Effect of norbornyl modified soybean oil on CB-filled chloroprene rubber

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ABSTRACT: Carbon black (CB)-filled chloroprene rubber (CR) compounds and vulcanizates containing naphthenic oil (NO), soybean oil (SO), and two different levels of norbornyl modified soybean oil (MSO) were prepared and investigated. The MSO was prepared through the reaction of SO and dicyclopentadiene (DCPD) at different ratios. Various properties including gel fraction, crosslink density, bound rubber fraction, curing behavior, thermal, mechanical, and aging properties of CB-filled CR containing different oils were compared. It was observed that the addition of SO and MSO could benefit the dispersion of the filler, lower the glass transition temperature, and increase the thermal stability of the CB-filled CR/MSO compounds and vulcanizates, and also slightly decrease the crosslink density of the CB-filled CR/MSO vulcanizates compared to that of the CR/NO vulcanizate. With the increase of the modification level of the MSO, the curing time of the CB-filled CR/MSO compounds was found to be decreased, the tensile property, tear strength, abrasion resistance, and aging resistance of the CB-filled CR/MSO vulcanizates were improved compared with those of the CB-filled CR/NO vulcanizate. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43809.

INTRODUCTION

Chloroprene rubber (CR), also known as "Neoprene," was first introduced by DuPont in 1931. CR is polymerized mainly from chloroprene monomers. Various modifiers and stabilizers are used during the polymerization of CR to meet different needs. CR exhibits outstanding physical properties with resistance to hydrocarbon oils, heat, ozone, and weather. It is also more flame retardant than most general purpose hydrocarbon-based elastomers. Due to its unique combination of properties, CR is used in a variety of applications including automotive parts, construction parts, cable jackets, coated fabrics, conveyor belts, hoses, etc.

Some types of CR are manufactured by the copolymerization of chloroprene and sulfur, stabilized with thiuram disulfide to control the molecular weight,[1] such as the Neoprene G type by DuPont. Although it was reported that the CR could be crosslinked by sulfur and also thermovulcanization,[2] the conventional sulfur curing systems used for diene rubbers cannot provide satisfactory performance of the vulcanizates. This is due to the electronegative chlorine atoms, which can inhibit the electrophilic substitution that is common for hydrocarbon-based diene rubbers. Metal oxides such as zinc oxide (ZnO) and magnesium oxide (MgO) are widely used for curing CR, and they are sufficient for curing G types CR in the absence of other organic accelerators. However, to achieve a better performance and a faster curing of CR compounds, ethylene thiourea (ETU) is widely used. The curing mechanism of CR compounds were studied by many researchers.[3–6] It is generally accepted that the major curing site of CR is the tertiary allylic chlorine atom. The ZnO can generate crosslinks between two chloroprene units via a cationic mechanism, and the ETU can crosslink the CR alone and also in combination with ZnO. CR can also be crosslinked with other ingredients such as amino acid derivatives,[7] thiophosphoryl disulfides,[8] and fillers.[9,10] CR can also be blended with other elastomers to improve properties such as low temperature flexibility and mechanical properties. Zheng et al. studied the blend of CR with butadiene rubber (BR).[11] It was found that the addition of BR could increase the low temperature resistance and electrical insulation but decrease the mechanical properties of the blend. Das et al. investigated the physical and electrical properties of CR and natural rubber (NR) blends.[12] It was observed that the blend exhibited significant improvement on curing behavior and physical property.

Similar to other elastomers, plasticizers are frequently added to CR to facilitate processing, enhance specific properties, and reduce cost. Highly aromatic oils are compatible with CR, however, it has been considered as carcinogenic.[13] Naphthenic oil (NO) is a safer petroleum plasticizer and can also be used in

Table I. Compounding Recipes

Ingredients	Amount (phr)
CR	100
Oil	15
CB	50
MgO	4
ZnO	5
Stearic Acid	1
ETU	0.75

CR compounds at low level. However, the production and use of these petroleum-based plasticizers heavily rely on petroleum oil resource. Soybean oil (SO) is an environmental friendly, low cost, and renewable oil resource. Many researchers studied the effect of SO in different rubber systems such as SBR, NR/BR/SBR blend, and EPDM.[14–17] It was found that the rubber products containing SO exhibited similar properties compared with rubbers containing conventional petroleum plasticizers. Our previous research showed that the modification of SO by introducing norbornyl groups could increase the reactivity of the SO, the CB-filled CR compounds, and vulcanizates compounded with modified soybean oil (MSO) exhibited excellent thermal and mechanical properties.[17]

In the present study, norbornyl modified SO, due to its environmental advantages over NO, is added into the CR compounds to extend a further utilization of the renewable and environmentally friendly oil by rubber industry. The aim is to investigate and compare the effect of NO, SO, and MSO on CB-filled CR compounds and vulcanizates. The rheological properties, gel fraction, crosslink density, bound rubber fraction, thermal properties, curing behavior, tensile property, hardness, abrasion resistance, tear strength, and aging properties are studied. To the best of our knowledge, the use of SO and MSO in CR was not reported in available literature.

EXPERIMENTAL

Materials

A CR under the trade name of Neoprene GW manufactured by DuPont (Wilmington, DE) was used. According to the manufacturer, sulfur is copolymerized with chloroprene monomer during the production. Carbon black (CB) N550 from Evonik Corporation (Parsippany, NJ) with a Brunauer–Emmet–Teller (BET) surface area of 40 m^2/g was used as a filler. ZnO under the trade name of Zinc Oxide RGT-M, MgO under the trade name of Elastomag 170, N-octadecanoic acid (stearic acid) under the trade name of Stearic Acid Rubber Grade, and ETU Akroform ETU-75/EPR/P from Akrochem Corporation (Akron, OH) were used as compounding additives. For conventional petroleum plasticizer, a NO under the trade name Plasticizer LN by Akrochem Corporation (Akron, OH) was used. A technical grade RBD SO manufactured by Cargill Industrial Oils & Lubricants (Minneapolis, MN) was used. The SO was also modified through the reaction with dicyclopentadiene (DCPD) of different ratios. During the modification, the C═C double

bonds on the fatty acid chains of the SO were converted into norbornyl groups. The C═C double bonds on the norbornyl groups exhibited higher reactivity than those on the fatty acid chains.[18] The preparation and characterization of the MSO were described in our previous study.[17] MSO with modification levels of 11% (11MSO) and 33% (33MSO), which means about 11% and 33% of the C═C bonds in the SO were converted into norbornyl groups, were selected in this study to show the effect of MSO on the rubber properties.

Compounding and Curing

The compounding recipe is shown in Table I and the compounding procedure is shown in Table II. The CR gum and other ingredients were compounded using an 85-mL Brabender mixer (Model Plasti-corder, C.W Brabender Instruments, Inc. South Hackensack, NJ). A rotor speed of 60 rpm and a setup temperature of 60 °C were used. Then the ZnO was mixed with compounds on a laboratory size two roll mill (Dependable Rubber Machinery Co., Cleveland, OH) for 20 passes. A rotor speed of 20 rpm, a gap size of 3 mm, and a cooling water temperature of 40 °C were used. The final compounds were stored overnight before the vulcanization.

The curing curves of various CB-filled CR compounds with curatives were obtained from an Advanced Polymer Analyzer (APA 2000, Alpha Technologies, Akron, OH) at a temperature of 160 °C, a frequency of 10.5 rad/s, and a strain amplitude of 4.2%. The curing time T_{95} of various CB-filled CR compounds with curatives was calculated based on the curing curves. Same test was also applied to CB-filled CR compounds without any curatives. An electrically heated compression-molding press (Carver, Wabash, IN) was used for vulcanization at a temperature of 160 °C and a pressure of 15 MPa. Vulcanized slabs with a dimension of 150 mm × 150 mm and a thickness range of 2.0–2.2 mm were obtained. Cylindrical samples with a diameter of 16 mm and a length of 12 mm for abrasion tests were also prepared.

Characterization

The Soxhlet extraction method was applied to measure the gel fraction and crosslink density of various CB-filled CR vulcanizates and also the bound rubber fraction of various CB-filled CR compounds. Benzene was selected as the solvent. CR vulcanizate around 0.8 g was first weighed, then the sample was placed inside a Whatman cellulose extraction thimble in the Soxhlet extractor heated on a heater. The weight of the swollen vulcanizate was measured after an extraction time of 48 h. Then the sample was dried in a heated vacuum oven at 65 °C for

Table II. Compounding Procedures

Time (min)	Action
0	Add CR
1	Add MgO + Stearic Acid
2	Add Oil
2.5	Add CB
11	Add ETU
12	Dump

24 h. Finally the weight of dry rubber was measured. The gel fraction was determined by the final weight of dried vulcanizate over the initial weight of the vulcanizate. The crosslink density was calculated using the Flory–Rehner equation[19] and the Kraus correction.[20] The bound rubber fraction was calculated by the weight of the rubber after the extraction over its initial weight within the compound. Various CB-filled CR compounds were stored for 3 weeks at room temperature prior to the bound rubber test.

Rheological properties of various CB-filled CR compounds were measured by the APA 2000. A frequency sweep was performed in a frequency range from 0.06 to 200 rad/s (logarithmic mode) at a temperature of 90 °C and a strain amplitude of 4.2%. The frequency dependence of the storage (G'), loss (G'') moduli, tan δ, and complex viscosity of various CB-filled CR compounds were measured. A strain sweep was performed in a strain amplitude range from 0.3% to 200% at a frequency of 0.6 rad/s and a temperature of 90 °C. The G', G'', and tan δ of CB-filled CR compounds as a function of strain amplitude were measured.

Thermogravimetric analysis (TGA Q50, TA Instruments, New Castle, DE) and differential scanning calorimeter (DSC Q200, TA Instruments, New Castle, DE) were used to evaluate the thermal properties of various CB-filled CR compounds and vulcanizates. The TGA curves in a range from room temperature to 700 °C at a heating rate of 20 °C/min were obtained under nitrogen atmosphere. The DSC curves in a temperature range from −90 °C to 30 °C at a heating rate of 10 °C/min were obtained under a nitrogen atmosphere.

Tensile, tear, hardness, and abrasion tests were performed for various CB-filled CR vulcanizates. The tensile tests were conducted at room temperature according to ASTM D412 using an Instron tensile tester (Model 5567, Instron, Canton, MA) equipped with an extensometer. At least five samples cut with an ASTM D412 Die C were tested and a crosshead speed of 500 mm/min was used. Tear strength of various CB-filled CR vulcanizates was measured using the Instron tensile tester according to ASTM D624. Hardness of various CB-filled CR vulcanizates was measured at room temperature using a Durometer Shore A according to ASTM 2240. The abrasion test was conducted using a Zwick Abrasion Tester 6102 according to DIN 53516. A load of 10 N and a pathway of 40 m were applied to the specimens without specimen rotation. The weight loss of the sample after the abrasion was measured. The densities of various CB-filled CR vulcanizates were measured using an Accupyc 1340 Helium Pycnometer (Micromeritics Instrument Corp., Norcross, GA). Then the volume loss of the abraded sample was calculated to report the abrasion resistance. At least four specimens of each type of vulcanizate were used in the test.

To study the aging effect of various CB-filled CR vulcanizates, a hot air aging test was performed according to ASTM D573 at 100 °C for 48 h. The tensile properties, tear strength, and hardness of the aged CB-filled CR vulcanizates were measured using the same conditions as described above. The volume of the same sample before and after the aging was measured using a pycnometer. The changes of properties in percentages of various CB-filled CR vulcanizates were compared.
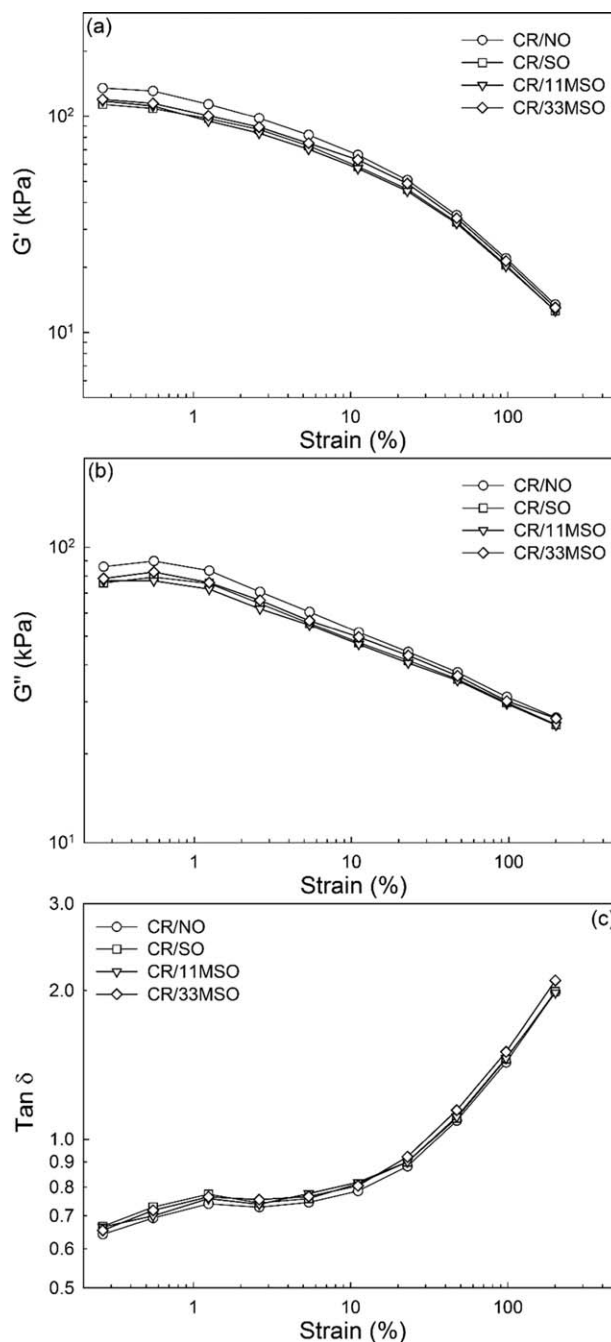

Figure 1. Storage (a), loss moduli (b), and tan δ (c) as a function of strain amplitude of various CB-filled CR compounds at 90 °C.

RESULTS AND DISCUSSION

Rheological Properties

Figure 1 shows the dependence of G' [Figure 1(a)], G'' [Figure 1(b)], and tan δ [Figure 1(c)] on the strain amplitude of various CB-filled CR compounds. From Figure 1(a), it is observed that all CB-filled CR compounds exhibit a reduction of G' with the increase of strain amplitude, which is also known as the Payne effect.[21] The CB-filled CR/SO and both CR/MSO compounds show similar G' values at low strain amplitudes. However, the CB-filled CR/NO compound exhibits a slightly
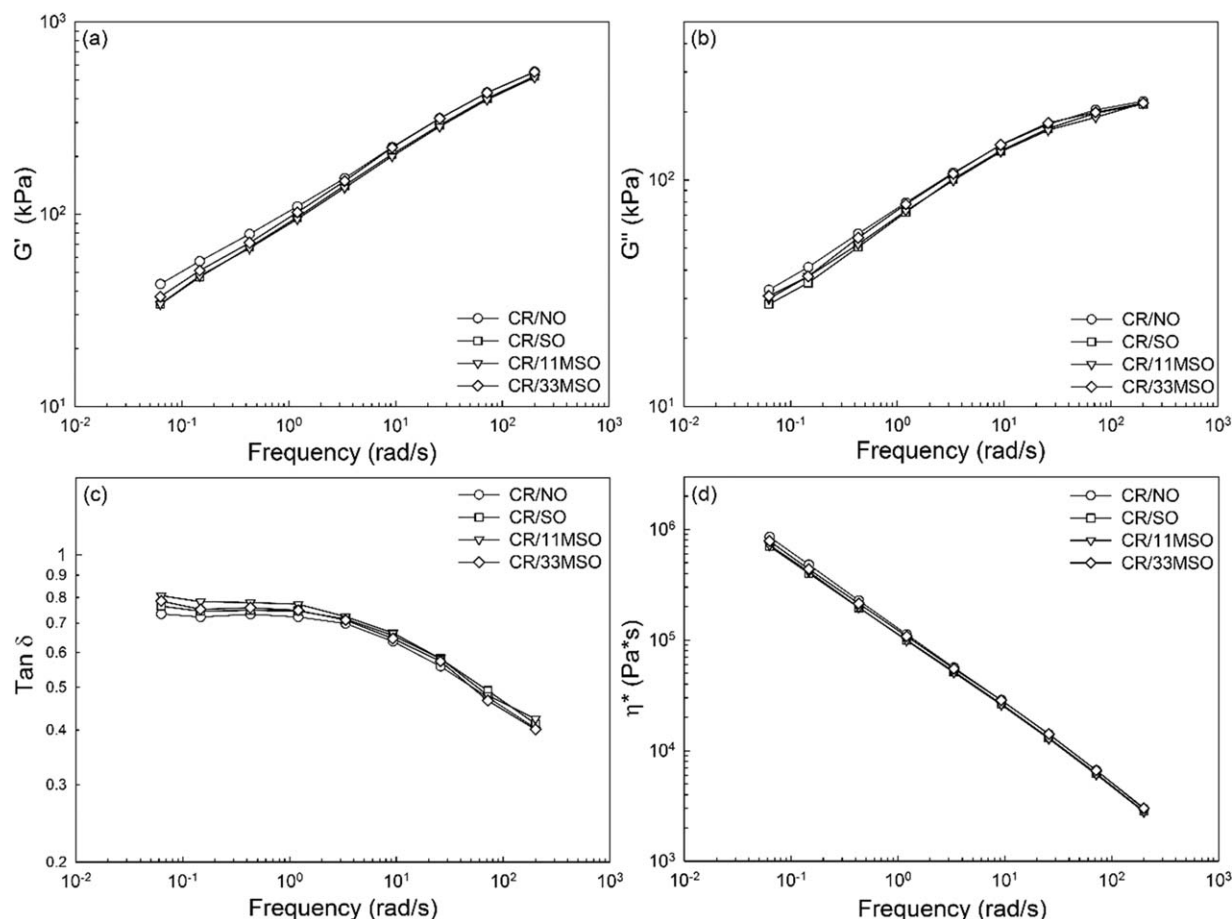
Figure 2. Storage (a), loss moduli (b), tan δ (c), and complex viscosity (d) as a function of frequency of various CB-filled CR compounds at 90°C.

higher G' at low strain amplitudes compared to those of the CB-filled CR/SO and CR/MSO compounds, indicating a stronger filler–filler interaction. At high strain amplitudes, all compounds exhibit similar values of G', which indicates a similar rubber–filler interaction. Figure 1(b) shows that the G'' values of various CB-filled CR compounds exhibit a small peak at a strain amplitude around 0.5%, and then the G'' values decrease rapidly with further increase in strain amplitudes. The value of G'' is dominated by the energy loss during dynamic strain, it is controlled by the breakdown and reformation of the filler network.[22] The CB-filled CR/NO compound exhibits a higher G'' value than other compounds at low strain amplitudes, indicating a more developed filler network breaking down and reforming during the dynamic strain. Figure 1(c) shows the tan δ of various CB-filled CR compounds. The value of tan δ is dominated by the state of filler network.[23] It can be observed that all compounds exhibit similar behavior. A peak of tan δ at a strain amplitude around 1.25% is observed, which corresponds to the breakdown of CB network. At high strain amplitudes, the tan δ values increase rapidly with the increase of strain amplitudes, indicating a further breakdown of rubber structure such as rubber–filler interaction. It is possible that the usage of SO and MSO can help the dispersion of CB in the CR matrix, which reduces the filler–filler interaction.

Figure 2 shows the frequency dependences of the G' [Figure 2(a)], G'' [Figure 2(b)], tan δ [Figure 2(c)], and complex viscosity (d) of various CB-filled CR compounds. From Figure 2(a,b), it is observed that the CB-filled CR compounds containing different oils exhibit similar frequency dependence of G' and G''. In particular, the CB-filled CR/NO compound exhibit the highest G' at low frequency region. This is due to the strong filler–filler network which can restrain the relaxation of the polymer chains, leading to a higher G' at low frequency region.[24] This result is in agreement with the strain sweep data shown in Figure 1. Figure 2(c) depicts the tan δ as a function of frequency of various CB-filled CR compounds. It is observed that various CB-filled CR compounds show similar tan δ values. All the compounds exhibit a plateau at lower frequency region, and a decrease at higher frequency region, indicating that the materials are approaching the rubbery plateau. Figure 2(d) shows the complex viscosity as a function of frequency of various CB-filled CR compounds. Various CR compounds exhibit a significant decrease of the complex viscosity with the increase of frequency. The addition of different oils gives negligible differences in the complex viscosity values. It can be concluded that the usage of SO and MSO has little influence on the rheological properties of the CB-filled CR compounds, indicating the addition of SO and MSO will not change the processability of CB-filled CR compounds during the processing.
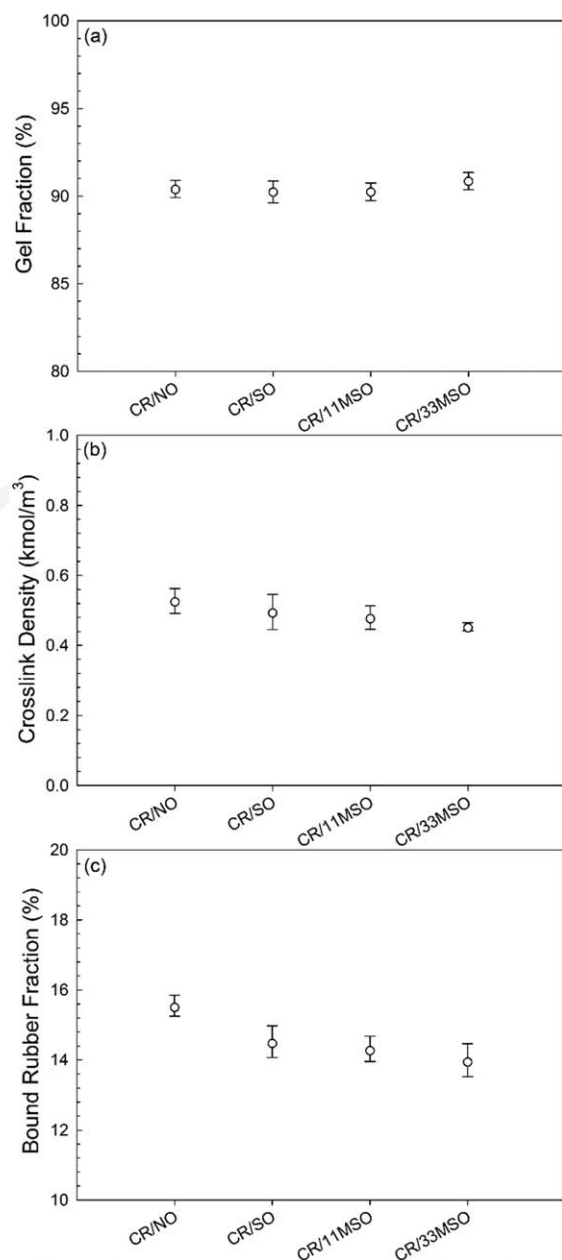
Figure 3. Gel fraction (a), crosslink density (b) of various CB-filled CR vulcanizates and bound rubber fraction (c) of various CB-filled CR compounds.

Gel Fraction, Crosslink Density, and Bound Rubber

Figure 3 shows gel fraction [Figure 3(a)], crosslink density [Figure 3(b)] of various CB-filled CR vulcanizates, and bound rubber fraction [Figure 3(c)] of various CB-filled CR compounds. It is observed from Figure 3(a) that the CB-filled CR/NO, CR/SO, and CR/11MSO vulcanizates have similar gel fraction, and with the increase of the modification level, the CR/33MSO vulcanizate exhibits a slightly higher gel fraction. Figure 3(b) shows that the CB-filled CR/NO vulcanizate exhibits the highest crosslink density. The CB-filled CR/SO and CR/11MSO vulcanizate have a similar crosslink density which is slightly lower than that of the CR/NO vulcanizate. The CB-filled CR/33MSO

vulcanizate exhibit the lowest crosslink density. It is observed from Figure 3(c) that the CB-filled CR/NO exhibit the highest bound rubber fraction, followed by the CB-filled CR/SO compound. With the increase of the modification level, the CB-filled CR/MSO compounds exhibit slightly decreased bound rubber fractions. The previous studies showed that the SO and MSO could react with curatives, slightly increase the gel fraction, and decrease the crosslink density of diene rubber vulcanizates compared to rubber vulcanizates containing conventional petroleum oils.[15–17] The increase of the gel fraction and decrease of the crosslink density of CB-filled CR/MSO vulcanizates is possibly due to the reaction of the highly reactive MSO with the sulfur
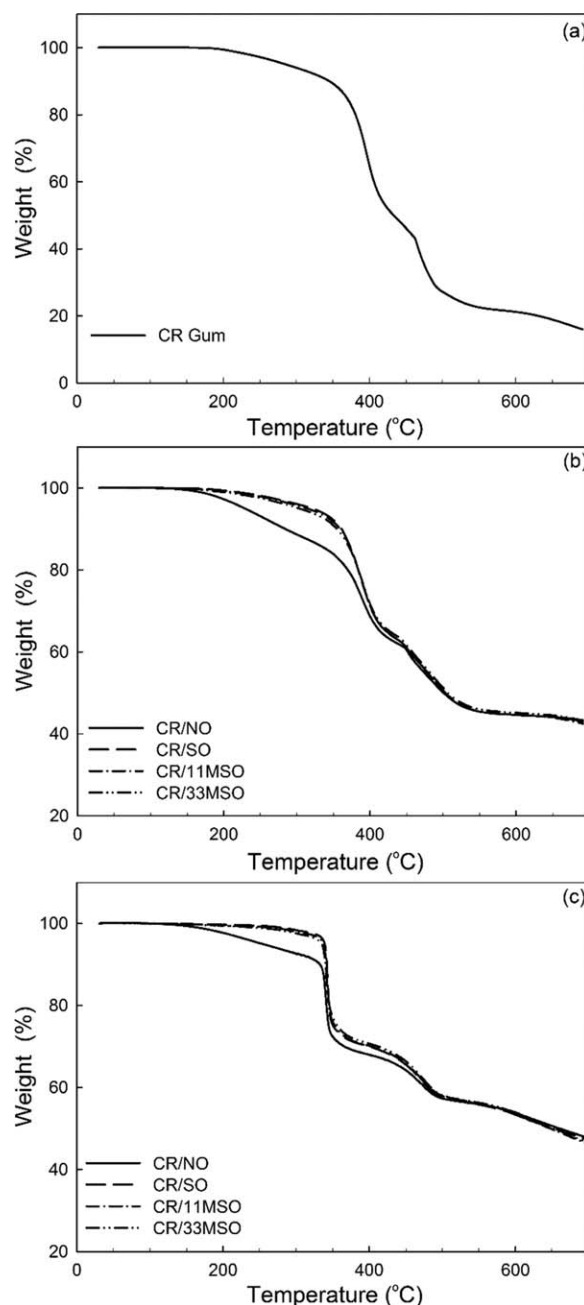

Figure 4. TGA curves of CR gum (a), various CB-filled CR compounds (b), and vulcanizates (c).
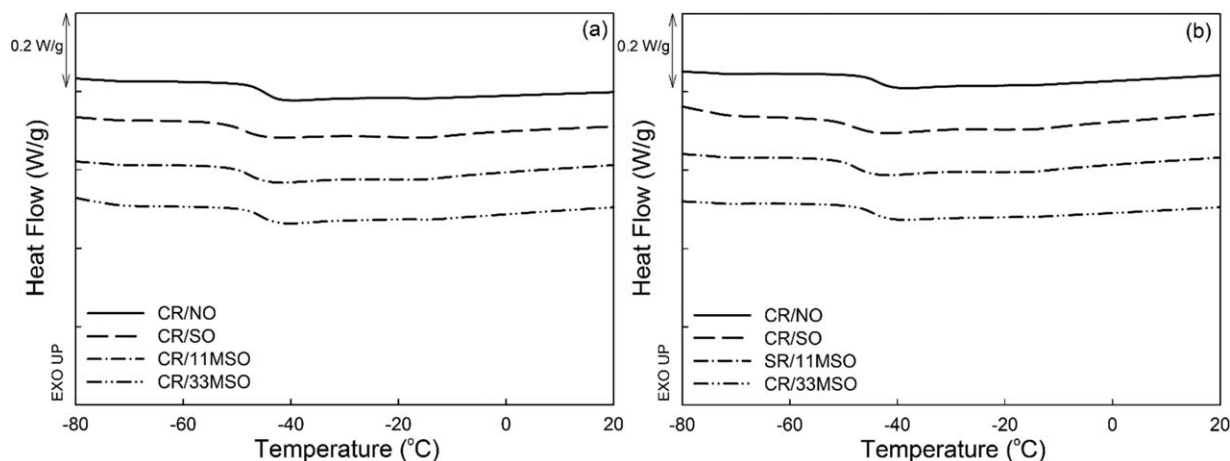
Figure 5. DSC curves of various CB-filled CR compounds (a) and vulcanizates (b).

Table III. Glass Transition Temperature of Various CB-Filled CR Compounds and Vulcanizates and Curing Time of Various CB-Filled CR Compounds

	T_{95} (min)	Compounds T_g (°C)	Vulcanizates T_g (°C)
CR/NO	19.7	−44.3	−43.9
CR/SO	19.2	−48.6	−48.0
CR/11MSO	17.3	−47.7	−47.1
CR/33MSO	12.0	−45.2	−44.3

and also the thiuram disulfide in the CR gum. The possible reaction will be discussed later.

Thermal Properties

Figure 4 shows the TGA curves of CR gum [Figure 4(a)], CB-filled CR compounds [Figure 4(b)], and CB-filled CR vulcanizates [Figure 4(c)]. From Figure 4(a), it is observed that the CR gum starts to slowly lose weight at 200 °C and then starts to degrade rapidly at about 350 °C. Above 500 °C, the CR gum has a second stage of slow degradation, and at 700 °C the CR gum

has a residue of 16%. The first stage of weight loss is due to the dehydrochlorination and then the autocatalytic chloroprene chain pyrolysis of CR, which was well studied by Kaiersberger et al.[25] The second stage of weight loss at 500 °C is due to the high pyrolysis shoot of CR. Similar effect was also observed in the previous study.[26] Figure 4(b) shows the TGA curves of CB-filled CR compounds containing various oils. The CB-filled CR compounds exhibit the thermal behavior similar to the CR gum. However, the CB-filled CR/NO compound exhibits a significant weight loss at a lower temperature due to the low thermal stability of the NO. On the contrary, the CB-filled CR/SO and CR/MSO compounds exhibit much better thermal stability than that of the CR/NO compound before the rapid degradation of the rubber matrix at high temperatures. The better thermal stability of the SO and MSO was also reported in previous studies.[16,17] It is observed from Figure 4(c) that the CB-filled CR/SO and CR/MSO vulcanizates exhibit a slightly better thermal stability below 350 °C than the CB-filled CR compounds. This is probably due to the addition of SO, MSO, steric acid, ZnO, and MgO that can slow down the autocatalytic decomposition of the rubber matrix. Similar to that of the CB-filled CR/NO compound, the CB-filled CR/NO vulcanizate starts to lose
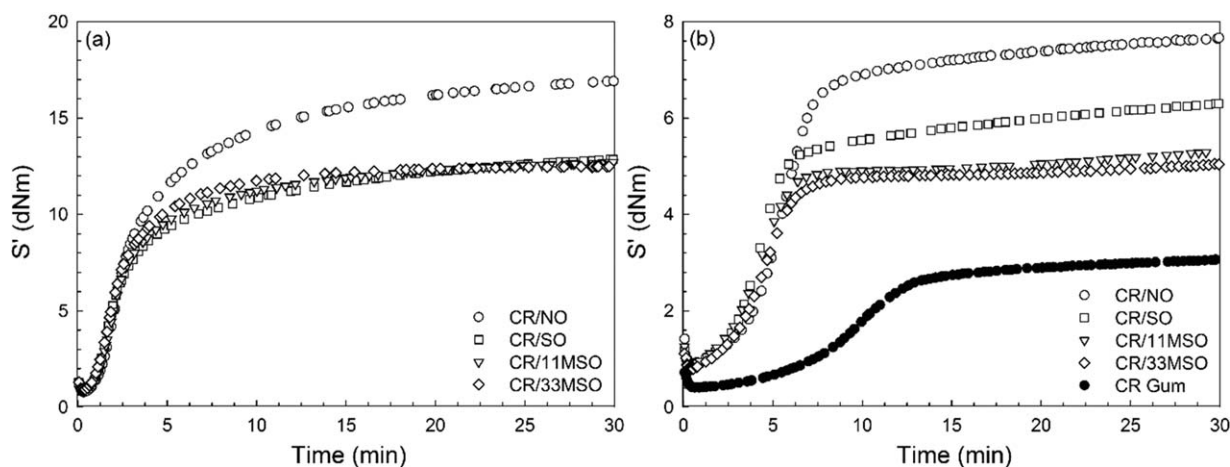

Figure 6. Curing curves of various CB-filled CR compounds with (a) and without (b) curatives.
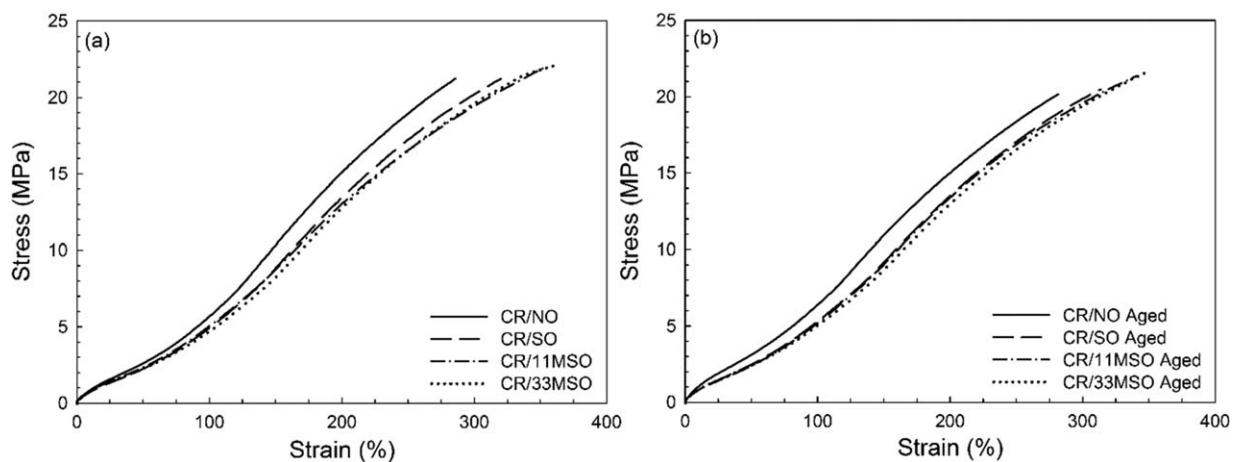
Figure 7. Stress–strain curves of various CB-filled CR vulcanizates before aging (a) and after aging (b).

weight at about 170 °C due to the evaporation of the NO. After the temperature reaches 350 °C, all the CB-filled CR vulcanizates exhibit similar weight loss process. In general, the addition of SO and MSO can enhance the thermal stability of CB-filled CR compounds and vulcanizates compared with conventional NO plasticizer. This advantage will improve the safety of the processing and application of rubber.

Figure 5 shows the DSC curves of various CB-filled CR compounds [Figure 5(a)] and vulcanizates [Figure 5(b)]. Table III shows the glass transition temperature T_g determined from the DSC curves. It is observed from the DSC curves that various CB-filled CR compounds and vulcanizates exhibit similar thermal behavior upon heating. From Table III, it is indicated that the CB-filled CR compound and vulcanizate containing NO

Table IV. Tensile Properties, Tear Strength, and Hardness of Various CB-Filled CR Vulcanizates Before and After Aging and Their Relative Change

|						
			Original Properties			
	M100 (MPa)	M300 (MPa)	E at B (%)	Tensile strength (MPa)	Tear strength (kN/m)	Hardness (Shore A)
CR/NO	5.69 ± 0.13	—	288.0 ± 1.8	21.3 ± 0.3	38.52 ± 0.79	74
CR/SO	4.96 ± 0.09	19.99 ± 0.20	321.7 ± 7.0	21.0 ± 0.3	40.45 ± 1.04	71
CR/11MSO	4.99 ± 0.07	19.59 ± 0.14	355.8 ± 8.4	22.2 ± 0.4	43.13 ± 1.10	72
CR/33MSO	4.79 ± 0.14	19.53 ± 0.26	362.0 ± 9.6	22.2 ± 0.5	45.69 ± 0.73	73
			Aged Properties (100 °C, 48 h)			
	M100 (MPa)	M300 (MPa)	E at B (%)	Tensile strength (MPa)	Tear strength (kN/m)	Hardness (Shore A)
CR/NO	6.42 ± 0.09	—	281.5 ± 6.7	20.2 ± 0.3	37.29 ± 0.92	78
CR/SO	5.33 ± 0.03	19.81 ± 0.10	313.3 ± 1.6	20.5 ± 0.1	40.00 ± 1.23	74
CR/11MSO	5.20 ± 0.07	19.49 ± 0.15	344.1 ± 11.6	21.6 ± 0.5	42.55 ± 0.77	73
CR/33MSO	5.05 ± 0.03	19.38 ± 0.14	350.6 ± 8.6	21.6 ± 0.6	44.58 ± 0.34	74
			Percentage of Change			
	M100 (%)	M300 (%)	E at B (%)	Tensile strength (%)	Tear strength (%)	Hardness (%)
CR/NO	+12.8	—	−2.3	−5.2	−3.2	+5.4
CR/SO	+8.1	−0.9	−2.6	−2.4	−1.1	+4.2
CR/11MSO	+4.2	−0.5	−3.3	−2.7	−1.3	+1.4
CR/33MSO	+5.4	−0.8	−3.1	−2.7	−2.4	+1.4
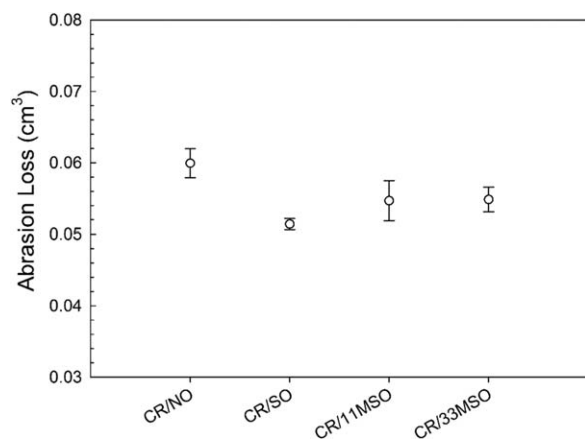
Figure 8. Abrasion loss of various CB-filled CR vulcanizates.

exhibit the highest T_g compared with the CR compounds and vulcanizates containing SO and MSO. The CB-filled CR/SO compound and vulcanizate exhibit the lowest T_g. Similar effect was also observed in the previous study on EPDM/SO,[16] which showed that SO had better plasticization effect than conventional petroleum-based plasticizer. With the increase of the modification level, the T_g of CB-filled CR/MSO compounds and vulcanizates is increased. This effect is due to the modification of the SO which introduces norbornyl groups on the fatty acid chain. Similar effect was also observed in the previous study.[17] It is also noticed that the T_g of the CB-filled CR vulcanizates slightly increases compared to those of the CB-filled CR compounds due to the vulcanization. In general, the addition of SO and MSO to the CB-filled CR compounds and vulcanizates can achieve a lower T_g value than NO, which can benefit the low temperature flexibility of the CR product.

Curing Behaviors

Figure 6 shows the curing curves of various CB-filled CR compounds with curatives [Figure 6(a)] and CB-filled CR compounds and pure CR gum without curatives [Figure 6(b)]. Table III shows the curing time T_{95} calculated from the curing curves shown in Figure 6(a). It is observed from this figure that all the CB-filled CR compounds exhibit a similar scorching time and minimum torque (M_L). The CB-filled CR/NO compound exhibits the highest maximum torque (M_H), while the CB-filled CR/SO and CR/MSO compounds exhibit similar values of M_H which are lower than that of the CB-filled CR/NO compound. The CB-filled CR/SO compound has a T_{95} of 19.2 min, slightly shorter than that of the CB-filled CR/NO compound (19.7 min). With the increase of the modification level, the CB-filled CR/11MSO and CR/33MSO compounds have a shorter T_{95}, with times being 17.3 min and 12.0 min, respectively.

There are two possible reasons that the CB-filled CR/NO compound exhibits a higher M_H than those of the CB-filled CR/SO and CR/MSO compounds. First, the filler–filler interaction of CB-filled CR/NO compound is slightly higher than those of the CR/SO and CR/MSO compounds and gives a higher torque, which was reflected by a higher value of G' in Figure 1(a). Second, the reactive SO and MSO can react with sulfur and thiuram disulfide in the CR gum, leading to a lower crosslink

density, which is shown in Figure 3(b). In order to prove this hypothesis, CR gum and CR compounds containing different oils were heated to a temperature of 160 °C corresponding to the curing test. Similar to the previous study,[2] the present study shows that the crosslinking of CR by sulfur copolymerized into CR during its manufacturing occurs during the vulcanization, as shown in the curves in Figure 6(b). In the absence of ZnO/MgO in curing system, the CB-filled CR compounds still can be partially cured by the sulfur and thiuram disulfide in the CR gum. The CB-filled CR/NO compound exhibit the highest torque, followed by the CR/SO compound. With an increase of the modification level, the CR/11MSO and CR/33MSO exhibit a lower maximum torque. This is due to the increasing consumption of sulfur with the increasing modification level of MSO.[17] The observation is in agreement with the gel fraction and crosslink density data shown in Figure 3.

Mechanical Properties

Figure 7 shows the stress–strain curves of various CB-filled CR vulcanizates before aging [Figure 7(a)] and after aging [Figure 7(b)]. The data of M100, M300, elongation at break, tensile strength, tear strength, and hardness before and after the aging of various CB-filled CR vulcanizates are shown in Table IV. Also the relative changes of properties after aging are shown in this table in percentages. From Figure 7(a) and Table IV, it is observed that the CB-filled CR/NO vulcanizate has the highest modulus, the CB-filled CR/SO and CR/11MSO vulcanizates have similar values of modulus but being lower than that of vulcanizate containing NO. The CB-filled CR/33MSO vulcanizate has the lowest modulus. Meanwhile, the CB-filled CR/SO vulcanizate exhibits higher elongation at break than that of the CR/NO vulcanizate, and with the increase of the modification level, the CB-filled CR/MSO vulcanizates exhibit higher elongation at break. The CB-filled CR/11MSO and CR/33MSO vulcanizates exhibit a slightly higher tensile strength than those of the CB-filled CR/NO and CR/SO vulcanizates. These effects are due to the reactions of the SO and MSO during the vulcanization which slightly decrease the crosslink density as shown in Figure 3(b). Similar effects of SO were also seen in previous studies on diene rubber.[14,15,17]

It is found that the CB-filled CR/SO vulcanizate exhibit a higher tear strength than that of the CB-filled CR/NO vulcanizate. With the increase of the modification level, the CB-filled CR/MSO vulcanizates exhibit progressively higher tear strength. The CB-filled CR/33MSO vulcanizate has a tear strength of 45.69 kN/m and is 18.6% higher than that of the CB-filled CR/NO vulcanizate. The tear strength of rubber vulcanizates is related to the filler dispersion, crosslink density, and crosslink type. Direct information about CB dispersion in various samples of CR is not available. However, the study[27] showed the effect of crosslink density and crosslink type on tear strength. Results indicated that with the decrease of the crosslink density, the tear strength of rubber vulcanizates first increased and then decreased. In addition, the study[28] showed that the inherent flaw size increased with the decrease of crosslink density increasing ability to blunt the crack tip. The CB-filled CR/SO vulcanizate has a lower crosslink density than that of the CB-filled CR/NO vulcanizate, and with the increase of modification level, the crosslink density is further decreased. The slightly

decreased crosslink density of CB-filled CR/MSO vulcanizates can enhance the tear strength of vulcanizates. The study[27] also found that rubber vulcanizates containing more polysulfidic crosslinks exhibited higher tear strength than those with shorter crosslinks. Our previous study[17] found that the use of MSO can alter the crosslink type, creating more flexible polysulfidic crosslinks. Therefore, the use of MSO in CB-filled CR vulcanizates can also increase their tear strength.

For the hardness of the various CR vulcanizates, the CB-filled CR/SO vulcanizate exhibits the lowest hardness with the value being 71 Shore A. With the increase of the modification level, the hardness of various CB-filled CR/MSO vulcanizates is increased gradually, but it is still lower than that of the CB-filled CR/NO vulcanizate.

To study the aging of various CB-filled CR vulcanizates, the properties described above before and after the hot air aging are compared. It is seen that after the aging, the M100 of various CB-filled CR vulcanizates is increased and the elongation at break and tensile strength are decreased. This is a typical behavior due to the post curing effect, similar behavior was also observed in previous studies on CR.[10,29] It is observed from Table IV that the CB-filled CR/NO vulcanizate exhibits the largest change in all the properties after aging, except the elongation at break. The CB-filled CR/MSO vulcanizates exhibit less change in M100 than that of the CR/SO vulcanizate. The change of M300 of various CB-filled CR/SO and CR/MSO is negligible. The CB-filled CR/MSO vulcanizates exhibit a slightly larger change in elongation at break than that of the CR/NO vulcanizate, but they have a smaller change in tensile strength. With the increase of the modification level, the CB-filled CR/MSO vulcanizates exhibit a slightly increased change in tear strength, but they still outperform the CR/NO vulcanizate. The CB-filled CR/11MSO and CR/33MSO vulcanizates exhibit the best hardness consistency during the aging among all the samples. In addition, the volume change after the aging was measured. The volume of CB-filled CR/NO vulcanizate decreases by about 4.8%, while the volume of CR/SO, CR/11MSO, and CR/33MSO vulcanizates only slightly increases by about 0.3%, 0.3%, and 0.2%, respectively. It is obvious that the CB-filled CR/SO and CR/MSO vulcanizates have a much better volume consistency during the aging. Clearly, the addition of SO and MSO can enhance the aging resistance.

Figure 8 depicts the abrasion loss of various CB-filled CR vulcanizates. It is noticed that the CB-filled CR/NO vulcanizate has the highest abrasion loss among all the samples. The CB-filled CR/SO and CR/MSO vulcanizates exhibit a similar level of abrasion resistance being better than that of the CB-filled CR/NO vulcanizate. In general, the addition of MSO to CR can increase the tensile properties, tear strength, aging resistance, and also abrasion resistance compared with CR with conventional NO, without changing other compounding ingredients.

CONCLUSIONS

MSO is a novel rubber plasticizer. It has the advantages of being the environmental friendly and low cost. It enhances the rubber performance without an additional cost. The addition of SO and MSO in CB-filled CR compounds can benefit the filler dispersion without changing the processability of the compounds. The SO and MSO can react with the CR modifier such as sulfur and thiuram disulfide during the vulcanization, slightly increase the gel fraction, and decrease the crosslink density. The use of SO and MSO can also slightly decrease the bound rubber fraction of the CB-filled CR compounds. The CB-filled CR compounds and vulcanizates containing SO and MSO exhibit much better thermal stability compared to those containing conventional NO, improving the safety of processing, and application. Also the SO and MSO can contribute to a lower T_g of the CR vulcanizates, which can improve the low temperature performance. With the increase of the modification level of the MSO, the curing time of the CB-filled CR/MSO compounds is shortened compared with the CB-filled CR/NO compound. The CB-filled CR/MSO vulcanizates exhibit better tensile properties and tear strength compared with the CB-filled CR/NO and CR/SO vulcanizates. The hardness of CB-filled CR/MSO vulcanizates is slightly increased with the increase of the modification level. The CB-filled CR vulcanizates containing SO and MSO exhibit better aging resistance compared with the CR vulcanizate containing NO. Also, the addition of SO and MSO to the CB-filled CR provides vulcanizates with a better abrasion resistance than that of the NO. In conclusion, the usage of MSO in rubber products is an inexpensive and effective way to improve their performance of the product. Its unique features make it a potential candidate to replace the conventional petroleum rubber plasticizers.

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