

COMPARATIVE PROPERTIES OF SILICA- AND CARBON BLACK-REINFORCED NATURAL RUBBER IN THE PRESENCE OF EPOXIDIZED LOW MOLECULAR WEIGHT POLYMER

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RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 87, No. 2, pp. 320–339 (2014)

ABSTRACT

This work investigates the effect of epoxidized low molecular weight natural rubber (ELMWNR) in silica- and carbon black-filled natural rubber (NR) compounds on processing and mechanical and dynamic mechanical properties. The ELMWNRs with different mol% epoxide content were prepared from depolymerization of epoxidized NR using periodic acid in latex state to have a molecular weight in a range of 50 000–60 000 g/mol. Their chemical structures and actual mol% of epoxide were analyzed by ¹H NMR. The ELMWNRs were added to the filled NR compounds as compatibilizers at varying loadings from 0 to 15 phr. The addition of ELMWNR decreases compound viscosity and the Payne effect, that is, filler–filler interaction, of the silica-filled compound. In the silica–silane compound and the compound with 28 mol% epoxide (ELMWNR-28), the compound viscosities are comparable. The optimal mechanical properties of silica-filled vulcanizates are obtained at the ELMWNR-28 loading of 10 phr. In contrast, the addition of ELMWNR to a carbon black-filled compound shows only a plasticizing effect. The incorporation of ELMWNR into NR compounds introduces a second glass transition temperature and affects their dynamic mechanical properties. Higher epoxide contents lead to higher loss tangent values of the rubber vulcanizates in the range of the normal service temperature of a tire. [doi:10.5254/rct.13.86970]

INTRODUCTION

The physical and mechanical properties of rubber vulcanizates can be improved by the incorporation of reinforcing fillers such as carbon black and silica. The addition of such fillers usually leads to an increase of hardness, modulus, tensile strength, and tear resistance. However, the reinforcement depends on type and amount of fillers used. Carbon black is not only the most widely used but also the oldest active filler in rubber compound.¹ The development of silica compounds was initially aimed at colored articles and later combined with silane coupling agents for high-performance products. This leads to an increasing use of silica as a reinforcing filler to replace carbon black either partly or completely. However, mixing of silica-filled compounds is more difficult and complicated compared with that of carbon black because silica is an inorganic filler that has a high concentration of very polar hydroxyl groups on the surface. Therefore, a basic difficulty lies in the incompatibility between highly polar silica and nonpolar hydrocarbon rubbers. In addition, silica-filled rubber compounds without coupling agents or organic compounds (e.g., amines and alcohols) have a high viscosity and generate a high amount of heat during mixing, which may lead to scorch. Moreover, a serious problem for the use of silica is its poor dispersion and reagglomeration in the hydrocarbon rubber matrix leading to inferior vulcanizate mechanical properties. Generally, high filler loadings in a compound require the use of processing oil to control compound viscosity and to improve filler dispersion during the processing stage.

In general, silane coupling agents are used to chemically bond the polymer to silica, thereby improving filler dispersion and increasing the level of reinforcement. However, they bear some

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disadvantages, such as high cost, toxicity, risk of precuring during the mixing stage, and the generation of ethanol during mixing. Therefore, some new alternatives have been researched and proposed to avoid or reduce the use of the silane coupling agent. The use of polar rubbers such as acrylonitrile butadiene rubber (NBR),² chloroprene rubber (CR),³ and epoxidized natural rubber (ENR)⁴ to improve filler dispersion and the properties of filled vulcanizates is one of the promising methods.

Epoxidized low molecular weight natural rubber (ELMWNR) constitutes a new family of polymers chemically modified from natural rubber (NR). It is a highly viscous rubber of relatively low molecular weight that is generally used as plasticizer or processing aid and it also has a random distribution of epoxide groups along the polymer backbone.⁵ The chemical structure contains both epoxide and unsaturated sites. Although the double bonds can be crosslinked by sulfur, the epoxide groups provide alternative sites for crosslinking or for chemically interacting with other functional chemicals. ELMWNR had been used as plasticizer during processing of some polymers, such as filled nitrile (NBR) and NR/NBR blends.⁶ The results showed a decrease in total mixing energy and compound viscosity with increasing low molecular weight rubber content. George et al.⁷ reported that an optimum concentration of about 15% of ENR relative to the total rubber in a silica-filled NBR compound improved bound rubber content and mechanical and dynamic mechanical properties. The presence of the polar epoxide groups permits a good compatibility between rubber and silica. This compatibility involves a hydrogen bonding and possibly also some chemical bonding,⁸ allowed by the ring opening of the oxirane ring caused by the acidity of the siloxane groups on the silica surface at vulcanization temperature.

In this study, the use of ELMWNR is aimed on enhancing the processing properties and compatibility between rubber and filler. The effect of ELMWNR with different degrees of epoxidation on cure characteristics, processing properties, and mechanical and dynamic mechanical properties of silica- and carbon black-reinforced NR compounds are investigated. The results of an ELMWNR-compatible system are compared with those of a conventional silane coupling agent used in silica-filled compounds. For comparison, the use of LMWNR bearing no epoxide groups is studied.

EXPERIMENTAL

MATERIALS

High ammonia natural rubber (HA-NR) latex (Yala Latex Industry, Thailand), non-ionic surfactant Teric N30 (Huntsman Corp., Australia), and formic acid and hydrogen peroxide (Acros Organics, Belgium) were used for the preparation of ENR. Periodic acid (Merck, Germany) was used for the molecular weight reduction of the rubber. The ingredients used for rubber compounding were natural rubber (Ribbed Smoked Sheet 3 [RSS3]), locally produced in Pattani, Thailand; high abrasion furnace black ([HAF], Thai carbon black PLC, Thailand); highly dispersible silica with CTAB 152 m²/g (Zeosil[®] 1165MP, Rhodia, France); bis-triethoxysilylpropyl tetrasulfide ([TESPT], Evonik, Germany); treated distillate aromatic extract (TDAE) oil (H&R, Germany); polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ), diphenylguanidine (DPG); and *N*-cyclohexyl-2-benzothiazole-sulfenamide ([CBS], all from Flexsys, Belgium). Zinc oxide (ZnO), stearic acid, and sulfur were of general commercial grades for the rubber industry.

EPOXIDIZED LOW MOLECULAR WEIGHT NATURAL RUBBER

Preparation of ENR. — The ENR latex was prepared by using HA-NR latex with a dry rubber content (DRC) of approximately 60%. The latex was diluted to approximately 20% DRC,

stabilized with 3 phr of 10% solution of Teric N30, and then stirred for 8 h at room temperature to eliminate ammonia. The epoxidation was carried out by using performic acid generated in situ by the reaction of formic acid (HCOOH) and hydrogen peroxide (H₂O₂) at 60 °C in 1000 mL glass reactor equipped with a control stirrer speed of 60 rpm. HCOOH was added dropwise and then H₂O₂ was slowly added under continuous stirring. The ratio of reagents used were [HCOOH]/[H₂O₂] = 1 mol mol⁻¹ and [H₂O₂]/[polyisoprene unit] = 0.15, 0.40, 0.60 mol mol⁻¹. The reaction was allowed to proceed for 24 h.

Degradation of NR and ENR by Periodic Acid. — The NR or ENR latex (20% DRC) from the previous step was treated with periodic acid solution⁹ at 30 °C under continuous stirring with a stirrer speed of 30 rpm for 48 and 36 h for NR and ENR latex, respectively. The latex was then neutralized by adding sodium bicarbonate, coagulated with methanol, washed with water, and finally dried in a vacuum oven until constant weight.

Characterization of ELMWNR. — The chemical structure of the modified LMWNR was characterized by means of the attenuated total reflection- Fourier transform infrared (FT-IR) spectrometry using a Spectrum One FT-IR spectrometer (PerkinElmer) under nitrogen atmosphere at room temperature. The samples were scanned in a spectral range of 4000 to 650 cm⁻¹ with a resolution of 4 cm⁻¹. ¹H NMR spectra were recorded with a Fourier Transform NMR spectrometer (500 MHz, Unity Inova, Varian, Germany) at room temperature using deuterated chloroform as a solvent for sample preparation. The epoxide group content, X_{epoxy} , was calculated by using the peak integral at 2.7 and 5.1 ppm, assigned to epoxy proton in ELMWNR and alkene proton in polyisoprene units, respectively, following Eq. 1:

$$X_{\text{epoxy}} = \frac{I_{2.7}}{I_{2.7} + I_{5.1}} \times 100. \quad (1)$$

Measurements of molecular weight and molecular weight distribution of the rubbers were made by gel permeation chromatography (GPC), consisting of a CBM 20 Alite system controller, Shodex GPC KF-806M and Shodex GPC KF-803L columns, and an RID-10A refractive index detector. The system was operated at 40 °C using tetrahydrofuran as a mobile phase with a flow rate of 1 ml/min and polystyrene as a standard calibrator.

PREPARATION OF RUBBER COMPOUNDS

The formulations of the silica- and carbon black-filled compounds are given in Tables I and II, respectively. For silica-filled compounds, a compound with TESPT as a coupling agent was used as the reference. A two-step mixing procedure as reported by Kaewsakul et al.¹¹ was used for the silica-filled compounds. The first step was done in an internal mixer with a mixing chamber volume of 370 cm³ (Brabender Plasticorder 350S) whereby the polymer and all chemicals except the curatives were mixed. The mixer temperature setting, rotor speed, and fill factor were 100 °C, 60 rpm and 0.7, respectively. The rubbers in different ratios as shown in Table I were masticated for 2 min. Half of the silica was added and mixed for 5 min, and then the second half of silica and TDAE oil (together with the silane for the reference compound using silica) were added and continuously mixed for 5 min. The ZnO, stearic acid, and TMQ were then added and mixed for 3 min, and the batch was finally dumped at a total mixing time of 15 min. Carbon black-filled compounds were mixed in HAAKE internal mixer (Rheomix 3000p) with a mixing chamber volume of 310 cm³ at a fill factor of 0.7. Mixer temperature setting and rotor speed were at 60 °C and 60 rpm, respectively. The mixing steps were similar to the silica compound to have the same total mixing time of 15 min. The curatives were incorporated in the second step of mixing on a two-roll mill.

TABLE I
SILICA-FILLED COMPOUND FORMULATION

Ingredient	Amount, phr						
NR (RSS3)	100.0	100.0	95.0	92.5	90.0	87.5	85.0
ELMWNR (or LMWNR) ^a	0.0	0.0	5.0	7.5	10.0	12.5	15.0
Silica (Zeosil 1165MP)	55.0	55.0	55.0	55.0	55.0	55.0	55.0
Silane (TESPT)	4.4 ^b	0.0	0.0	0.0	0.0	0.0	0.0
Process oil (TDAE)	5.0	5.0	5.0	5.0	5.0	5.0	5.0
ZnO	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Stearic acid	1.0	1.0	1.0	1.0	1.0	1.0	1.0
TMQ	1.0	1.0	1.0	1.0	1.0	1.0	1.0
DPG ^c	1.1	1.1	1.1	1.1	1.1	1.1	1.1
CBS	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5

^a ELMWNRs with 12, 28, and 51 mol% epoxide were used; LMWNr was used for comparison.

^b Amount of TESPT (phr) = 0.00053 × Q × CTAB, where Q is the silica content (phr) and CTAB is specific surface area of the silica (m²/g).¹⁰

^c Amount of DPG (phr) = 0.00012 × Q × CTAB, where Q is the silica content (phr) and CTAB is specific surface area of the silica (m²/g).¹⁰

DETERMINATION OF RUBBER COMPOUND AND VULCANIZATE PROPERTIES

Compound Viscosity. — The Mooney viscosities were determined using a Mooney viscometer (MV2000 VS, Alpha Technologies, Akron, OH) at 100 °C with a large rotor according to ASTM D1646-04. The complex viscosities were analyzed using an RPA2000 Rubber Process Analyzer (Alpha Technologies). The frequency sweep was performed from 0.1 to 33 Hz at 14% strain and 80 °C.

Payne Effect. — Storage shear moduli (G') of uncured compounds were measured under shear deformation using the RPA2000 analyzer. The strain was varied from 0.56 to 100% at 0.50 Hz and 100 °C.

TABLE II
CARBON BLACK-FILLED COMPOUND FORMULATION

Ingredient	Amount, phr			
NR (RSS3)	100.0	95.0	90.0	85.0
ELMWNR (or LMWNR) ^a	0.0	5.0	10.0	15.0
HAF N330	55.0	55.0	55.0	55.0
Process oil (TDAE)	5.0	5.0	5.0	5.0
ZnO	3.0	3.0	3.0	3.0
Stearic acid	1.0	1.0	1.0	1.0
TMQ	1.0	1.0	1.0	1.0
DPG	0.3	0.3	0.3	0.3
CBS	1.2	1.2	1.2	1.2
Sulfur	1.5	1.5	1.5	1.5

^a ELMWNRs with 12, 28, and 51 mol% epoxide were used; LMWNr was used for comparison.

Cure Characteristics. — The cure characteristics were determined using the RPA2000 analyzer at 150 °C according to ASTM D5289-95. The samples were tested at a frequency of 0.833 Hz and 2.79% strain for 30 min.

Mechanical Properties. — The test specimens were press-vulcanized in an electrically heated hydraulic press (Wickert laboratory press WLP1600) at 150 °C to optimal cure time (t_{90}) as predetermined from the rheograph. Tensile properties (i.e., modulus, tensile strength, and elongation at break) of the vulcanizates 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 412-98a. For tear strength, angle-shape specimens (die type C) were tested according to ASTM 624-98.

Dynamic Mechanical Properties. — The dynamic mechanical properties of the filled vulcanizates were measured by a Metravib Viscoanalyser VA2000, under tension mode from –90 to 80 °C at 0.01% strain, a frequency of 10 Hz, and a heating rate of 2 °C/min. The storage modulus and loss tangent ($\tan \delta$) of both carbon black- and silica-filled vulcanizates were characterized under identical conditions.

Kinetics of the Self-Crosslinking Reaction of ELMWNR. — As the chemical bonding between –OH groups of ring-opened ENR itself¹² and between –OH groups of the polymer and silica can possibly take place,⁸ this work investigated the self-crosslinking behavior of ELMWNR-12, –28, and –51 with and without silica (30 phr) by monitoring a change of the rheometer torque using the RPA2000 analyzer at various temperatures varying from 160 to 220 °C. The masterbatches of ELMWNRs and silica were prepared by using an internal mixer with 50 cm³ mixing chamber volume, at a fill factor of 0.8, a rotor speed of 60 rpm, and a mixer temperature setting of 60 °C. ELMWNR was masticated for 1 min, and then silica was added and mixed for 4 min. The kinetics of the reactions were elucidated from the torque–time values of the vulcanization curve via the kinetic Eqs. 2 and 3:¹³

$$\ln\left(\frac{M_H - M_L}{M_H - M_t}\right) = kt, \quad (2)$$

$$\ln(M_H - M_L) - \ln(M_H - M_t) = kt. \quad (3)$$

The M_H , M_L , and M_t are maximum torque, minimum torque, and the torque at time (t), respectively. The reaction rate constants (k) are obtained from the slope of the plot of $\ln(M_H - M_t)$ versus time, t , with the $\ln(M_H - M_L)$ being constant. Moreover, the activation energy (E_a) can be calculated according to the Arrhenius equation, as shown in Eqs. 4 and 5:

$$k = A \times \exp\left(\frac{-E_a}{RT}\right), \quad (4)$$

$$\ln k = \ln A - \frac{E_a}{R} \times \frac{1}{T}, \quad (5)$$

where A is the pre-exponential factor, R represents the gas constant (8.314 J.K^{–1}mol^{–1}), T is the absolute temperature, and E_a indicates the apparent activation energy for the crosslinking reaction.

RESULTS AND DISCUSSION

EPOXIDIZED LOW MOLECULAR WEIGHT NATURAL RUBBER

The weight average molecular weight (\bar{M}_w) of the LMWNR is 65 000 g/mol and the \bar{M}_w of ELMWNRs are in the range of 50 000–65 000 g/mol as measured by GPC, and detailed in Table

TABLE III
WEIGHT-AVERAGE MOLECULAR WEIGHT OF ELMWNR

ELMWNR, mol% epoxide	\bar{M}_w , g/mol
0	65 000
12	55 000
28	49 000
51	N.A. ^a

^a Not applicable (N.A.) because the sample was not completely dissolved in tetrahydrofuran.

III. The degradation of ENR latex containing a higher mol% epoxide is expressed in lower \bar{M}_w ; the chain breakdown may be caused by residual H_2O_2 in addition to periodic acid. The chemical structure of ELMWNR was analyzed by FT-IR and 1H NMR. Figure 1 shows the infrared spectra of ELMWNRs with different epoxide contents in comparison with the spectra of NR and LMWNR. The characteristic peaks of isoprene units are observed at wave numbers of 1663 cm^{-1} (C=C stretching) and 835 cm^{-1} (=C-H out of plane deformation). After degrading NR with periodic acid, the low molecular weight rubber displays additional peaks at 1720 cm^{-1} (C=O stretching) and 3440 cm^{-1} (OH stretching) as a result of molecular chain breakdown. The functional groups such as carbonyl and hydroxyl groups that arise from the oxidative degradation of rubber molecule have been previously demonstrated by using the FT-IR characterization technique.¹⁴⁻¹⁶ For the structure of ELMWNR, the infrared spectra show the peaks at wave number of 870 cm^{-1} , which is attributed to epoxide asymmetric stretching and more intensified with increasing epoxide content. At high epoxide content, the peak at 1140 cm^{-1} caused by C-O stretching vibrations also becomes clearly visible. Furthermore, the intensity of carbonyl peak at 1720 cm^{-1} is getting stronger, whereas the

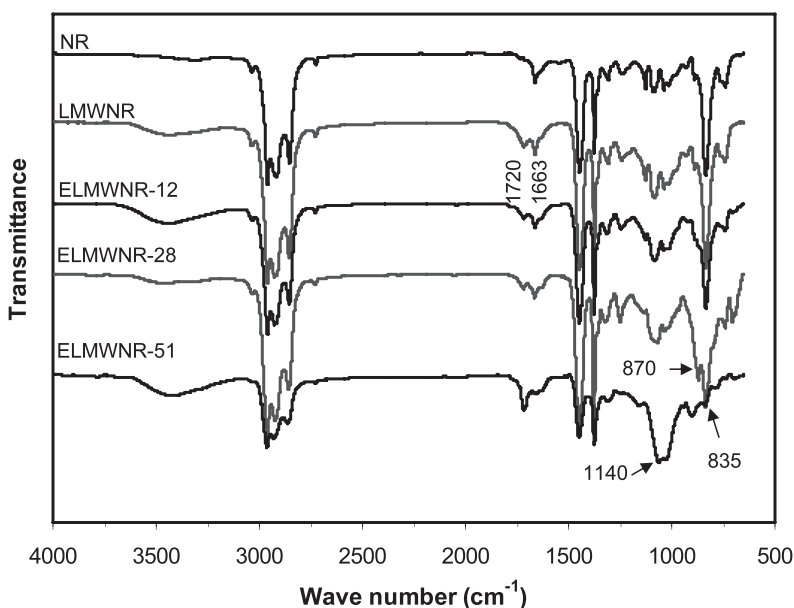


FIG. 1. — Infrared spectra of NR, LMWNR, and ELMWNR with different epoxide contents.

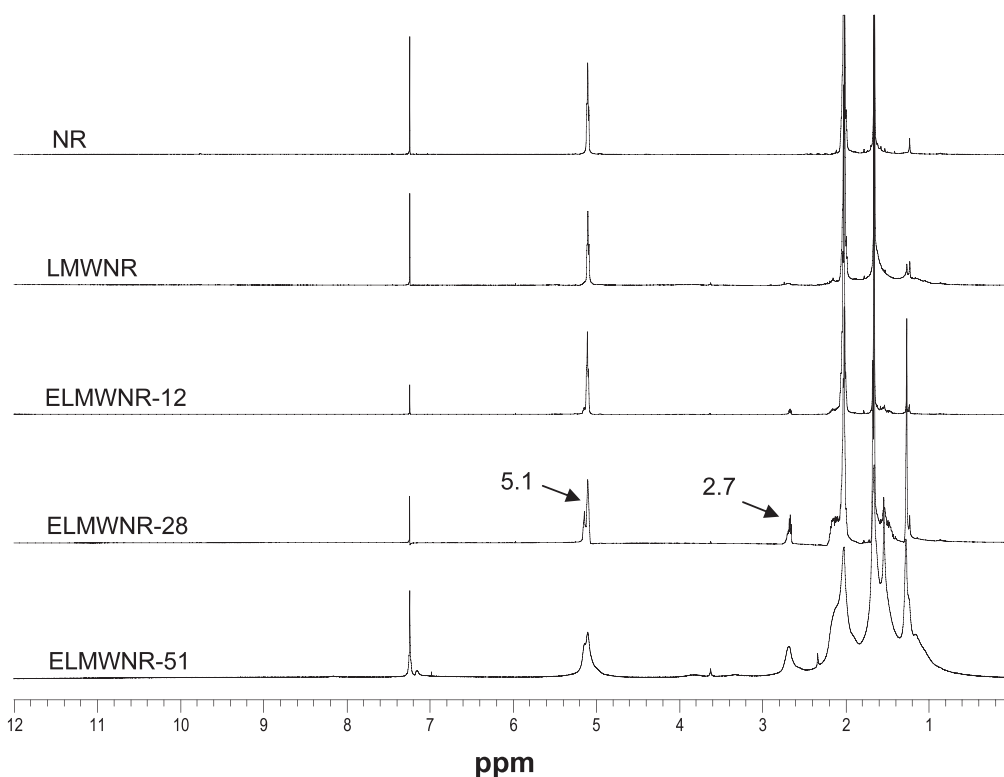


FIG. 2. — ^1H NMR spectra of NR, LMWNR and ELMWNR with different epoxide contents.

intensity of the peaks at 1663 and 835 cm^{-1} decreased, indicating the reduction of double bonds as the epoxidation reaction proceeds.

The ^1H NMR spectra of ELMWNRs (Figure 2) exhibit the characteristic peak of protons adjacent to the epoxide ring corresponding to the epoxide structure on the rubber chain at 2.7 ppm. The actual epoxide content of ELMWNRs, calculated from the integrated area of proton peaks obtained from the ^1H NMR using Eq. 1, are 12, 28, and 51 mol% epoxide. The materials are denoted as ELMWNR-12, ELMWNR-28, and ELMWNR-51, respectively.

COMPOUND PROPERTIES

Compound viscosity is a very important parameter for rubber processing. Figure 3 shows Mooney viscosities of silica- and carbon black-filled NR compounds containing various amounts of low molecular weight rubber, compared with that of the compounds with and without TESPT in the case of silica-filled compounds. The Mooney viscosity of carbon black-filled compound shows no significant change by the incorporation of either LMWNR or ELMWNR, whereas Mooney viscosities of the silica-filled compounds are clearly reduced by the addition of 5 phr of low molecular weight rubber-bearing epoxide groups and further decreased with an increasing amount of ELMWNR. The use of LMWNR at 5 and 10 phr shows almost no effect on the viscosity of a silica-filled compound, and the increasing amount of LMWNR to 15 phr decreases the compound viscosity, which is mainly due to the plasticizing effect as the incorporation of smaller molecules of polymer increases chain mobility. In addition, when a high loading of LMWNR (i.e., 15 phr) was

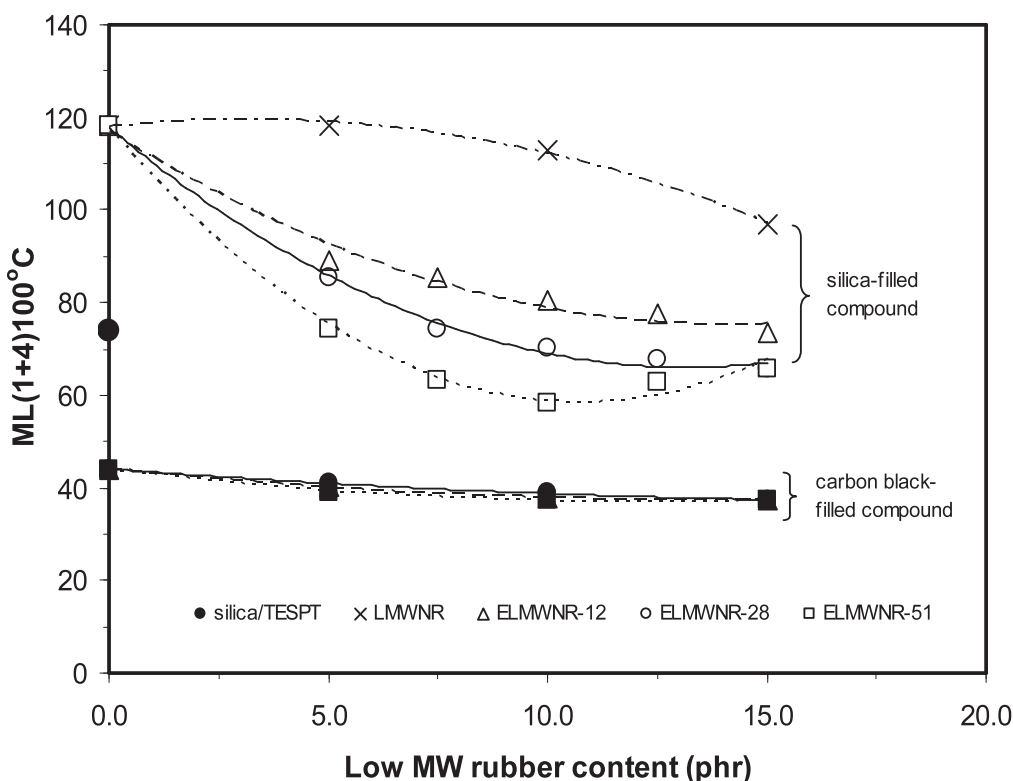


FIG. 3. — Mooney viscosity of silica- and carbon black-filled NR compounds at various amounts of low molecular weight rubber.

used, the carbonyl groups at the chain ends⁹ of the LMWNR can possibly interact with the silanol groups on the silica surface, thereby positively affecting filler dispersion and lower Mooney viscosity. The use of a sufficient amount of ELMWNR-28 and ELMWNR-51 in silica-filled compounds can decrease the Mooney viscosity to match the level of the compound with TESPT. This is caused by the interactions between epoxide groups and silanol groups on the silica surface resulting in a better dispersion of silica in the NR matrix, and also by suppression of silica reagglomeration.¹⁷ However, the use of ELMWNR-51 at a high concentration (>10 phr) results in an upward turn of Mooney viscosity that can be due to self-association of epoxide groups, leading to a decreasing amount of epoxide groups to interact with silanols and resulting in poorer silica dispersion. The self-association itself also would increase viscosity.

Pseudoplastic material typically shows a decrease in viscosity with increasing shear rate. Figures 4 and 5 show the plots of the complex viscosity versus frequency for silica- and carbon black-filled NR compounds containing 10 phr of low molecular weight rubber, respectively. The silica-filled NR compound without any compatibilizer shows the highest complex viscosity; by the addition of silane, a drop in the complex viscosity is observed. The use of low molecular weight rubber without epoxide groups shows only a slight decrease, whereas the addition of ELMWNR with 28 and 51 mol% epoxide significantly decreases the complex viscosity to match the viscosity level of the compound with the silane coupling agent. The silica compounds show different viscosities reflecting their different degree of filler dispersion. Herein, the filler dispersion is improved by adding ELMWNR, as discussed previously. For the carbon black-filled compounds, the viscosities in terms of Mooney viscosity (Figure 3) and complex viscosity (Figure 5) are lower

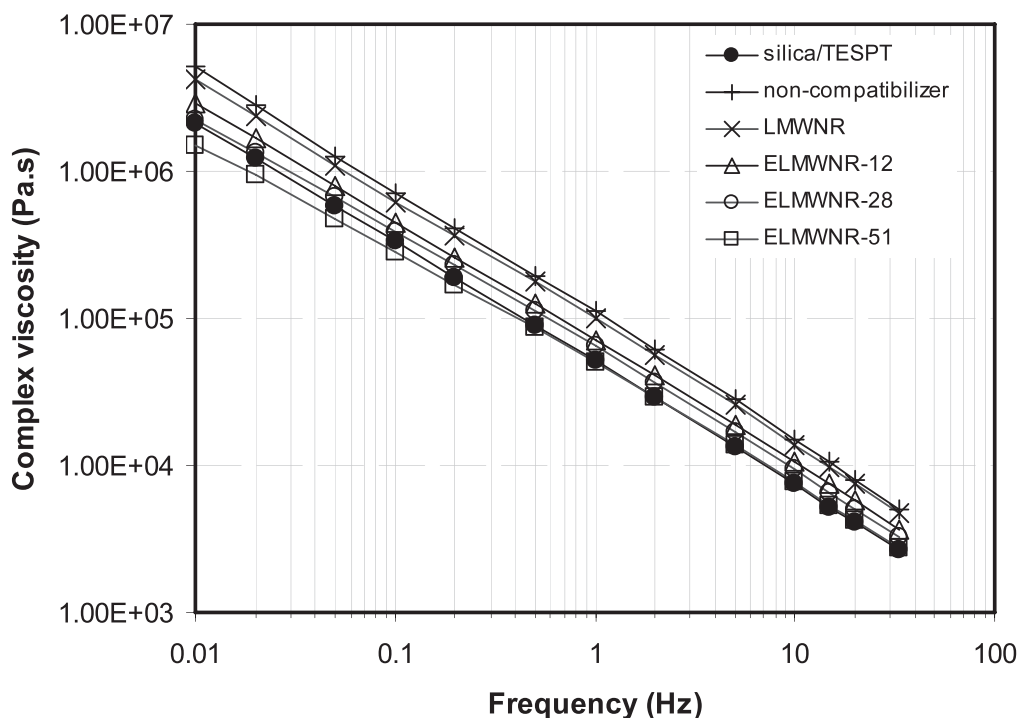


FIG. 4. — Complex viscosity of silica-filled compounds containing 10 phr of low molecular weight rubber with various epoxide contents.

compared with those of the silica-filled compound because of the lower inter-particle attractive forces between carbon black particle aggregates. However, the addition of LMWNR both with and without epoxide groups shows almost no influence on Mooney viscosity and complex viscosity of carbon black-filled compounds.

In filled rubber compounds, the G' value is dependent on the rubber network, the hydrodynamic effect of the filler, and the filler–rubber and filler–filler interactions. The first three contributions remain constant with the deformation, in contrast to the filler–filler interaction that is strain-dependent. 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, or the Payne effect.¹⁸ Figure 6a,b shows the storage shear modulus of silica- and carbon black-filled uncured compounds containing 10 phr of low molecular weight rubber. The Payne effect of the silica-filled compound without compatibilizer is much higher than that of the carbon black-filled compound. This is attributed to the hydroxyl groups on the silica surface that form hydrogen bonds and result in strong filler–filler interaction. Carbon black is composed of graphitic layers with only a very small quantity of polar functional groups, such as hydroxyl, carboxyl, or ketone, on its surface.¹⁹ Thus, the filler–filler interaction of silica is much stronger than that of carbon black. Compared with the silica-filled compounds without compatibilizer, the storage modulus of carbon black-filled compounds gradually drops with increasing strain amplitude because of less filler–filler interactions. For silica filled-compounds, the use of low molecular weight NR without epoxide groups slightly lowers the Payne effect compared with the effect with only original NR. However, the use of 10 phr ELMWNR with 28 and 51 mol% epoxide significantly lessens the Payne effect by reducing the storage modulus of the compounds to a level close the silane-containing compound. This indicates that the incorporation of ELMWNR weakens the filler–filler interactions and can

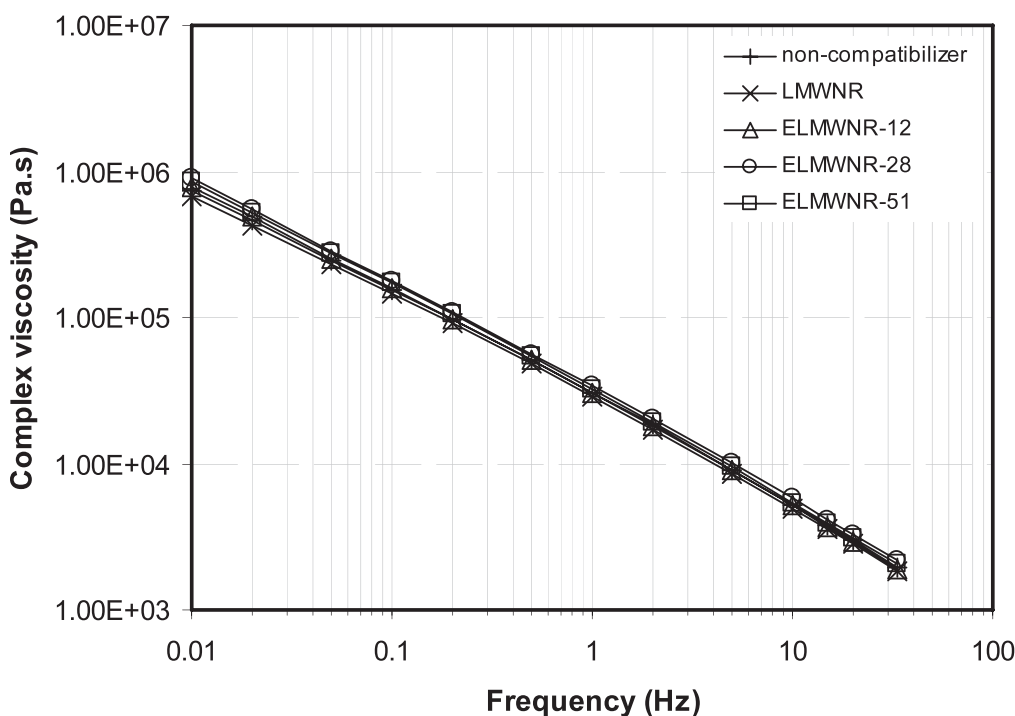


FIG. 5. — Complex viscosity of carbon black-filled compounds containing 10 phr of low molecular weight rubber with various epoxide contents.

further imply to a possible formation of hydrogen bond between epoxide groups of ELMWNR and silanol groups of silica during the mixing stage, thereby promoting the filler–rubber interaction. The effect of low molecular weight rubber in silica-filled and carbon black-filled compounds on the Payne effect can be clearly seen in Figure 7. The Payne effect of the silica-filled compounds decreases with increasing amounts of low molecular weight rubber and epoxide content and can be explained by two different contributions. First, the low molecular weight rubber molecules act as internal plasticizers in rubber compounds, thereby improving the mobility of both rubber chains and filler and facilitating filler dispersion. Second, the relatively strong interaction between the epoxide group of ELMWNR and the silanol groups on the silica surface via hydrogen bonds, chemical bonds, or both formed after epoxide ring opening,²⁰ and a covering of the silanol groups by the ELMWNR molecules, prevent filler–filler interactions. For the silica-filled compound with 15 phr of LMWNR, a clear decrease of the Payne effect also can be attributed in part to the possible interaction between carbonyl groups at the rubber chain ends and silanol groups of silica, resulting in better filler–rubber interaction and filler dispersion. The increasing amount of ELMWNR-12 and ELMWNR-28 further decreases the Payne effect, but the use of ELMWNR with 51 mol% epoxide at high concentrations, that is, >10 phr, shows an upturn in Payne effect that is ascribed to self-association of epoxide groups, leading to a reduced tendency of epoxide–silanol interactions. This self-association behavior is discussed later in the study of the self-crosslinking reaction kinetics of ELMWNR. The incorporation of low molecular weight rubber without epoxide groups shows no effect in carbon black-filled compounds, and the level of storage modulus difference [$G'(0.56\%) - G'(100\%)$] is comparable to that of the silica–TESPT compound.

The curing characteristics of filled NR compounds in terms of scorch time (t_{c10}), t_{90} , M_L , and M_H are displayed in Figure 8. With regard to the silica compounds, the addition of low molecular

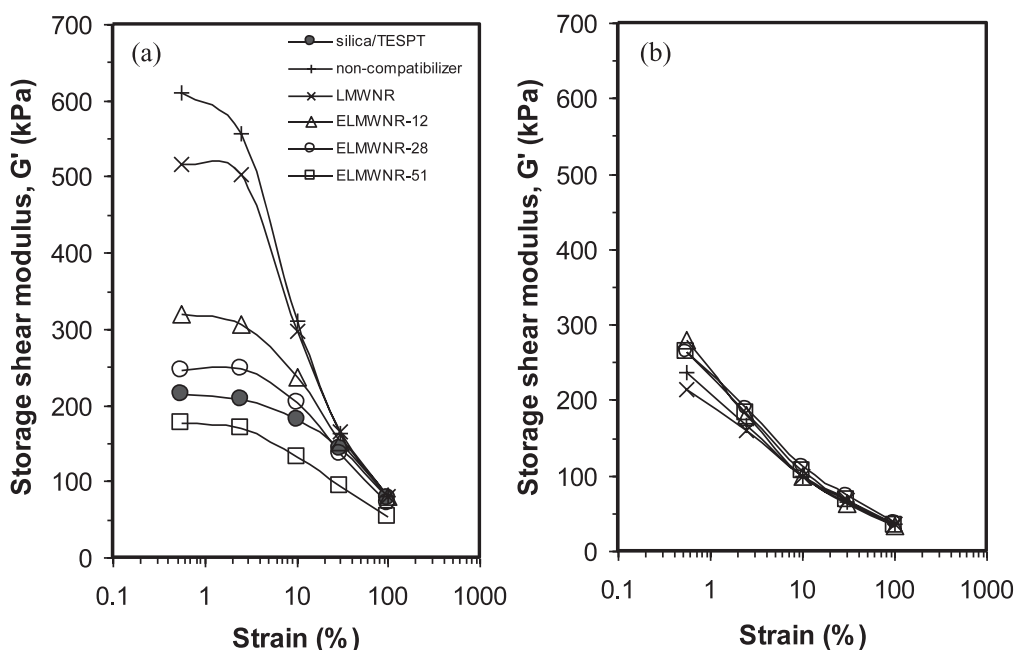


FIG. 6. — Payne effect of silica-filled (a) and carbon black-filled (b) NR compounds containing 10 phr of low molecular weight rubber with various epoxide contents.

weight rubber without epoxide groups shows no effect on scorch and cure times, but the use of ELMWNR delays both scorch and cure times, compared with the compound without any compatibilizer (Figure 8a). This difference can be attributed to the presence of polar functional groups on both silica surface and rubber chains that can absorb or interact with the basic accelerators, causing longer scorch and cure time. However, when a sufficient amount of modified LMWNR is present in the system, that is, when ELMWNR-28 content is >10 phr or ELMWNR-51 is >7.5 phr, the cure times tend to decrease. This decrease indicates that, after having sufficient epoxide–silanol interactions and the covering of the silanol groups by the ELMWNR molecules, the polar groups have no further interference in the curing reaction. In contrast, the presence of smaller rubber molecules and overall less reactive double bond sites in the system decreases the cure times. For carbon black-filled compounds, different cure characteristics are observed compared with the silica-filled compounds as the scorch and cure times tend to decrease when the amount of low molecular weight rubber is increased, especially when ELMWNR with 28 and 51 mol% epoxide is used (Figure 8c). In this case, there is no interference of curative absorption by polar functional groups, so the presence of the smaller rubber molecules increases the reactivity toward a vulcanization reaction. It has been reported by Sadequl et al.²¹ that the epoxide groups can activate an adjacent double bond, and the apparent activation energy for the curing reaction of ENR is lower than that of NR, so the incorporation of ELMWNR reduces both cure and scorch times. The M_L is related to the viscosity or plasticity of filled compounds, and the results are in accordance with the Mooney viscosity (Figure 3). Incorporation of ELMWNR in silica-filled compound drastically drops the M_L to the same level as that of the compound with the silane coupling agent (Figure 8b), due to a combination of decreased filler–filler interaction and plasticizing effect, whereas the use of low molecular weight rubber without epoxide groups shows a decrease of torque as a result of the plasticizing effect only. The M_H values of both, silica- and carbon black-filled compounds decrease

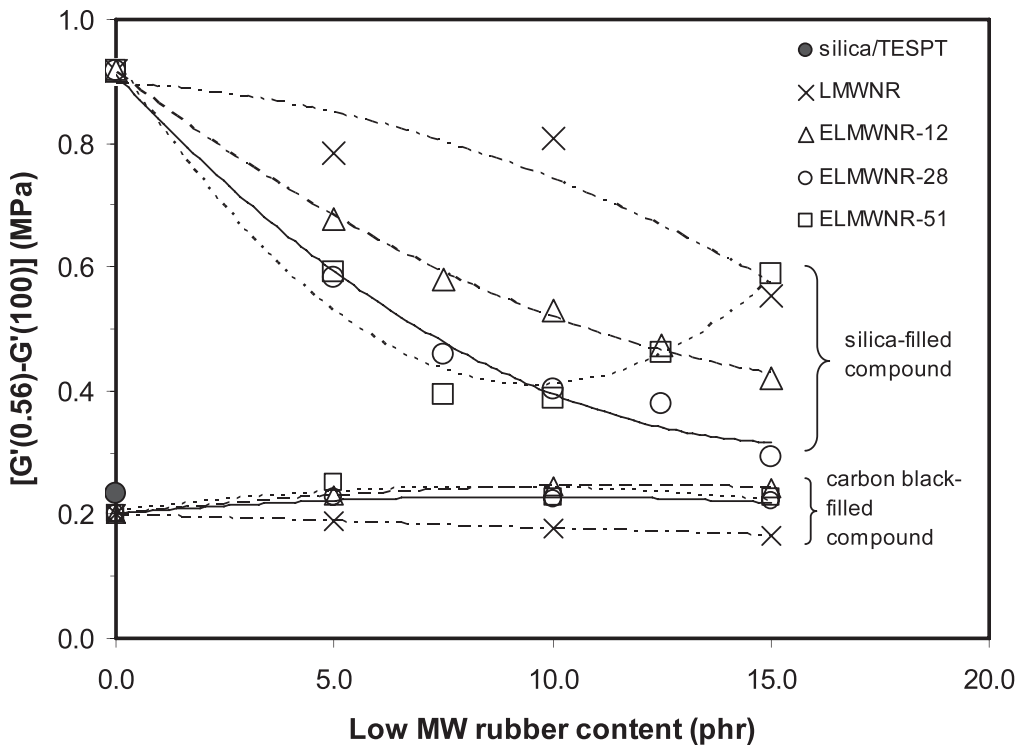


FIG. 7. — Payne effect of silica-filled and carbon black-filled NR compounds at various amounts of low molecular weight rubber.

with increasing amount of low molecular weight rubber, because the addition of shorter rubber chains into the original high molecular weight matrix leads to an increase of loose or dangling chain ends and lower stiffness. However, the use of ELMWNR with 51 mol% epoxide at a high concentration shows an increase of the M_H in the silica-filled compound, most likely due to poor filler dispersion after the large amount of epoxide groups interact with themselves rather than to interact with the silanol group on silica surface, and an extra crosslinking caused by the self-association.

KINETICS OF SELF-CROSSLINKING REACTION OF ELMWNR

Mooney viscosity, the Payne effect, and the minimum and maximum cure torques of silica-filled compounds showed an upward trend when ELMWNR-51 was used at high concentrations, that is, >10 phr. This phenomenon was explained by self-association of epoxide groups that leads to a decreasing amount of epoxide moieties to interact with the silanol groups and consequently results in poor silica dispersion. In addition, such a self-crosslinking reaction between polymer molecules leads to more crosslinks. Due to its strong influence on the properties of the material, the kinetics of this self-crosslinking reaction of neat ELMWNRs with different epoxide contents and ELMWNRs-silica masterbatch were studied. The rheographs of ELMWNR-51-silica masterbatch (Figure 9a) and neat ELMWNR-51 (Figure 9b) at various temperatures show that the torques of both unfilled ELMWNR-51 and ELMWNR-51-silica masterbatch increase at all temperatures studied in the range of 160–220 °C, but the increase is bigger when the temperature is higher. The increase of torques indicates self-crosslinking via epoxide ring opening followed by condensation,

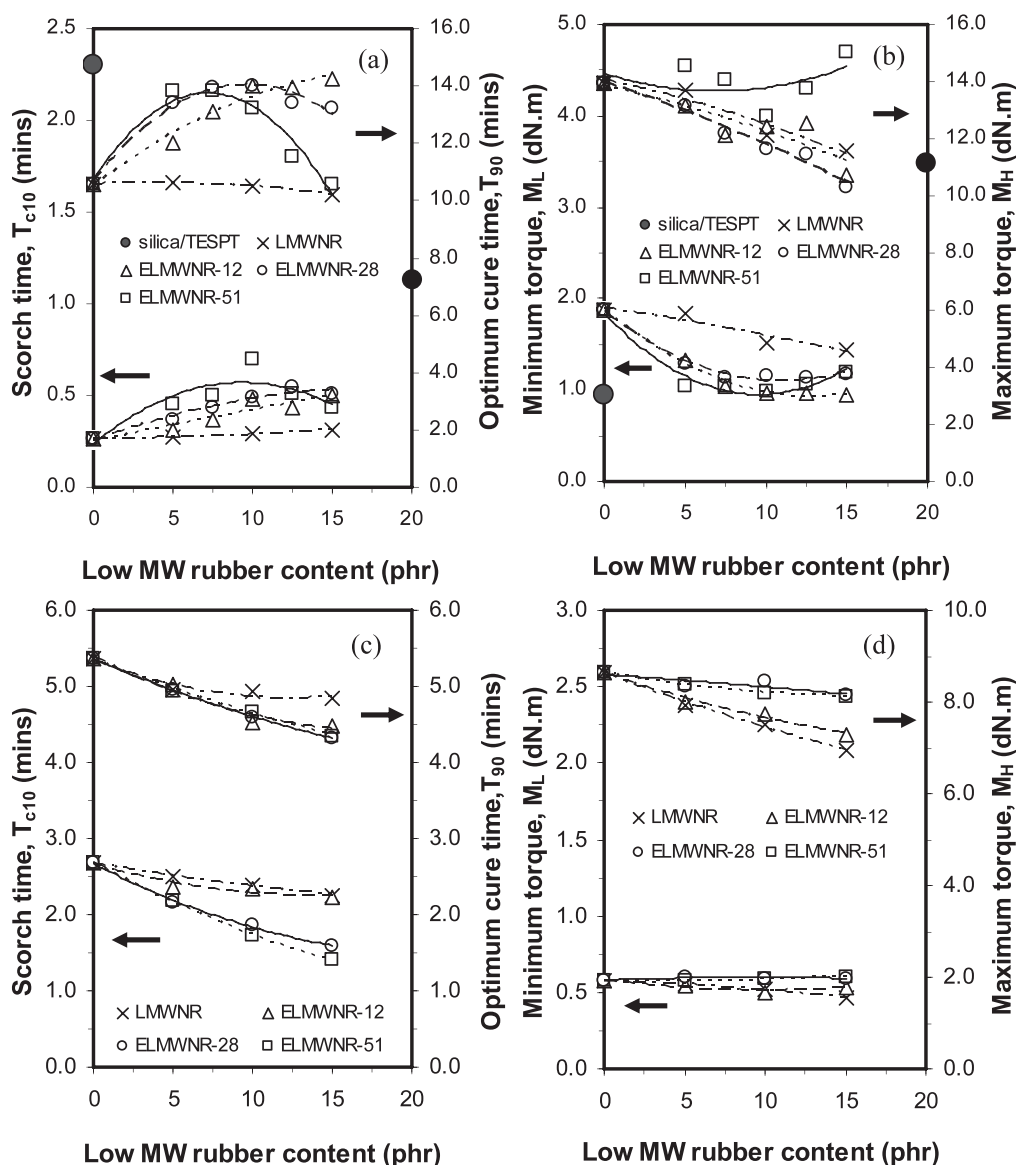


FIG. 8. — Scorch time, cure time, and minimum and maximum torque values of silica-filled (a, b) and carbon black-filled (c, d) NR compounds at various amounts of low molecular weight rubber.

and interactions or bonding between epoxide groups and silanol groups of silica surface in the case of rubber–silica masterbatch. Higher torque increases are observed at increasing temperatures, indicating a higher degree of network formation, either between epoxide groups themselves or between epoxide groups and silanol groups of silica surface, or both.

The kinetics of the self-crosslinking reaction can be calculated by using the kinetic reaction equations, according to Zhang et al.¹³ The k values can be taken from the slope of the plot of $\ln(M_H - M_t)$ versus t (Figure 9c,d). Kinetic parameters, that is, k and activation energy, of the ELMWNRs with 12, 28, and 51 mol% epoxide and silica–ELMWNR masterbatches are summarized in Table

TABLE IV
KINETIC PARAMETERS OF ELMWNRs AND SILICA-FILLED ELMWNR MASTERBATCHES

Sample	Rate constant, $k \times 10^{-2}, \text{min}^{-1}$				$E_a, \text{kJ/mol}$
	160 °C	180 °C	200 °C	220 °C	
ELMWNR-12	4.43	4.70	7.10	8.60	21.19
ELMWNR-28	6.25	9.00	11.00	11.80	18.90
ELMWNR-51	9.40	11.20	13.50	16.10	15.96
ELMWNR-12-silica	5.67	11.23	14.38	8.96	15.24
ELMWNR-28-silica	12.35	14.56	14.80	16.70	8.20
ELMWNR-51-silica	12.20	15.70	15.90	16.70	8.61

IV. The reaction rate constant increases with increasing temperature and epoxide content. The E_a values of the self-crosslinking reaction between epoxide groups and the additional reaction between epoxide groups and silanol groups in the silica–rubber masterbatch can be calculated by using the Arrhenius equation (Eq. 4). The neat ELMWNR with 51 mol% epoxide shows the lowest E_a of the unfilled compounds, whereas the ELMWNR-28 and ELMWNR-51 with silica show similarly a very low E_a . A lower E_a value indicates that the reaction can occur easier at lower temperatures. This result implies that a higher epoxide content would promote a higher degree of self-crosslink reaction. In the absence of silica, the kinetic parameters of the ELMWNRs clearly depend on the epoxide contents. Although in the silica-filled ELMWNR-28 and –51, the similarly low values of k and E_a indicate the faster cross-linking reaction promoted by the epoxide–silanol interactions. This observation supports the upturn in Mooney viscosity (Figure 3), storage modulus difference (Figure 7), and minimum cure torque (Figure 8b) in the silica compounds containing ELMWNR-51 in a concentration > 10 phr.

MECHANICAL PROPERTIES OF VULCANIZATES

The effect of ELMWNR on tensile strength, elongation at break, reinforcement index (M300/M100), and tear resistance of filled NR vulcanizates is presented in Figure 10. The silica–TESPT vulcanizate shows the highest tensile strength, followed by the vulcanizates filled with carbon black and silica with ELMWNR, respectively. The efficient use of TESPT enhances the reinforcement activity of silica in NR through the silanization reaction of the silanol groups of silica with the ethoxy groups of silane during mixing, and by the formation of crosslinks with the rubber molecule during vulcanization. It also has been proven that depending on the availability of sulfur in the compound, TESPT can act as a sulfur donor and increase the crosslink density of the vulcanizates.²² For silica-filled vulcanizates, tensile strength shows an increase up to 10 phr of ELMWNR with 28 and 51 mol% epoxide and then tends to decrease. The reduction of tensile strength as well as reinforcement index, when ELMWNR-28 and –51 were used at high loading, can be attributed to the incompatibility between less polar NR matrix and more polar ELMWNR compatibilizer. The improved dispersion of silica particles obtained by the addition of ELMWNR not only improves processability of the rubber compounds but also influences on the mechanical properties of the vulcanizates. The tensile strength of the vulcanizates is improved when ELMWNR-28 and ELMWNR-51 are added as the compatibilizer, compared with the use of silica without any compatibilizer. The use of ELMWNR-28 at 10 phr shows the highest tensile strength. The incorporation of low molecular weight rubber without epoxide group or a low epoxide content, that is, ELMWNR-12, shows no effect on tensile strength. The poor properties of the compound with an

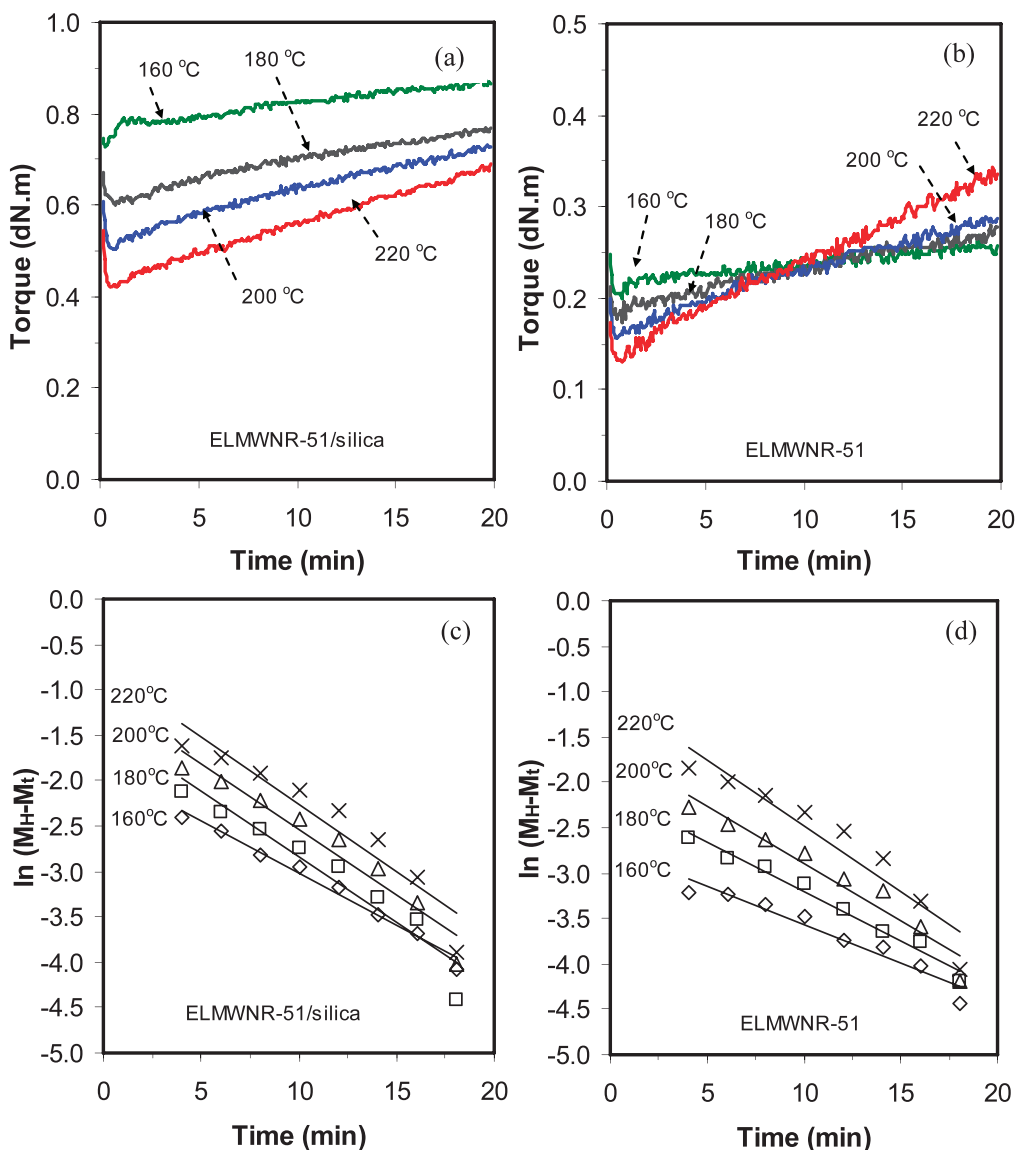


FIG. 9. — Rheograph of ELMWNR-51-silica masterbatch (a) and ELMWNR-51 (b) and plots of $\ln(M_H - M_t)$ vs time (according to Eq. 2) for ELMWNR-51-silica masterbatch (c) and ELMWNR-51 (d) at various temperatures.

insufficient amount of compatibilizer are caused by the filler–filler interaction, incompatibility between silica and rubber and thus poor filler dispersion. Elongation at break of the silica-filled vulcanizates decreases with increasing ELMWNR concentration, whereas for the carbon black-filled material, it is almost independent of low molecular weight rubber content. This difference is attributed to an increased interaction between rubber and silica in the presence of ELMWNR. However, elongation at break of silica-filled vulcanizates is much higher than that of the carbon black-filled vulcanizates. This high value is in accordance with the reinforcement index (Figure 10c). The use of ELMWNR in carbon black-filled vulcanizates has only small effect on tensile strength (Figure 10a) and elongation at break (Figure 10b), but it lowers the reinforcement index

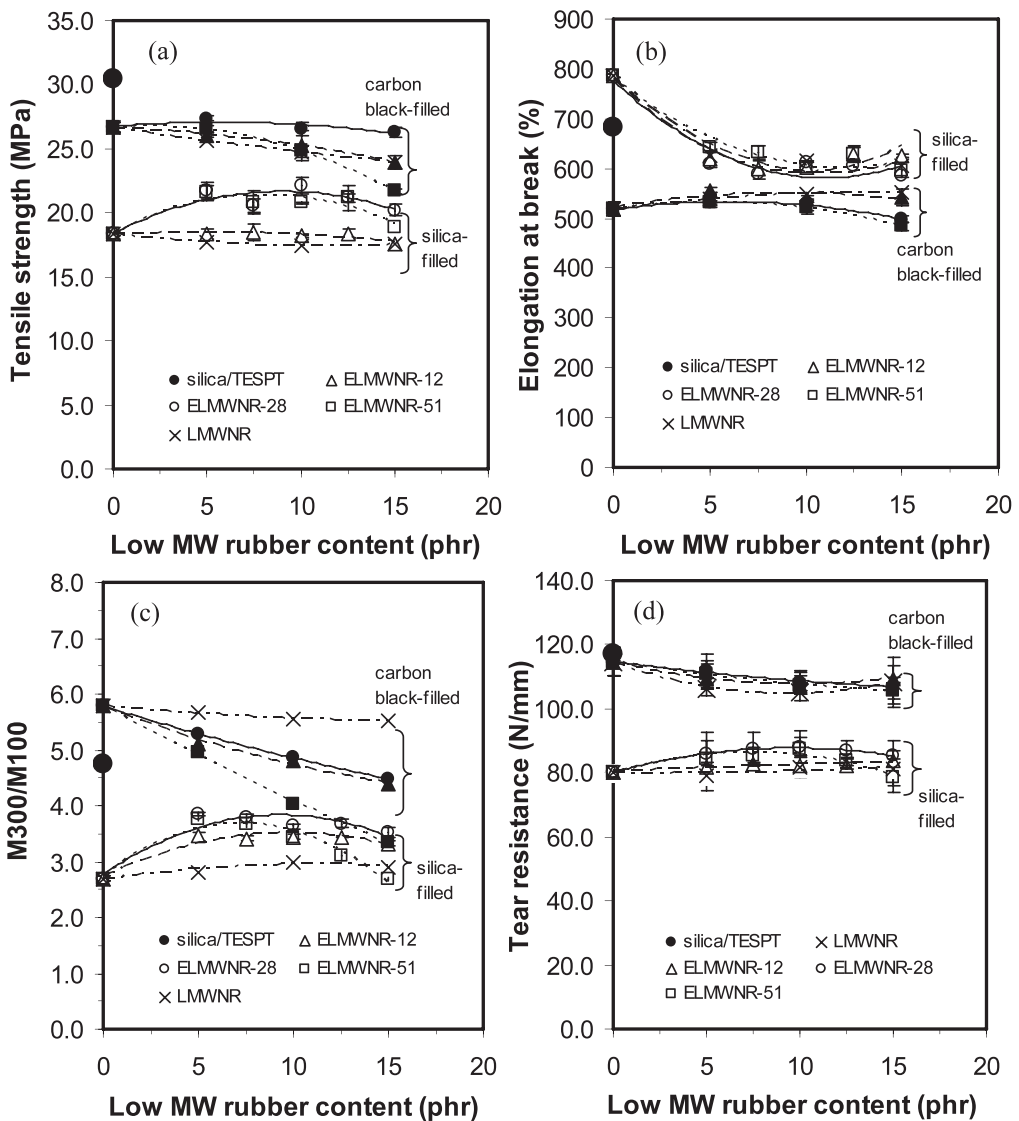


FIG. 10. — Tensile strength (a), elongation at break (b), M300/M100 (c), and tear resistance (d) of silica-filled and carbon black-filled NR vulcanizates.

(Figure 10c). Thus, for the carbon black-filled compound, the addition of ELMWNR shows only a plasticizing effect. Figure 10d displays the tear strength of the various filled NR vulcanizates. The tear strength of carbon black-filled vulcanizates is higher than that of the silica-filled vulcanizates, and an increase in ELMWNR content slightly decreases tear strength. The ELMWNR-28 and ELMWNR-51 compatibilized silica-filled compounds exhibit a marginal improvement of tear strength. Considering the overall mechanical properties, the use of ELMWNR-28 and ELMWNR-51 can improve these properties, but in the case of the silica-filled compounds, they are still lower compared with the use of TESPT. The silica-TESPT combination results in vulcanizates with excellent tensile strength, elongation at break, and tear resistance but with inferior M300/M100 values compared with the carbon black-filled vulcanizates. The carbon black-filled rubber exhibits

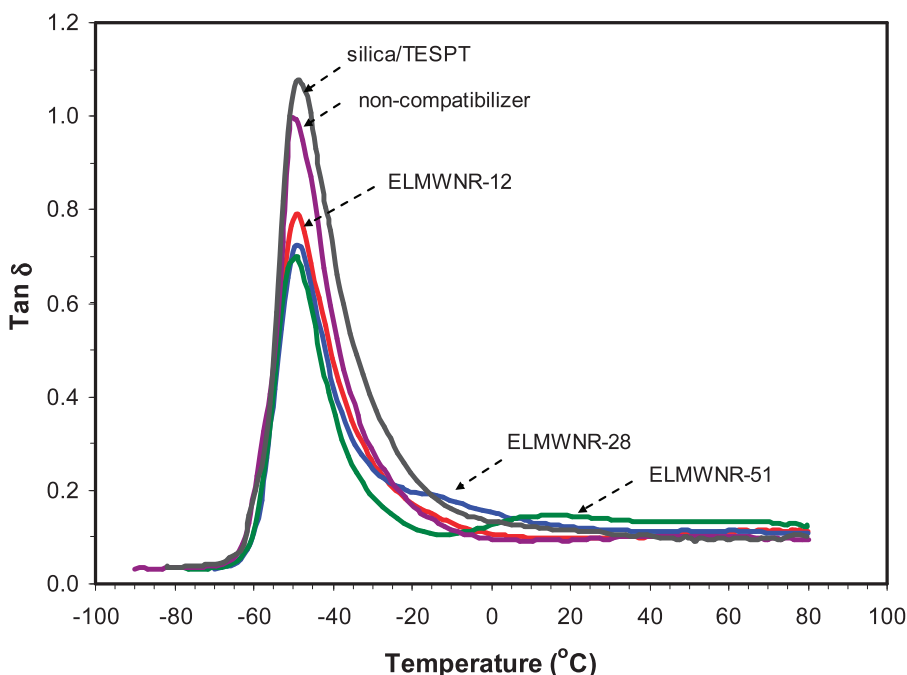


FIG. 11. — Tan δ curves of silica-filled NR vulcanizates containing 10 phr of low molecular weight rubber.

superior M300/M100 values due to a better compatibility of NR with carbon black and strong rubber chain adsorption at the crystal boundaries of carbon black particles. These physical junctions restrict chain mobility in the rubbery matrix outside the interface.²³

DYNAMIC MECHANICAL PROPERTIES OF VULCANIZATES

The dynamic mechanical properties were determined by a DMA viscoanalyser in tension mode at a frequency of 10 Hz and dynamic strain of 0.1%. Figure 11 shows the loss tangent ($\tan \delta$) as a function of the temperature in the range of -90 to 80 °C of the silica-filled vulcanizates. Without any compatibilizer, the rubber vulcanizate shows a glass transition temperature, T_g , of -50 °C. The T_g is slightly shifted to higher temperatures, that is, -48 °C when using TESPT as a coupling agent in the vulcanizate. The increase in the T_g is due to a reduction in the molecular mobility of the polymer chains that are in contact with the filler surfaces.^{24,25} For the silica–TESPT system, this is caused by the increase of filler–rubber interactions and enhanced rubber network formation by additional sulfur in TESPT. The direct bonding of the rubber chains to the filler via the silane coupling reaction reduces local segmental mobility and influences on T_g ,²⁵ as determined by using loss tangent peak. However, the T_g value of the silica-filled NR with ELMWNRs as the compatibilizer remains unchanged compared to the vulcanizate without a compatibilizer. For the ELMWNR-compatibilized systems, the filler–rubber interactions are contributed mainly to the hydrogen bonding between epoxide groups and silanol groups of silica, with a possible small fraction of directly bonded rubber chains on the filler surface via the condensation reaction between the $-OH$ groups of ring-opened epoxidized rubber and silanol groups of silica.⁸ Therefore, it has no influence on the T_g of the vulcanizates. The silica-filled vulcanizates that containing ELMWNRs show a second peak of T_g associated with the T_g of ELMWNR, and a higher T_g at higher epoxide contents. The silica-filled vulcanizate with TESPT displays a larger peak height of $\tan \delta$ compared with the

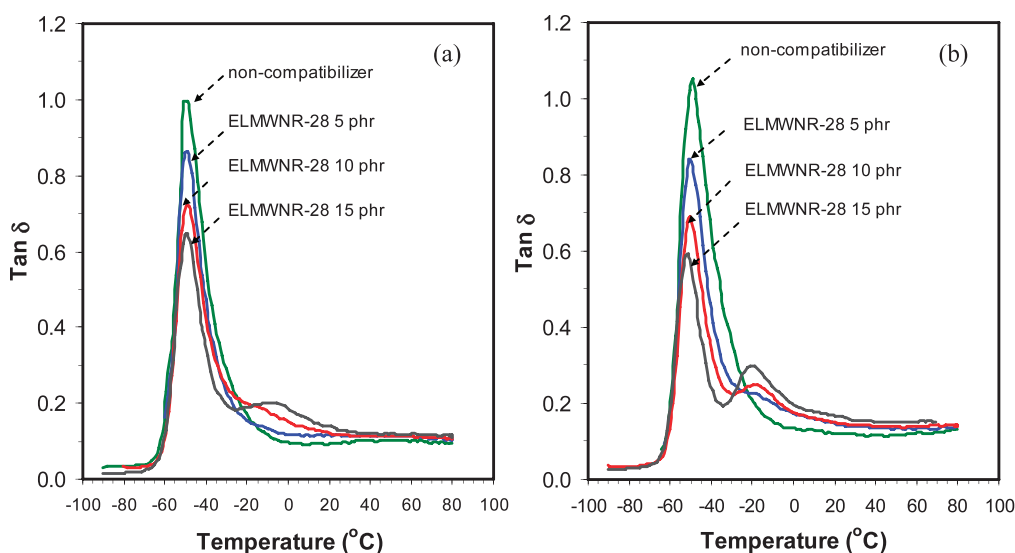


FIG. 12. — Variation of $\tan \delta$ with temperature for silica-filled (a) and carbon black-filled (b) NR vulcanizates with various amounts of ELMWNR-28.

vulcanizates without TESPT. It is well known that filled rubber compounds show a lower $\tan \delta$ value at the maximum [$(\tan \delta)_{\max}$] than gum compounds, because the viscous component of the compound decreases.²⁶ In the filled system, filler–polymer and filler–filler interactions lead to an effective immobilization of the elastomer segments. These segments lose the rubbery behavior, thereby increasing the effective volume of the filler and reducing the viscous component of the compound. When comparing the NR–silica vulcanizates with and without TESPT, the better filler dispersion of the rubber containing TESPT reduces the formation of a secondary filler–filler network and thus decreases the amount of rubber trapped within that filler network. This means that more rubber molecules are involved in segmental relaxation.²⁷ In contrast, the incorporation of 10 phr of ELMWNR in NR vulcanizates leads to lower $\tan \delta$ values at the maximum of the curve due to the reduction of the NR proportion by the addition of ELMWNR and the lower chain mobility of the epoxidized rubber. The height of the $\tan \delta$ peak for ELMWNR-51 compatibilized silica-filled vulcanizates is lower than that of the ELMWNR-28 and ELMWNR-12, respectively. This suggests a higher polar–polar interaction and a possible self-association of epoxide groups in ELMWNR that are less mobile to resonate with the externally applied sinusoidal stress at the glass transition regions. Consequently, the vulcanizates that contain the ELMWNR show higher hysteresis at normal service temperature, from which some applications such as damping materials, for example, rubber engine mounts, can benefit. However, it increases rolling resistance for tires ($\tan \delta$ value measured at 60 °C). Figure 12 shows the effect of the presence of ELMWNR with 28 mol% epoxide as the compatibilizer at various contents in silica- and carbon black-filled vulcanizates on the $\tan \delta$ curve. The same decreasing trend of the $\tan \delta$ values at the maximum of NR phase with increasing ELMWNR-28 contents is observed for both types of vulcanizates. Looking at the second peak of the $\tan \delta$ curve, which represents the T_g of ELMWNR, this peak is broader and less pronounced in the silica compound compared with the carbon black-filled vulcanizate. The T_g also shifts to higher temperature. The interactions between epoxide groups and silanol groups on the silica surface lead to a weaker characteristic peak of epoxidized rubber, and these interactions introduce more physical and chemical crosslinks that result in a shift of T_g to a higher value. In the carbon black-filled compounds, where weak physical interactions are dominant, the T_g peak of ELMWNR is clearly

visible. The difference in the $\tan \delta$ peaks of ELMWNRs in the silica- and carbon black-filled NR vulcanizates evidently supports the occurrence of interactions between epoxide groups and silanol groups of silica.

CONCLUSIONS

Epoxide groups in ELMWNR play a major role in silica-filled NR compounds and affect both processing and vulcanizate properties, due to epoxide–silica interactions. The addition of ELMWNR to a carbon black-filled NR compound shows only a plasticizing effect. Blending of ELMWNR into a silica-filled NR compound decreases Mooney viscosity, complex viscosity, and Payne effect. Epoxide groups can self-crosslink at higher temperatures, and epoxide–silica interaction and coupling are evidenced by a further increase of torque. The optimal mechanical properties of silica-filled NR vulcanizates can be obtained by using 10 phr of ELMWNR-28. ELMWNR shows its own T_g in the NR vulcanizates, but due to the interaction between epoxide and silanol groups, the T_g peak of ELMWNR in a silica-filled compound is less pronounced compared with that of the carbon black-filled compound.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support from the Thailand Research Fund through the Royal Golden Jubilee Ph.D. Program (grant number PHD/0268/2552).

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[Received May 2013, Revised August 2013]