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Preparation and characterization of polymethyltrifluoropropylsilicone modified acrylonitrile–butadiene rubber/fluorosilicon rubber blend

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ABSTRACT: The blending of polymethyltrifluoropropylsilicone-modified acrylonitrile–butadiene rubber (MNBR) and fluorosilicon rubber (FSR) at 70 : 30 ratio was investigated. The grafting of mercapto-functionalized polymethyltrifluoropropylsilicone onto acrylonitrile-butadiene rubber (NBR) by thiol-ene reaction was carried out with 2,2′-azobisisobutyronitrile as initiator in a Haake torque rheometer. The rheological properties of NBR grafting obtained at varying dosages of polymethyltrifluoropropylsilicone in a Haake torque rheometer were studied using torque curves. Grafting reaction was confirmed by ^{1}H nuclear magnetic resonance and energy-dispersive X-ray spectroscopy. Results of scanning electron microscopy and dynamic mechanical analysis showed better compatibility of MNBR/FSR blend than NBR/FSR reference blend. Meanwhile, the macro-mechanical properties of the blend significantly improved. The tensile strength and tear strength of MNBR/FSR blend were improved to 14.34 MPa and 44.94 KN/m, respectively, which were 2.92 MPa and 13.03 KN/m higher than those of NBR/FSR reference blend. The low-temperature brittleness of the blend was improved to $-57°C$, an increase of $-6°C$ compared with that of NBR. These results indicated that MNBR/FSR blend at 70 : 30 ratio had improved compatibility because of the grafting chains that acted as interfacial agents. The low-temperature resistance of the blend was also enhanced. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42328.

INTRODUCTION

Polymer blending is an efficient technique to improve the properties of individual polymers. Acrylonitrile–butadiene rubber (NBR) is a diene-based unsaturated polymer[1] that has excellent oil resistance, abrasion resistance, and mechanical properties[2] but poor low-temperature resistance.[3] Fluorosilicon rubber (FSR) offers a broader range of low temperature and oil resistance properties,[4] but it is costly and has poor mechanical properties. Thus, blending NBR with FSR retains superior oil resistance, improves low-temperature resistance, and leads to a flexible property–cost balance. However, this blending system has not yet been studied because FSR is not widely commercialized.

Most polymer blends are immiscible at the molecular level and exhibit poor mechanical properties because of unfavorable interactions among their molecular segments. Thus, addition or *in situ* generation of interracially active copolymers is often used to enhance compatibility.[5–7] The modification of polymer according to tailor-made specifications designed prior to blend-ing is also another effective mechanism to improve compatibility. Carone[8] performed compatibilization by adding maleic anhydride to natural rubber in a roll mill at room temperature prior to blending with polyamide 6. Zhao *et al.*[9] used 1.5 wt % maleic anhydride to improve the interfacial adhesion and morphology of PP/EPDM blend after EPDM grafting. Based on this method, we could modify one polymer with a similar molecular chain of another polymer prior to blending. The modifier should have the capacity to localize at the blend interface, decrease interfacial tension between two phases, inhibit coalescence between domains of the minor phase, and improve adhesion between constituents of the blend.

Polymer modification by grating is a very beneficial mechanism. It entails the easy and controllable introduction of branch chains and exact localization of branch chains on the surface, with bulk properties remaining unchanged. The covalent attachment of branch chains onto a polymer surface also prevents their delamination and ensures long-term chemical stability.[10] However, when grafting a heterogeneous polymer onto another

polymer, their compatibility has to be considered because a modified reaction can possibly occur in solution, although this process is extremely expensive and relatively complex. The large quantity involved in solvent recycling also makes this process impractical for large-scale production and is harmful to the environment.[11] Thus, reactions conducted in a Haake torque rheometer through melting is a feasible mechanism. In reactive processing, a Haake torque rheometer mixer can be used as a reaction vessel in which a reactive polymer can be grafted onto a second polymer.[12] The rheological characterization of polymer in the reaction process can also be shown by the torque curve. Li *et al.* studied the rheological properties of long-chain branches grafted onto linear PP through melt-grafting reaction in the presence of a novel chain extender [i.e., poly(hexamethy-lendiamine-guanidine hydrochloride) (PHGH)]. The branching reactions between the functionalized PP and PHGH are confirmed by transient torque curves.[13] Thus, polymers modified in a Haake torque rheometer is industrially important and scientifically meaningful.

When polymers are modified in a Haake torque rheometer, a reaction that rapidly proceeds and has high yield under a variety of experimental conditions is sought. A thiol-ene reaction directed by the attack of radically initiated functional thiols on unsaturated bonds is more efficient and versatile. Modified polymers have been explored by numerous research groups through thiol-ene chemistry because of their advantages, such as mild reaction conditions, tolerance to oxygen and water, simple purification, and high reaction rates.[14–16] Thiol-ene polymer grafting is a simple and straightforward method of forming polymer grafts on glass and silicon surfaces, as presented by Harant *et al.*[17]

In the present work, mercapto-functionalized polymethyltri-fluoropropylsilicone was introduced onto NBR in a Haake torque rheometer through thiol-ene reaction in the presence of 2,2′-azobisisobutyronitrile (AIBN). The modified NBR (modified acrylonitrile–butadiene rubber [MNBR])/FSR blend at a ratio of 70 : 30 was studied. MNBR was used as the main component of the blend to retain the good mechanical performance of NBR.

EXPERIMENTAL

Materials
NBR [trade name 1965; acrylonitrile group content of 19 wt %; Mooney viscosity (ML {1 + 4}) at $100°C = 65$] was purchased from Zhenjiang Nancar Co., Ltd. (Chloromethyl)dimethylchlor-osilane was purchased from Shanghai Xianwei Co., Ltd. AIBN, thiourea, and diethylamine were supplied by Aladdin. Purlite CT-175 (a type of cation exchanger with $-SO_3H$ groups) was purchased from Zhejiang Purlite Co., Ltd. 2,5-Bis(tert-butylper-oxy)-2,5-dimethylhexane (DBPMH) was obtained from Akzo-Nobel Co., Ltd. FSR was obtained from Shanghai Sanaifu Co., Ltd. Fumed silica (TS-530) with a specific surface area of $220 m^2/g$ was purchased from Cabot Co., Ltd.

Material Preparation
Mercapto-Functionalized Polymethyltrifluoropropylsilicone.
The synthesis of 1,3-bis(mercaptomethyl)tetramethyldisiloxane
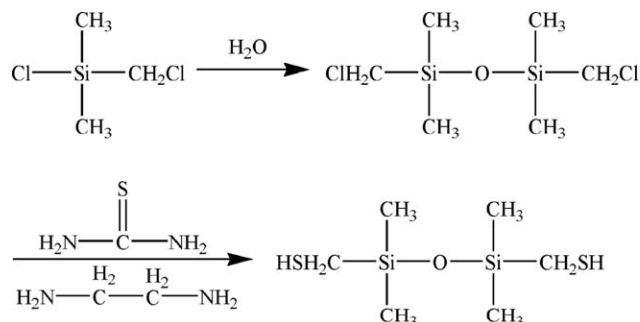
Scheme 1. The synthesis of 1,3-bis(mercaptomethyl)tetramethyldisiloxane.

is shown in Scheme 1.[18] Mercapto-functionalized polymethyltri-fluoropropylsilicone with low-molecular weight was prepared according to the controlled acid-catalyzed ring opening polymer-ization of 1,3,5-tris[(3,3,3-trifluoropropyl)methyl]cyclotrisiloxane (D_3F) and 1,3-bis(mercaptomethyl)tetramethyldisiloxane.[19–21] The mixture of D_3F (70.2 g, 1.5 mol), 1,3-bis(mercaptomethyl)te-tramethyldisiloxane (3.39 g, 0.15 mol), and purolite CT-175 (2.5 g, 3 wt %) were stirred at 90°C for 8 h. The catalyst was then removed by filtration. The reaction mixture was devolatilized by heating at 160°C/5 mmHg. Finally, the mercapto-functionalized polymethyltrifluoropropylsilicone was obtained.

Polymethyltrifluoropropylsilicone-Modified NBR. MNBR was prepared in a Haake Torque Rheomix 600 OS mixer, as shown in Scheme 2. NBR was modified with mercapto-functionalized polymethyltrifluoropropylsilicone in the presence of AIBN. NBR (40 g) was added to the mixer at room temperature at a rotor speed of 40 rpm. When the torque was stabilized approximately 6 min later, different percentages of mercapto-functionalized polymethyltrifluoropropylsilicone were added stepwise from 6 to 15 min until uniformly mixed. AIBN (0.5 g) was then added to the mixer. After 20 min, the temperature was raised to 100°C for reaction. After approximately 48 min, the torque became balanced and the reaction was completed.

Blends of MNBR/FSR Blend at a Ratio of 70 : 30. MNBR was mixed with silica TS-530 (50 wt % of rubber) in a Haake Rheo-mix 600 OS mixer at room temperature with a rotor speed of 40 rpm for approximately 10 min. FSR compounds were prepared by FSR and TS-530 (50 wt % of rubber) using the same
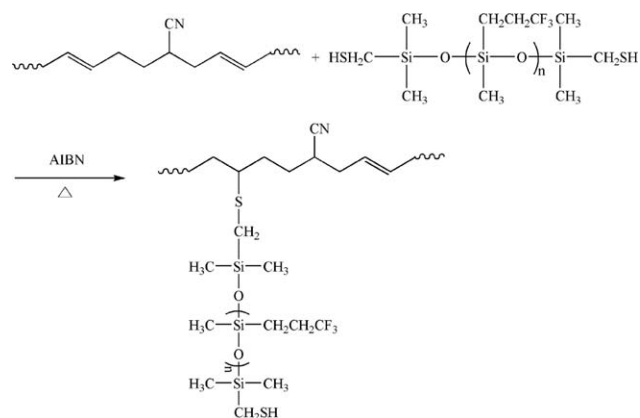
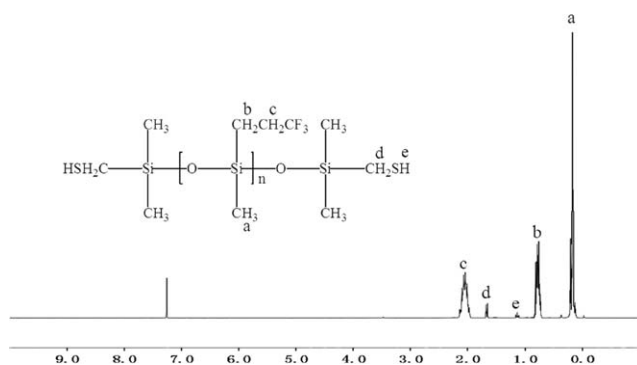

Scheme 2. NBR modified via thiol-ene reaction.

Figure 1. The ^{1}H NMR spectrum of mercapto-functionalized polymethyltrifluoropropylsilicone.

method. The MNBR compounds (28 g) were then placed in the Haake mixer at room temperature at a rotor speed of 40 rpm, and the FSR compounds (12 g) were gradually added. DBPMH (0.27 g, 1 wt % of rubber) was mixed until uniformly compounded. Thin sheets of approximately 2 mm thickness were compression molded at 170°C under a pressure of 10 MPa.

Material Characterization
The rheological behavior of grafting reaction was confirmed by transient torque curves (Haake Torque Rheometer with Banbury rotors, Thermo Fisher Scientific, Germany). The variation in torque was adopted to assess the reaction.

^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a BRUKER AVANCE-400 spectrometer in deuterated chloroform without tetramethylsilane.

The elemental composition of the grafted copolymer was determined by energy-dispersive X-ray (EDX) analysis (Hitachi S-4800).

High-resolution scanning electron microscopy (SEM) images were obtained using Hitachi S-4800 (5 kV). Samples were cut and coated with a thin layer of Pt before analyses.

Dynamic mechanical analysis (DMA) of the blended vulcanizate was conducted on a DMA analyzer (METTLER DMA/SDTA 861e) in sheer mode. The specimens ($3 \times 3 \times 1.7$ mm^3) were analyzed in sheer mode at frequency of 1 Hz rom -100°C to 25°C, with a heating rate of 3 K/min in nitrogen atmosphere.

Mechanical properties of the blended vulcanizate, including tensile strength, tear strength, and elongation at breaking, were measured based on ASTM D412 and D624 procedures at a crosshead speed of 500 mm/min using a Universal Testing Machine (100CX, Lloyd Instruments, UK) at room temperature. Hardness test was carried out using a shore type A Durometer based on ASTM D2240.

The low-temperature brittleness temperature of the blended vulcanizate was measured using a rubber cryogenic brittleness tester (Daochun Machinery Factory, Yangzhou, China).

RESULTS AND DISCUSSION
Mercapto-Functionalized Polymethyltrifluoropropylsilicone
Mercaptomethyl-terminated polymethyltrifluoropropylsilicone was synthesized with D$_3$F as raw material and 1,3-bis(mercapto-

methyl)tetramethyldisiloxane as end-capping reagent. The ^{1}H NMR spectrum is shown in Figure 1. According to the ratio of the functional groups —CH$_2$SH and —CH$_2$CH$_2$CF$_3$, a certain degree of polymerization was obtained, and a molecular weight of about 6400 g/mol was calculated.

Grafting Reaction in Haake and Rheological Properties
The torque trace of the branching reaction between mercapto-functionalized polymethyltrifluoropropylsilicone and NBR is shown in Figure 2. For sample #1, NBR was prepared without polymethyltrifluoropropylsilicone. In about 20–25 min, torque decreased with decreased viscosity, which can be attributed to the increased temperature from room temperature to 100°C. Final temperatures were higher than 100°C because of shear stress.

For sample #s 2–5, NBR was modified with various percentages of polymethyltrifluoropropylsilicone: 3, 5, 6, and 7 wt %, respectively. When polymethyltrifluoropropylsilicone was added to the mixer approximately 6 min later, the torque of samples decreased because of the lubrication effects of the flexible molecules of polymethyltrifluoropropylsilicone. In about 20–25 min, the torque of samples continued to decrease because of the reduced viscosity of compounds attributed to the increased temperature. About 30 min later, the temperature remained nearly constant, and the torque of samples gradually increased, indicating increased viscosity of compounds and decreased free-state polymethyltrifluoropropylsilicone. Therefore, a branching reaction between mercapto-functionalized polymethyltrifluoropropylsilicone and NBR occurred.

As shown in Figure 2, the final balanced torque was varied by altering the dosage of polymethyltrifluoropropylsilicone. For sample #s 2 and 3, the final torque remained nearly the same with sample #1 because all polymethyltrifluoropropylsilicone molecules participated in the reaction. No other polymethyltrifluoropropylsilicone provided lubrication effects to make the rotor slip with the copolymer. For sample #s 4 and 5, the final balanced torque decreased because the unreacted polymethyltrifluoropropylsilicone made the rotor slip rather than shear with
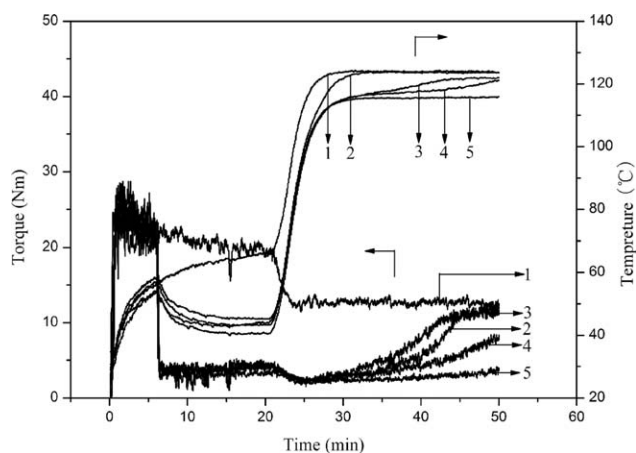

Figure 2. Torque curves of polymethyltrifluoropropylsilicone MNBR, percentage of polymethyltrifluoropropylsilicone: (1) 0 wt %; (2) 3 wt %; (3) 5 wt %; (4) 6 wt %; and (5) 7 wt %.
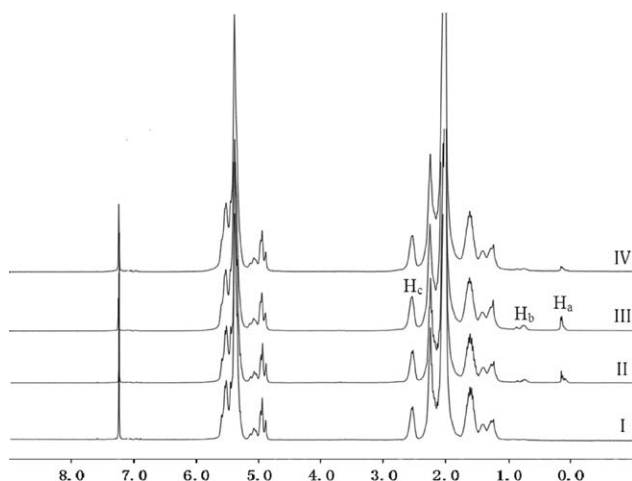
Figure 3. ^{1}H NMR spectrum of virgin NBR (I) and purified MNBR (II, III, IV), percentage of polymethyltrifluoropropylsilicone: (II) 3 wt %; (III) 5 wt %; (IV) 6 wt %.
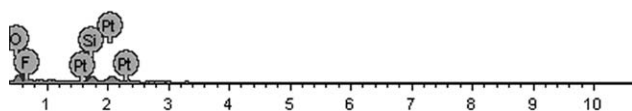

Figure 4. The EDX spectrum of the purified MNBR.

the copolymer, and the force counter-acting the rotor decreased. The final torque further decreased with increased unreacted polymethyltrifluoropropylsilicone. However, shear force played an important role in promoting the uniform mixing and the grafting reactions.[22] Thus, the excess dosage of polymethyltrifluoropropylsilicone did not contribute to the reaction in this system. The optimal dosage of polymethyltrifluoropropylsilicone was approximately 5 wt %.

^{1}H NMR Spectrum Analyses of MNBR Samples

For ^{1}H NMR spectrum analysis, the modified sample was dissolved in xylene at 80°C and then precipitated with excess ethanol. Purified MNBR was obtained by washing, filtering, and drying in a vacuum for 9 h at 90°C. Figure 3 shows the ^{1}H NMR spectrum of virgin NBR (sample #1) and MNBR (sample #s 2–4). Signals at 0.05−0.2 and 0.7−0.9 ppm were the

Table I. The EDX Analysis Data of the Purified MNBR

Element	Weight %	Atomic %
C	86.91	94.55
O	4.28	3.49
F	1.61	1.11
Si	0.91	0.42
Pt	6.29	0.42
Total	100	

resonances of —SiCH$_3$ protons (H_a) and —CH$_2$CH$_2$CF$_3$ protons (H_b), respectively. This finding indicated that polymethyltrifluoropropylsilicone was successfully introduced onto NBR. The signal at 2.5−2.6 ppm was due to —CH—protons (H_c) in the —CH(CN)CH$_2$— group.

For sample #s 2–4, the number of group C (—CH (CN) CH$_2$—) was constant. Reaction degree could be estimated by the ratio of groups A (—SiCH$_3$) to C. This ratio had the maximum value of 0.06 in sample #3 compared with 0.043 and 0.027 in sample #s 2 and 4, respectively. Therefore, when the dosage of polymethyltrifluoropropylsilicone was 5 wt %, the maximum reaction degree was achieved. This result was confirmed by the Haake torque curves.

EDX of Purified MNBR

As shown in Figure 4, the EDX spectrum of purified MNBR (5 wt % polymethyltrifluoropropylsilicone) revealed the presence of silicon, oxygen, and fluorine. Given that no silicon or fluorine signal was observed in virgin NBR, silicon and fluorine signals in the EDX spectrum indicated that polymethyltrifluoropropylsilicone was successfully introduced onto NBR. The relative atomic weights of the different constituents of MNBR are listed in Table I.

SEM Analysis

The SEM morphologies of the blend vulcanizates NBR/FSR and MNBR/FSR blends at a ratio of 70 : 30 are shown in Figure 5. The micrograph in Figure 5(a) indicated a loose matrix with irregular domain size and shape, which meant that NBR/FSR blend was incompatible. However, Figure 5(b) shows that
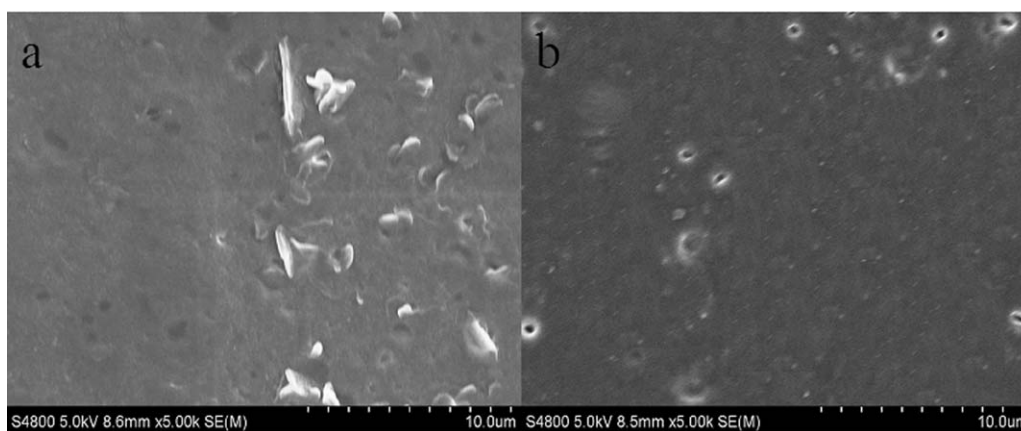

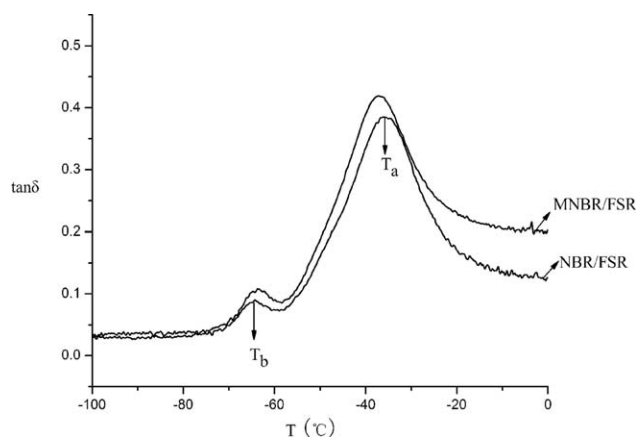**Figure 5.** The SEM of the blend vulcanizates: (**a**) NBR/FSR; (**b**) MNBR/FSR.

Figure 6. DMA curves of the effect temperature on the loss tangent (tan δ).

Figure 7. Mechanical properties of the blend vulcanizates.

surface texture was smoother and no gross phase separation was present in the blend. Therefore, grafting chains in MNBR acted as interfacial agents improved blend compatibility.

DMA Measurements of Blend Vulcanizates

DMA is a technology used to assess the compatibility of polymer blends.[23,24] Figure 6 exhibits the temperature dependence of loss tangent (tan δ) of the blend vulcanizates. Two peaks T_a and T_b showed two separate glass transition relaxations corresponding with the NBR and FSR phases, respectively. Figure 6 shows that the separation between two peaks T_a ($-63.5°C$) and T_b ($-37.2°C$) in MNBR/FSR blend decreased by 2.4°C compared with T_a ($-64.6°C$) and T_b ($-35.9°C$) in NBR/FSR blend. Thus, the grafting chains offered compatibility between the two hetero-rubbers.

Mechanical Properties of MNBR/FSR Blend

MNBR (5 wt % polymethyltrifluoropropylsilicone) blended with FSR at a ratio of 70 : 30 was further investigated. For comparison, the process used to prepare NBR/FSR 70 : 30 blend was the same. Incompatible rubber blends generally exhibited poor mechanical properties because of inhomogeneous mixing and phase separation. Figure 7 shows that the tensile strength, tear strength, and elongation at breaking of MNBR/FSR blend vulcanizate were all better than those of NBR/FSR blend vulcanizate. Compared with NBR/FSR blend, MNBR enabled the tensile strength and tear strength of MNBR/FSR blend to increase by 2.92 MPa and 13.03 KN/m to 14.34 MPa and 44.94 KN/m, respectively. Elongation at breaking increased by 117%, whereas hardness was nearly unchanged. Considering that polymethyltrifluoropropylsilicone was successfully introduced onto the NBR surface, the branching chain significantly affected the mechanical properties of MNBR/FSR blends at a ratio of 70 : 30. The interfacial adhesion between the blend components improved.

Low-Temperature Resistance of MNBR/FSR Blend

Low-temperature brittleness is an important indicator of the low-temperature resistance of rubber. The brittleness temperature of NBR was $-51°C$, whereas that of MNBR/FSR blend at a ratio of 70 : 30 was $-57°C$. Thus, the low-temperature resistance of MNBR/FSR blend can be much better than that of NBR
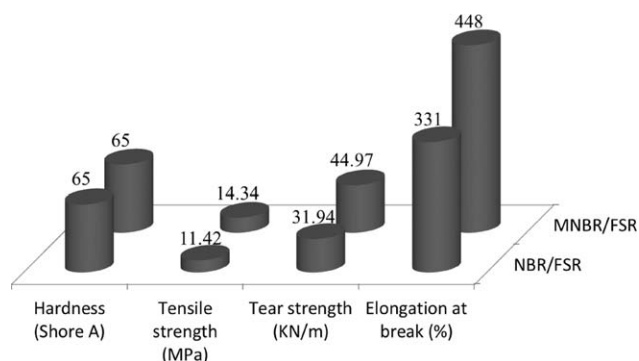
by modifying NBR with polysiloxane first and then blending MNBR with FSR.

CONCLUSIONS

MNBR was prepared by branching reaction with mercapto-functionalized polymethyltrifluoropropylsilicone through a thiol-ene reaction in a Haake torque rheometer. Rheological behaviors of MNBR were studied in detail. The optimal dosage of modifier was approximately 5%. ^{1}H NMR spectrum and EDX confirmed that polymethyltrifluoropropylsilicone was successfully introduced onto NBR.

The blending system of at 70 : 30 ratio was studied. Compatibility between MNBR and FSR was observed because the polysiloxane grafting chain acted as interfacial agent. This compatibility significantly improved the mechanical properties compared with those of NBR/FSR blend. The tensile strength and tear strength of MNBR/FSR blend increased by 2.92 MPa and 13.03 KN/m, respectively, compared with that of NBR/FSR blend. Brittleness temperature also increased by 6°C compared with NBR. Therefore, both the excellent mechanical properties and the good low-temperature resistance of the blend indicated that it was a high-performance material.

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