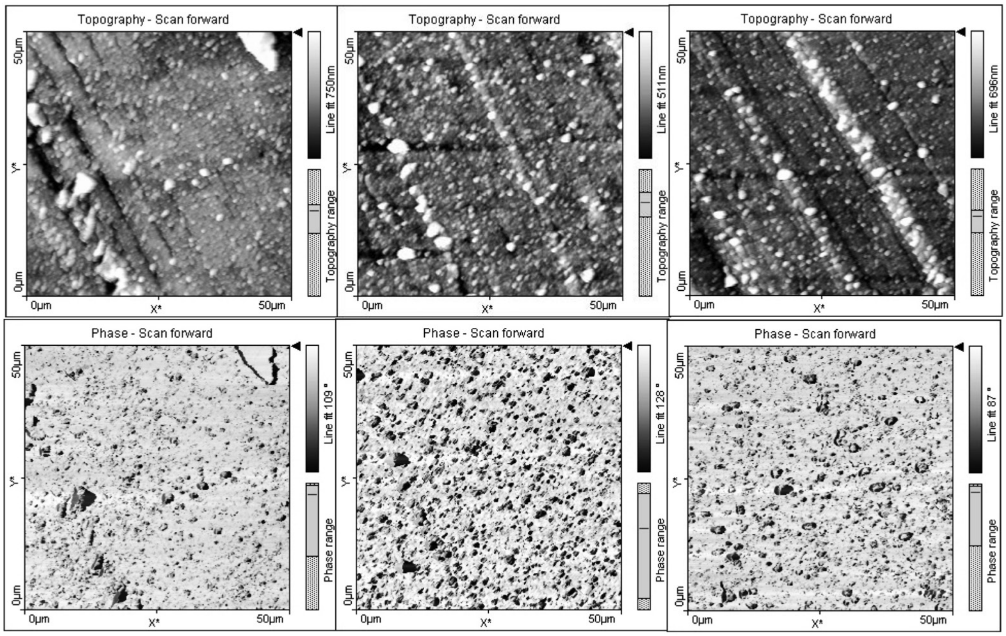


Figure 6. Tan δ at 0ºC and 60ºC of silica-filled NR vulcanisates containing 10 phr of ELMWNRs compared to the compounds with and without TESPT.



(a) (b) (c)

Figure 7. AFM topography (top) and phase images (bottom) of silica-filled NR vulcanisates (a) Without compatibiliser (b) With 10 phr ELMWNR-28 and (c) With TESPT .

results correlate well with the processing (*i.e*. Mooney viscosity), Payne effect and the mechanical properties of the compounds, as previously discussed. The presence of epoxide groups, which can be adsorbed or interact with the silanol groups on the silica surface, leads to a reduction in filler-filler interaction and a better silica dispersion/distribution in the rubber matrix. The silica-filled NR compound without compatibiliser in *Figure 7(a)* shows bigger clusters of silica aggregates or agglomerates, *i.e*. poorer filler dispersion and distribution than compounds with compatibilisers. The use of TESPT results in the most uniform silica dispersion and a smoother surface than the compounds with ELMWNR-28 and without compatibiliser, respectively. The phase images of the filled-NR without compatibiliser: *Figures 7(a)* and with ELMWNR as compatibiliser: *Figure 7(b)*, look different. In the presence of ELMWNR, the surface is coarser due to the effect of the polymer blend, but silica is still uniformly dispersed and distributed in the material.

CONCLUSION

Epoxide groups in ELMWNRs play a major role in the silica-filled NR compounds and affect both processing and vulcanisate properties, due to epoxide-silica interactions and their plasticising effect. The addition of ELMWNRs into the silica-filled NR compounds decreases mixing torque, Mooney viscosity and Payne effect, and increases epoxide-silica interactions as evidenced by the increase of bound rubber content and enhancement of filler dispersion as well as mechanical properties. By applying ELMWNRs as compatibiliser, the best mechanical properties of the silica-filled NR vulcanisates are obtained when 10 phr of ELMWNR-28 is used. For application on tyre tread compounds, the presence of ELMWNRs as compatibilisers positively influences wet grip, but slightly affects tyre rolling resistance negatively, as indicated by a much higher tan δ at a temperature of 0 and somewhat higher at 60ºC, respectively.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support from Thailand Research Fund through the Royal Golden Jubilee PhD. Program (Grant No. PHD/0268/2552) and the Graduate School of Prince of Songkla University. Also, the hospitality rendered by the Elastomer Technology and Engineering Department of the University of Twente, Enschede, the Netherlands for several experiments is highly appreciated.

Date of receipt: May 2015
Date of acceptance: January 2016

REFERENCES

1. WOLFF, S. (1996) Chemical Aspects of Rubber Reinforcement by Fillers. *Rubber Chem. Technol*., **69(3)**, 325–346.

2. CHOI, S.S. (2002) Improvement of Properties of Silica-filled Natural Rubber Using Polychloroprene Compound. *J. Appl. Polym. Sci*., **83(12)**, 2609–2616.

3. CHOI, S.S. (2001) Improvement of Properties of Silica-filled Styrene–Butadiene Rubber Compounds Using Acrylonitrile–Butadiene Rubber. *J. Appl. Polym. Sci*., **79(6)**, 1127–1133.

4. YAN, H., SUN, K., ZHANG, Y. AND ZHANG, Y. (2005) Effect of Nitrile Rubber on Properties of Silica-filled Natural Rubber Compounds. *Polym. Test*., **24(1)**, 32–38.

5. SEO, B., KIM, H., PAIK, H.J., KWAG, G.H. AND KIM, W. (2013) Characterization of

AN-SBR/silica Compound with Acrylonitrile as A Polar Group in SBR. *Macromol. Res*., **21(7)**, 738–746.

6. BANDYOPADHYAY, S., DE, P.P., TRIPATHY, D.K. AND DE, S.K. (1996) Interaction between Carboxylated Nitrile Rubber and Precipitated Silica: Role of (3-Aminopropyl) Triethoxysilane. *Rubber Chem. Technol*., **69(4)**, 637–647.
7. SAHAKARO, K. AND BERAHENG, S. (2008) Reinforcement of Maleated Natural Rubber by Precipitated Silica. *J. Appl. Polym. Sci*., **109(6)**, 3839–3848.
8. CHRISSOPOULOU, K. AND ANASTASIADIS, S.H. (2011) Polyolefin/layered Silicate Nanocomposites with Functional Compatibilizers. *Eur. Polym. J*., **47(4)**, 600–613.
9. MANNA, A.K., DE, P.P., TRIPATHY, D.K., DE, S.K. AND PEIFFER, D.G. (1999) Bonding between Precipitated Silica and Epoxidized Natural Rubber in the Presence of Silane Coupling Agent. *J. Appl. Polym. Sci*., **74(2)**, 389–398.
10. CATALDO, F. (2002) Preparation of Silica-based Rubber Compounds without the Use of a Silane Coupling Agent through the Use of Epoxidized Natural Rubber. *Macromol. Mat. Eng*., **287(5)**, 348–352.
11. XU, H., LIU, J., FANG, L. AND WU, C. (2007) In Situ Grafting Onto Silica Surface With Epoxidized Natural Rubber Via Solid State Method. *J. Macromol. Sci. Part B Physics*., **46(4)**, 693–703.
12. VARKEY, J.K., SUMANNA, J., THOMAS, K.T. AND MATHEW, N.M. (1998) Epoxidised Natural Rubber − An Interface Modifier for Natural Rubber-silica Composites. In: *Proceedings of the International Rubber Conference (IRC)*, Chennai, India. December 7-9, 1998.
13. GEORGE, K.M., VARKEY, J.K., THOMAS, K.T. AND MATHEW, N.M. (2002) Epoxidized Natural Rubber as a Reinforcement Modifier for Silica-filled Nitrile Rubber. *J. Appl. Polym. Sci*., **85(2)**, 292–306.
14. SENGLOYLUAN, K., SAHAKARO, K., DIERKES, W.K. AND NOORDERMEER, J.W.M. (2014) Silica-reinforced Tire Tread Compounds Compatibilized by Using Epoxidized Natural Rubber. *Eur. Polym. J*., **51(Feb 28)**, 69–79.
15. KANTALA, C., WIMONMALA, E., SIRISINHA, C. AND SOMBATSOMPOP, N. (2009) Reinforcement of Compatibilized NR/NBR Blends by Fly Ash Particles and Precipitated Silica. *Polym. Adv. Technol*., **20(5)**, 448–458.
16. BAKER, C.S.L., GELLING, I.R. AND NEWELL, R. (1985) Epoxidized Natural Rubber. *Rubber Chem. Technol*., **58(1)**, 67–85.
17. CHAPMAN, A.V. (2007) Natural rubber and NR-based polymers: renewable materials with unique properties. In: *The 24th International H.F. Mark-Symposium, Advances in the Field of Elastomers & Thermoplastic Elastomers*, Vienna, Austria. November 15-16, 2007.
18. SARAMOLEE, P., SAHAKARO, K., LOPATTANANON, N., DIERKES, W.K. AND NOORDERMEER, J.W.M. (2014) Comparative Properties of Silica and Carbon Black-reinforced Natural Rubber in the Presence of Epoxidized Low Molecular Weight Polymer. *Rubber Chem. Technol*., **87(2)**, 320–339.
19. KAEWSAKUL, W., SAHAKARO, K., DIERKES, W.K. AND NOORDERMEER, J.W.M. (2012) Optimization of Mixing Conditions for Silica-reinforced Natural Rubber Tire Tread Compounds. *Rubber Chem. Technol*., **85(2)**, 277–294.
20. GUY, L., DAUDEY, S., COCHET, P. AND BOMAL, Y. (2009) New Insights in the Dynamic Properties of Precipitated Silica Filled Rubber Using a New High Surface

Silica. *KGK Kautsch. Gummi Kunstst*., **62(7-8)**, 383–391.

21. WOLFF, S., WANG, M.J. AND TAN, E.H. (1993) Filler-elastomer interactions. Part VII. Study on Bound Rubber. *Rubber Chem. Technol*., **66(2)**, 163–177.

22. ROCHA, T.L.A.C., JACOBI, M.M., SAMIOS, D. AND SCHUSTER, R.H. (2006) Evaluation of the Influence of the Polymer-filler Interaction on Compounds Based on Epoxidized Elastomeric Matrix and Precipitated Silica. *Polímeros*., **16(2)**, 111–115.

23. PHINYOCHEEP, P., PHETPHAISIT, C.W., DEROUET, D., CAMPISTRON, I. AND BROSSE, J.C. (2005) Chemical Degradation of Epoxidized Natural Rubber Using Periodic Acid: Preparation of Epoxidized Liquid Natural Rubber. *J. Appl. Polym. Sci*., **95(1)**, 6–15.

24. PAYNE, A.R. AND WHITTAKER, R.E. (1971) Low Strain Dynamic Properties of Filled Rubbers. *Rubber Chem. Technol*., **44(2)**, 440–478.

25. KAEWSAKUL, W., SAHAKARO, K., DIERKES, W.K. AND NOORDERMEER, J.W.M. (2013) Optimization of Rubber Formulation for Silica-reinforced Natural Rubber Compounds. *Rubber Chem. Technol*., **86(2)**, 313–329.

26. LUGINSLAND, H.D. (2000) Reactivity of the Sulfur Chains of the Tetra Sulfane Silane Si69 and the Disulfane Silane TESPD. *Kautsch. Gummi Kunstst*., **53(1)**, 10–19.