Reinforcement of Maleated Natural Rubber by Precipitated Silica

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ABSTRACT: Graft copolymers of maleic anhydride and natural rubber or so-called maleated natural rubbers (MNRs) were prepared in a molten state with varying maleic anhydride contents from 4 to 10 phr. In this work, the filler–filler and filler–rubber interactions of the MNR and precipitated silica were investigated. The MNR compounds containing 40 phr of silica both with and without 9 wt % of silane coupling agent were prepared. By increasing the maleic anhydride contents, the Mooney viscosity and cure times were increased, but the torque differences and cure rate indices were decreased. Bound rubber was increased with increasing maleic anhydride content, indicating an increase of filler–rubber interaction. In case of the compounds without silane, the MNR with 6 phr of maleic anhydride showed the lowest filler–filler interaction as indicated by a decrease of storage modulus upon an increase of strain in the filled compound i.e., Payne effect. This MNR compound also yielded the optimum mechanical properties. It has been demonstrated that a use of MNR with appropriate maleic anhydride content can reduce filler–filler interaction dramatically and hence improve a silica dispersion, as confirmed by SEM micrographs, resulting in an enhancement of the mechanical and dynamical properties. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3839–3848, 2008

Key words: rubber; silica; reinforcement; fillers; maleic anhydride

INTRODUCTION

Rubber reinforcement can be achieved either by a use of conventional active fillers, i.e., carbon black and silica, or an introduction of nano-fillers such as nano-sized silica and organoclay.[1–6] Carbon black is the oldest and most widely used filler in rubber industry[7] whereas silica is previously mainly used for colored articles. The large-scale replacement of carbon black by silica in tire compounds: the ''Green Tire Technology,'' first invented by Michelin,[8] to reduce rolling resistance and hence fuel consumption, boosts the silica consumption and leads to a significant development in silica/rubber technology. Incorporation of silica to rubber is considered more difficult than the carbon black due to its polar surface resulting in a strong filler–filler interaction and thus filler aggregates.[2] Silica is less compatible with rubbers and more difficult to disperse. In addition, silica can reduce the effectiveness of some ingredients of the vulcanization system. The addition of filler to rubber compounds has a strong impact on the static and dynamic behaviors of rubber.[9,10] The dynamic modulus of filled samples attributes to both the strain-independent part contributed by the polymer network, hydrodynamic effect, and in-rubber structure, i.e., filler–rubber interaction, and a strain-dependent part contributed by the filler–filler interaction. The stress softening at small deformations, well known as Payne effect, is attributed to the breakdown of the filler–filler network.[9]

Utilization of silica generally requires coupling agents especially sulfur functional organosilanes to make the surface more hydrophobic and therefore more compatible with rubber. This results in the reduction of filler–filler interaction and a lower Payne effect.[9–12] The silica/silane technology is known but considered to be expensive relative to carbon black-filled systems.[2,13] Enhancement of silica–polymer interaction can also be obtained through some functional groups such as maleic anhydride (MA). Bikiaris et al.[14] utilized PP-*g*-MA to compatibilize between polypropylene and nano-sized silica. It has been demonstrated that a use of PP-*g*-MA results in a reduction of silica agglomerates and hence finer dispersion. This has been attributed to a reaction between the hydroxyl groups on silica surface and maleic anhydride groups of the modified polymer. Interaction between hydroxyl groups of the paper sludge and maleic anhydride groups of the maleated natural rubber has also been proposed.[15] Since silica has been extensively used in a

production of rubber articles, in this work, enhancement of silica-rubber compatibilization by a use of maleic anhydride grafted natural rubber called maleated natural rubber (MNR) was studied. The silica filled MNRs were investigated in comparison with the normal natural rubber, both with and without silane coupling agent.

EXPERIMENTAL

Materials

Air-dried sheet (ADS) typed NR produced by Local Farmer Cooperation and maleic anhydride (MA) manufactured by Riedel-deHaen (Germany) were used to prepare the maleate natural rubber. The compound ingredients were zinc oxide (Global Chemical, Thailand), stearic acid (Imperial Chemical, Thailand), Wingstay L (Eliokem, USA), N-tert-butyl-2-benzothiazyl sulfenamide or TBBS (Flexys, USA), sulfur (Siam Chemical, Thailand), bis(3-triethoxysilylpropyl) tetrasulfide under the trade name of Couplink 89 (Behn Meyer, Germany), and silica Ultrasil VN3 (Degussa, Germany). All ingredients were used as received.

Preparation and characterization of maleated natural rubber

The MNRs were prepared by melt mixing of NR with maleic anhydride (MA) in the Brabender Plasticorder at 145°C for 10 min with a rotor speed of 60 rpm under normal atmosphere. The MA contents were varied at 0, 2, 4, 6, 8, and 10 phr. The MNRs were purified by reprecipitation technique only for a purpose of characterization by FTIR and titration techniques. This was done by dissolving the MNR in toluene at room temperature for 24 h and then at 60°C for 2 h, filtering out the gel part, precipitating the soluble part in acetone, and finally drying in a vacuum oven at 40°C for 24 h. The gel part was also dried at 40°C for 24 h before weighing to calculate a gel content. The purified MNRs were characterized for their infrared spectra using FTIR-1600 (Perkin–Elmer) over the wavenumber of 4000–400 cm^{-1}. The rubber samples were prepared by dissolving in toluene, casting on the KBR disk and finally evaporating the solvent out in a hot air oven at 60°C for 30 min prior to recording the IR spectra. A grafted MA content was determined by the titration technique following the method reported by Nakason et al.[16] The grafted MA content was calculated based on a concentration of carboxylic acid groups derived from the anhydride functions which was determined by titration with 0.025N KOH in methanol/benzyl alcohol 1/9 (v/v) using 1% phenolphthalein in methanol

TABLE I
Compound Formulation

Ingredient	Quantity (phr)
Rubber (NR or MNR)	100
Stearic acid	0.5
ZnO	6
Wingstay L	1
TBBS	2.5
Silica VN3	40
Silane[a]	9 wt % of silica
Sulphur	1.5

[a] Silane was added into some compounds only.

as an indicator.[16] The remaining MNRs were used for compounding as neat.

Preparation of rubber compounds and Mooney viscosity measurement

All compounding ingredients were mixed on a 6″ × 14″ two roll mill using the formulation given in Table I. The rubber was first masticated, then stearic acid, ZnO, Wingstay L, TBBS, silica plus silane coupling agent, and sulfur were added consecutively. Total mixing time was about 15 min.

The compounds were tested for their Mooney viscosity at 100°C using large rotor according to ASTM D 1646. The value is reported as ML1 + 4(100°C) after the specimen was preheated for 1 min and hence tested for 4 min.

Characterization of filler–filler and filler–rubber interactions

Measurement of bound rubber

Bound rubber content indicates filler–rubber interaction in the rubber compound. In this study, the method reported by Wolff et al.[17] was employed. The compounds were left at room temperature for 1 week before extraction in toluene. The 0.2 g of compound was cut into small pieces and placed into a cage of known weight. The cage was immersed in 25 mL of toluene for 7 days at room temperature in which the solvent was renewed after 3 days. After that the rubber and cage were dried for 1 day in air at room temperature and then at 105°C in an oven for 24 h. The bound rubber was calculated according to the following equation.[17]

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

where W_{fg} is the weight of silica and gel, W is the weight of the specimen, and m_f and m_p are the weights of filler and polymer in the compound, respectively.

Determination of filler–filler interactions

Storage shear modulus (G') and complex modulus (G^*) of uncured rubber compounds were measured under shear deformation using the Moving Die Processability Tester or MDPt (TechPro, USA). A strain sweep test was set at 1 Hz in a range of 1–30% strain at 100°C. All specimens were preconditioned at 100°C, frequency 0.5 Hz and strain 1% for 1 min prior to starting the test.

Vulcanization and measurement of tensile properties

The compounds were tested for their cure characteristics at 160°C using Oscillating Disk Rheometer according to ASTM D 2084 and later press vulcanized at the same temperature to their 90% cure times (T_{c90}). The vulcanized sheet having a thickness of about 2 mm was die-cut to a dumbbell shaped specimen and tested at a crosshead speed of 500 mm/min according to ASTM D 412 using Hounsfield Tensile Tester. The values of tensile properties were an average of five specimens.

Determination of dynamic mechanical properties

The vulcanizates cured to their T_{c90} were tested for their dynamic mechanical properties under frequency sweep test using the Moving Die Processability Tester or MDPt (TechPro, USA). The frequencies were varied in a range of 0.1–20 Hz whereas the strain and temperature were fixed at 7% (0.5° arc) and 60°C, respectively. All specimens were preconditioned at 60°C, frequency 0.1 Hz and strain 2.8% (0.2° arc) for 1 min prior to starting the test.

Morphological characterization by scanning electron microscopy

The vulcanized sheet was immersed in liquid nitrogen for 10 min and then cryogenically fractured to
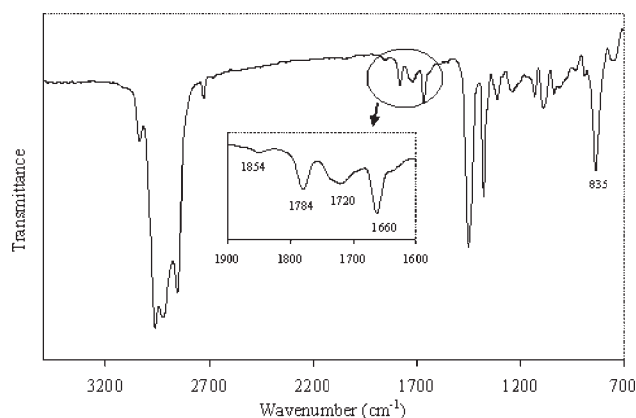
Figure 1 FTIR spectrum of maleated natural rubber.
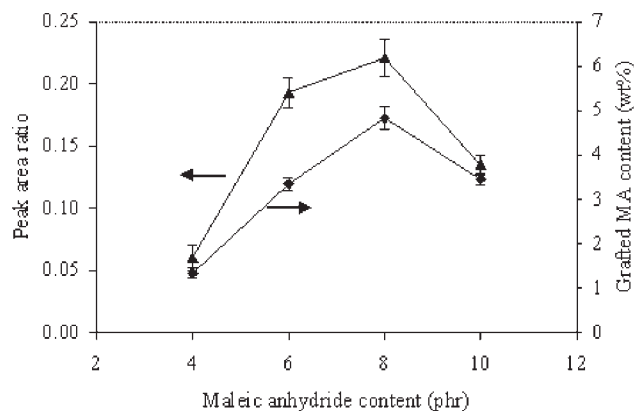
Figure 2 Peak area ratio and grafted maleic anhydride content of MNRs with varying maleic anhydride contents.

open a new surface. The surface was gold coated and SEM micrographs were taken by using JEOL SEM 5200 operating at an accelerating voltage of 20 kV. The magnification of each sample was at 2000×.

RESULTS AND DISCUSSION

Maleated natural rubber

FTIR spectra of the purified MNRs confirmed a presence of succinic anhydride groups grafted onto natural rubber molecules. The FTIR spectrum of the MNR prepared using 8 phr of MA is shown in Figure 1 as an example.

The cyclic anhydride shows the absorption peaks at wavenumbers of 1854 and 1784 cm^{-1} whereas the carbonyl functional group of opened ring is at 1720 cm^{-1}. To take an account of all grafted succinic anhydride groups presented in different forms, the peak area ratio was calculated in this study instead of the peak height ratio. The calculation based on the integrated absorption band area ratio was adapted from the method reported by Grigoryeva and Karger-Kocsis[18] for the EPDM-g-MA The peak area ratios of the succinic anhydride function groups integrated in the range of 1810–1690 cm^{-1} to the
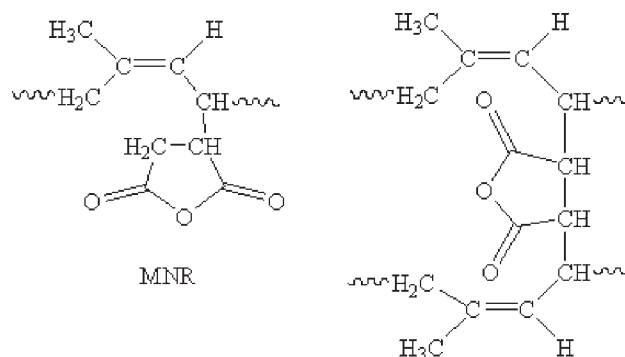
Figure 3 A formation of maleate crosslink in the MNR.
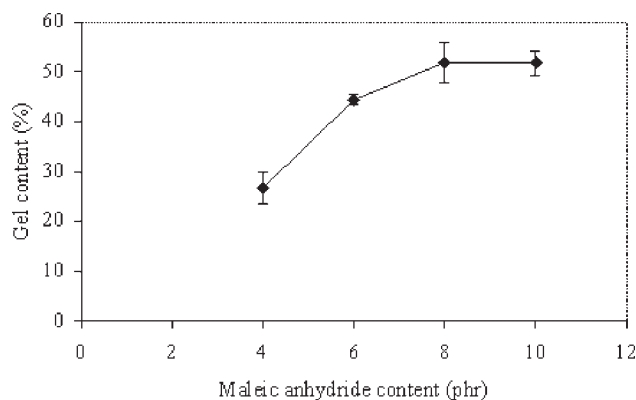
Figure 4 Gel content of the MNRs with varying maleic anhydride contents.
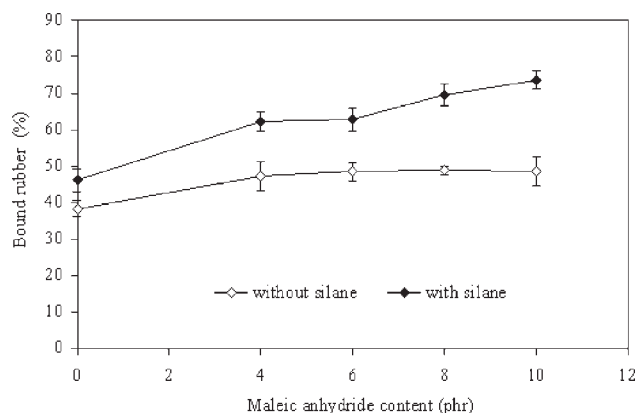
Figure 5 Bound rubber of MNR compounds at various maleic anhydride contents.

characteristic peak of NR at 835 cm^{-1} integrated in the range of 877–780 cm^{-1} are plotted in Figure 2. The very weak absorption band at 1854 cm^{-1} attributed to asymmetric C=O stretching of succinic anhydride ring was negligible and omitted in this calculation. The amount of maleic anhydride grafted onto NR molecules analyzed by titration technique was also plotted in the same figure.

The peak area ratios and grafted MA contents increased accordingly with increasing maleic anhydride contents and reached a maximum at a MA content of 8 phr. The increase of grafted MA content on NR molecules with increasing MA concentrations added into the reaction mixture was also observed for the MNRs synthesized in a solution state.[16] For their MNRs prepared in a toluene solution, the grafted MA content reached a maximum when 10 phr of MA was used. A further increase of MA concentration also resulted in a decrease of grafted MA content. Nakason et al.[16] stated that at higher monomer concentrations, higher side reactions such as chain transfer to monomer may compete with the grafting reaction and hence reduce the grafting efficiency. In our case, the MNR was prepared in a molten state without a use of initiator and the grafted MA content reached a maximum when MA = 8 phr was employed. In this molten state, rubber molecules are more in contact compared with the solution

state. A further increase of MA resulted in a decrease of grafting level which could be partly attributed to a formation of maleate crosslink[19] under a shearing action at high temperature, as shown in Figure 3, and partly due to a lower mixing efficiency. The increase of gel contents with increasing concentrations of MA is plotted in Figure 4. It shows that the gel content increased significantly up to the MA content of 8 phr where after it leveled off. In this study, in addition to the gel formation and other possible side reactions as suggested by Nakason et al.,[16] we found that the addition of 10 phr of MA caused a slip between rubber and mixing chamber and thus reduced mixing efficiency.
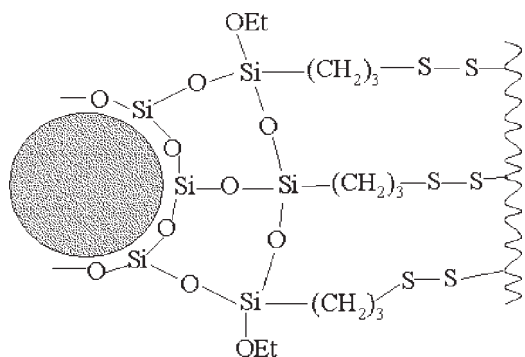
Filler–rubber and filler–filler interactions of unvulcanized compounds

This work aims to increase silica–rubber interaction as well as to reduce silica-silica interaction through the maleic anhydride functional groups on the modified NR. The bound rubber content of compounds both with and without silane after extraction with toluene is shown in Figure 5.

It is clearly seen in Figure 5 that, in the case of compounds without silane, the bound rubber content of the MNRs is higher than that of NR (i.e., at the maleic anhydride content = 0 phr) indicating an
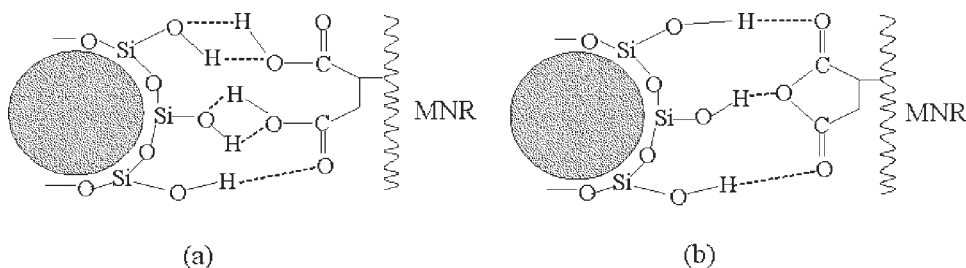
Figure 6 Postulated interactions between the maleic anhydride groups of the MNR and the hydroxyl group on silica surface.

**Figure 7** Reaction of silica with silane and unsaturated rubber.

increase of filler–rubber interaction, but an increase of maleic anhydride content results in only a slight increase of bound rubber. In addition, all compounds without silane coupling agent depict significant lower bound rubber compared with those containing silane.

The succinic anhydride groups grafted onto natural rubber molecules of the MNRs enhance a polarity of rubber and an interaction between the succinic anhydride groups and the hydroxyl groups on silica surface. Such interactions between the succinic anhydride group of the MNR and the surface hydroxyl group of the silica particle are postulated in Figure 6. The succinic anhydride groups could be in the form of either opened ring (a) or cyclic (b) structure. Similar interactions between the hydroxyl and maleic anhydride groups have previously proposed such as in the cases of PP-g-MA versus nano-silica[14] and MNR versus paper sludge filler.[15]

The polar interactions due to hydrogen bonds between the hydroxyl groups of the silica surface and the carboxyl group of the grafted NR or the hydroxyl group of the succinic acid improve the compatibility between rubber and silica, reduce the filler aggregates and as a consequence increase the degree of dispersion in the rubber compounds. In the case of silane treated compounds, in addition to such interactions postulated in Figure 6, the silica-rubber compatibility is promoted through the reactions of sulfur atom in silane and rubber molecule and between the ethoxy group of silane and the hydroxyl group of the silica, as shown in Figure 7.

Considering the storage modulus (G') of the uncured compounds formulated both with and without silane coupling agent under varying strain deformation as shown in Figures 8 and 9, the filler–filler interaction as indicated by a decrease of storage modulus upon an increase of strain, i.e., Payne effect, is significantly reduced by using the MNRs in stead of NR. The lowest Payne effect is observed for the MNR produced by using 6 phr of MA, and the storage moduli of the MNRs with MA contents = 6 and 8 phr are similar. A further increase of maleic anhydride content results in an increase of strain-dependent storage modulus. This could be attributed to a lower grafted MA content as seen in Figure 2, and hence reduce the interaction between the succinic anhydride groups and the hydroxyl groups of silica. In the case of MNR with MA = 8 phr, even though it shows the higher grafting degree than the MNR with MA = 6 phr, because of its higher gel content due to a formation of maleate network[18] so that it may have less reactive maleic ahnydride groups to interact with the hydroxyl groups of the silica surface. In the case of silane containing compounds, a dramatically decrease of filler–filler interaction is demonstrated resulting from a combination
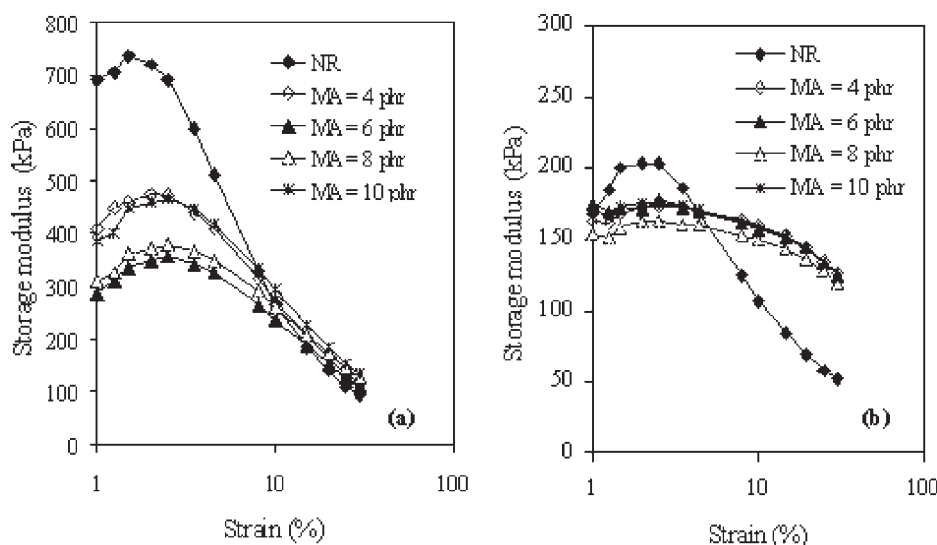
Figure 8 Strain amplitude dependence of storage modulus of MNR compounds at various maleic anhydride contents (1st sweep): (a) without silane and (b) with silane.
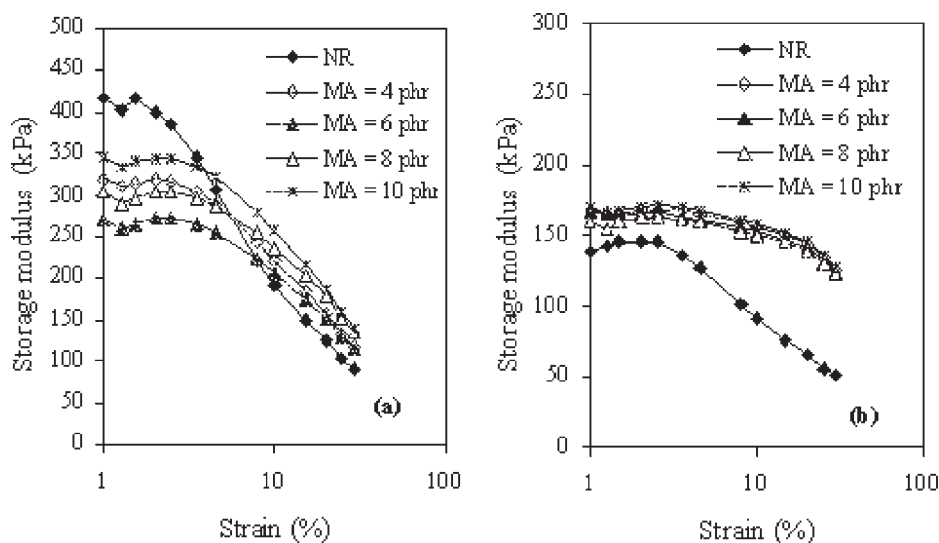
Figure 9 Strain amplitude dependence of storage modulus of MNR compounds at various maleic anhydride contents (2nd sweep): (a) without silane and (b) with silane.

of silane coupling agent effect and compatibilization effect by the succinic anhydride groups. The NR (MA = 0 phr) with silane still shows a distinct Payne effect but the MNRs with silane exhibits only a small decrease of storage modulus with increasing strain, indicated that the MNR filled compounds have less silica aggregates i.e., less filler–filler interaction.

## Mooney viscosity and cure characteristics of the compounds

The compounds without silane of NR (i.e., MA = 0 phr) and MNRs with varying contents of maleic anhydride display quite similar value of Mooney viscosity and distinctively higher than those compounds containing silane coupling agent as tabulated in Table II. Incorporation of silane into the compounds reduces the viscosity as a result of better filler dispersion and therefore less filler aggregates. The Mooney viscosity of the compounds with silane has a tendency to increase with increasing maleic anhydride content attributed to an increase of filler–

rubber interaction induced by the succinic anhydride functional groups of the MNR.

The MNR compounds display significant longer scorch and cure times compared with the NR, as shown in Figure 10 and Table II, due to a presence of acids from ring opening of succinic anhydride groups. It is seen that increasing the maleic anhydride content has only a little effect on scorch and cure times. The minimum torques of both NR and MNR compounds are similar, in accordance with the Mooney viscosity values. Their differences in a degree of filler–filler interaction can not be seen under these Mooney and ODR tests since the materials were deformed far exceed the strain needed to break up the filler aggregates. As seen in Figures 8 and 9, the filler aggregates break up at an approximate strain of 2–3%. The cure curves of the MNR compounds with silane coupling agent display the same pattern as those of the compounds without silane. However, the compounds with silane coupling agent show longer scorch and cure times, and lower minimum and maximum torques as a results of better filler dispersion as discussed earlier. The NR

TABLE II
Mooney Viscosities and Cure Characteristics at 160°C of the Compounds

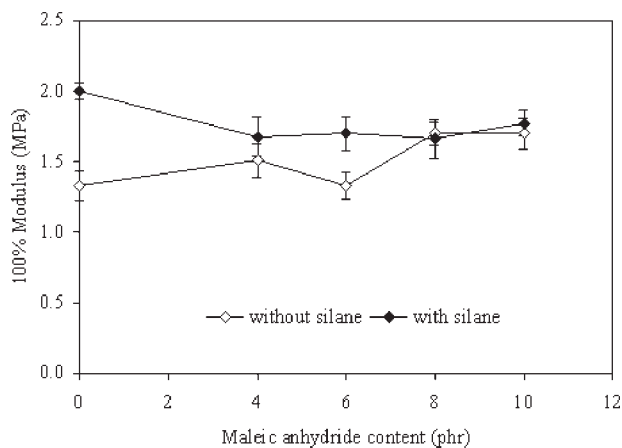| MA content (phr)	Mooney viscosity ML1+4(100°C)		Cure characteristics at 160°C					
			Scorch time, T_{s1} (min)		Cure time, T_{c90} (min)		Torque difference (dN m)	
	Silane	No silane	Silane	No silane	Silane	No silane	Silane	No silane
0	25.2	50.1	2.4	1.9	4.7	4.0	39.9	39.2
4	42.1	48.0	4.3	3.0	7.1	6.0	24.5	31.5
6	40.0	49.2	5.0	2.9	7.5	5.3	22.5	31.2
8	44.3	51.0	4.0	3.1	8.1	6.4	23.1	27.9
10	45.0	52.0	4.0	3.1	8.2	7.0	21.6	24.5
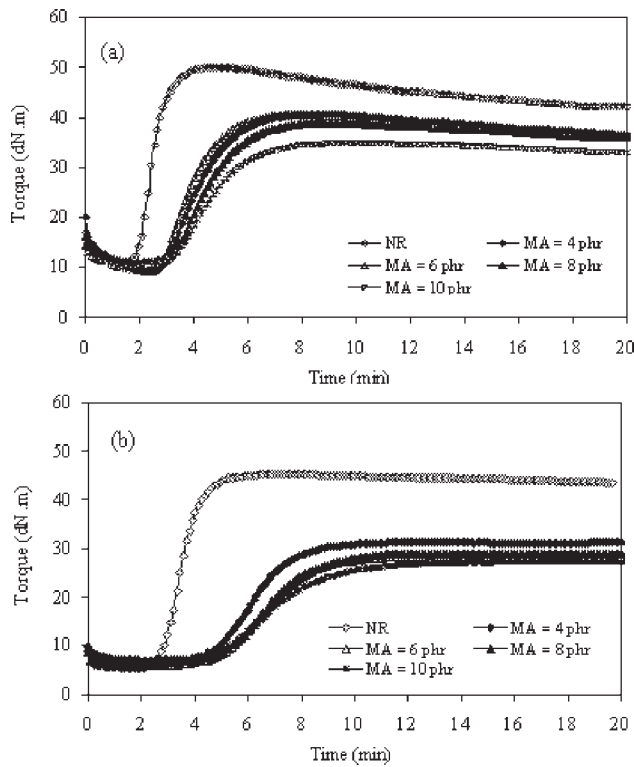
Figure 10 Cure characteristics at 160°C of MNR compounds containing 40 phr of silica: (a) without silane and (b) with silane.
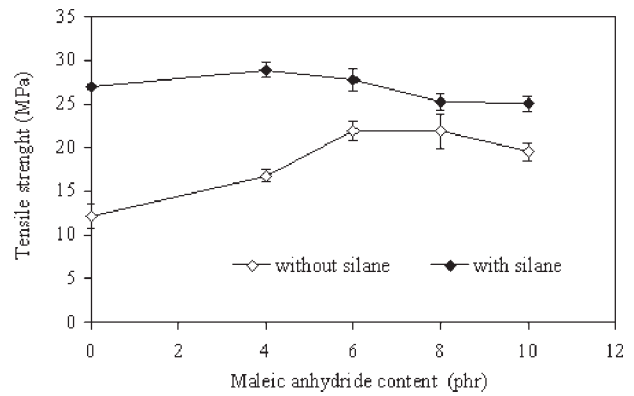
compounds show a significant higher maximum torque compared to the MNR compounds and this could be a result of either their differences in silica dispersion or their different extent of crosslink.

Tensile properties and SEM micrographs

The modulus at 100% elongation, tensile strength and elongation at break of the vulcanizates after press-curing to their 90% cure times at 160°C, both


Figure 12 Tensile strength of MNR vulcanizates at various maleic anhydride contents.

with and without silane coupling agent in the formulation, are shown in Figures 11–13.

The use of silane coupling agent results in the vulcanizates with higher 100%modulus and tensile strength but similar elongation at break, compared with those without silane. Figure 12 shows that the vulcanizates of NR (i.e., MA = 0 phr) and MNRs with silane depict similar tensile strength but the tensile strength of the MNRs containing MA content higher than 6 phr tends to decrease. However, importantly the tensile strength of the filled MNR compounds without silane is dramatically improved in comparison with that of the NR without silane. The highest tensile strength is observed when 6 phr of MA was used, indicating that the optimum silica dispersion was achieved when this MNRs were employed with no silane. The MNR with MA = 8 phr gives similar value of tensile strength to the MNR with MA = 6 phr. This is in agreement with their low levels of filler–filler interaction as seen in Figures 8 and 9. A further increase of maleic anhydride content also results in a reduction of tensile strength since a maleate network[19] may also be formed resulting in a less uniform network structure.

Figure 11 100% Modulus of MNR vulcanizates at various maleic anhydride contents.
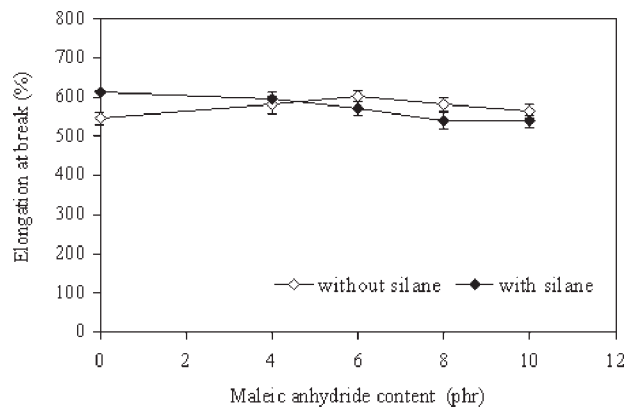
Figure 13 Elongation at break of MNR vulcanizates at various maleic anhydride contents.
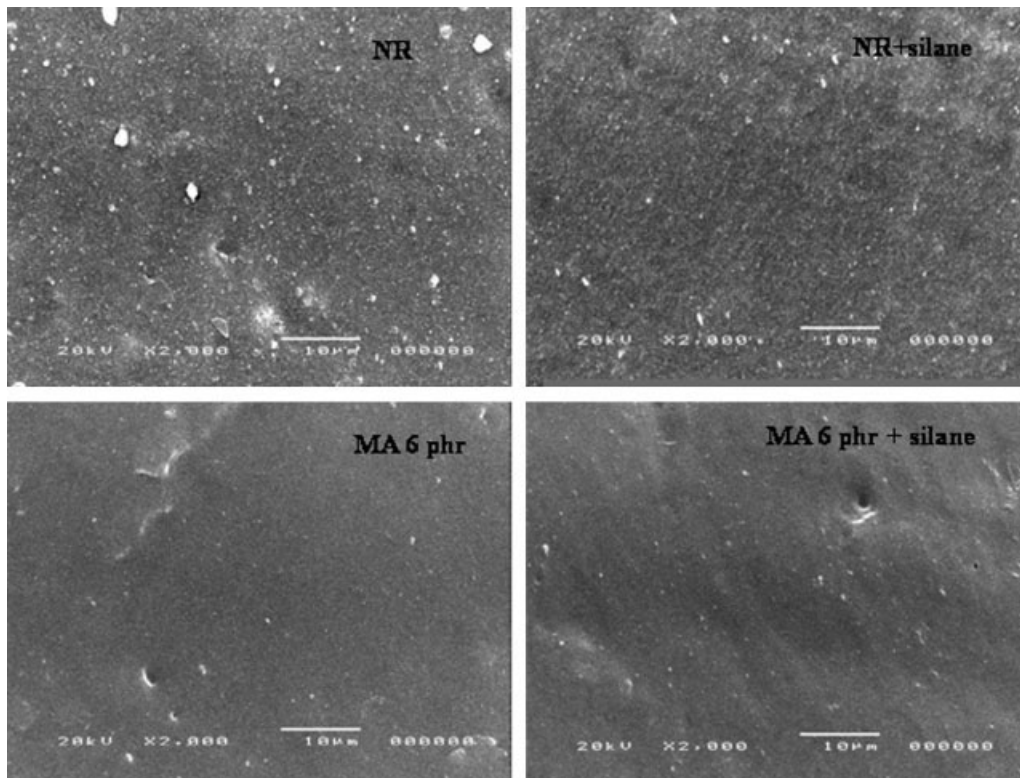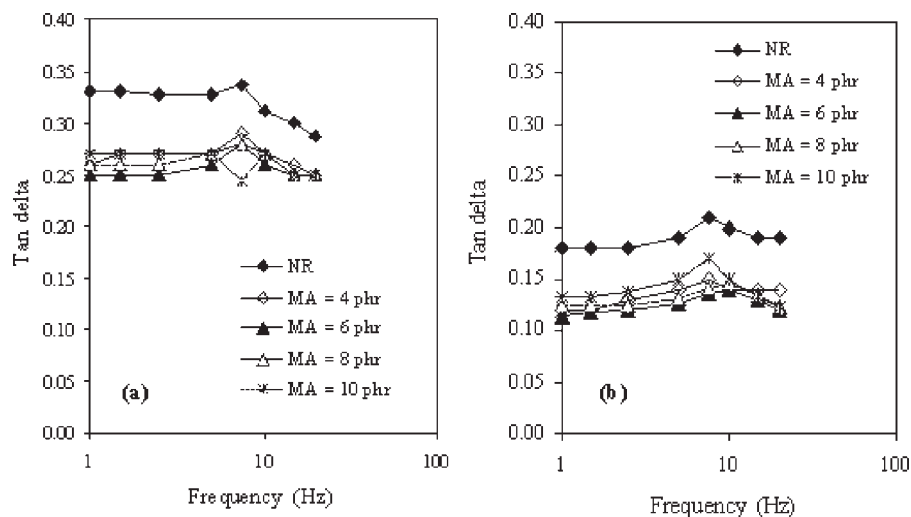
Figure 14 SEM micrographs of NR and MNR vulcanizates with and without silane.
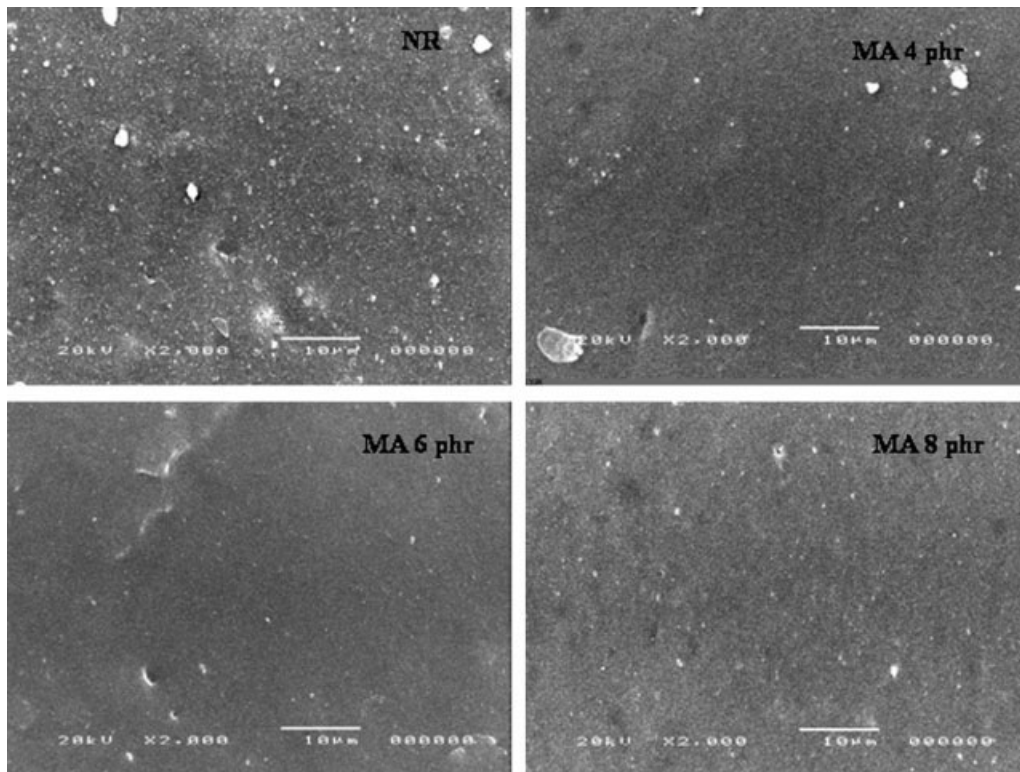
Figure 15 SEM micrographs of NR and MNR vulcanizates at various MA contents without silane.

Figure 16 Tan delta versus frequency of MNR vulcanizates at various maleic anhydride contents : (a) without silane and (b) with silane.

Comparing the compounds without silane of NR and MNRs, an increase of tensile strength in the MNR compounds without silane is surely because of an improved degree of compatibility between rubber and silica, as schematically described in Figure 6. In the case of silane containing compounds, the influence of maleic anhydride content is marginal since the silane itself effectively enhances the interfacial adhesion through the reaction between silica, silane and rubber as described in Figure 7. The tensile properties reflected degree of silica dispersion in the vulcanizates and this is in accordance with the morphology of the blends observed by SEM, as shown in Figures 14 and 15. Silica aggregates can be clearly seen in the unmodified NR without silane coupling agent, and they are less silica aggregates observed in silane containing compound. The MNR vulcanizates clearly showed better filler dispersion and so that improvement of tensile properties was achieved.

Dynamic mechanical properties

The increase of silica–filler interaction in the MNR compounds and hence better silica dispersion has also an influence on dynamic mechanical properties of the vulcanizates. As shown in Figure 16, the MNRs have lower tangent delta, which is a result of loss modulus over storage modulus, in comparison with the conventional NR and the incorporation of silane into the compounds further decrease tangent delta. An improvement of silica–rubber compatibility enhances an interfacial adhesion and results in an improved elastic property of the vulcanizates.

It has been clearly demonstrated in this work that the utilization of maleic anhydride grafted NR instead of unmodified NR results in an improved

silica-rubber interaction and a reduced silica–silica interaction which gives benefits to the mechanical and dynamical properties of the rubber vulcanizates. Therefore, the modified NR is a potential alternative for compatibilizing a polar surface of silica with a hydrocarbon rubber.

CONCLUSIONS

The silica–rubber interaction is increased whereas the silica-silica interaction is decreased when the maleated natural rubber (MNR) is used in stead of the unmodified natural rubber, indicating by an increase of bound rubber and a reduction of Payne effect in the MNR compounds. Incorporation of maleic anhydride functional groups retards the vulcanization as both the scorch and cure times increase, however further increasing the maleic anhydride content has marginal effect on cure characteristics. Without adding silane coupling agent, the MNR compound containing 6 phr of maleic anhydride shows the lowest silica–silica interaction and optimum tensile strength and elongation at break. Furthermore, the silica filled MNR vulcanizates depict lower tangent delta, i.e., better elastic property, in comparison with the NR counterpart. The addition of silane into the rubber compounds further increases filler–rubber interaction and decreases filler–filler interaction, hence results in an improvement of the mechanical and dynamical properties. The use of the MNRs clearly enhances a rubber-silica compatibilization and, to some extent, could lead to an improvement of processing behavior without the need of complicated and costly silane coupling agent systems.

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