Influence of Liquid Isoprene on Rheological Behavior and Mechanical Properties of Polyisoprene Rubber

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ABSTRACT: Prevention of plasticizer leaching from polymers has been a difficult task. Conventional oily plasticizers (COPs) often migrate from rubber matrix, leading to a poor stability of rubber products and serious environmental problem during long-term use. In the present study, liquid isoprene (LIP) with appropriate molecular weight and no migration was prepared by anionic polymerization. The effects of LIP on the comprehensive properties of carbon black filled polyisoprene rubber (CB/IR) composites were compared with those of one COP, naphthenic oil (NPO). The results showed that LIP reduced the Mooney viscosity and apparent viscosity, and improved the processability of CB/IR composites. LIP improved the mixing efficiency and the dispersion of the CB particles because its compatibility with CB/IR composites was higher than the compatibility of NPO and CB/IR composites. Furthermore, LIP did not migrate from the CB/IR composites because of its participation in the vulcanization reaction. Compared with CB/IR/NPO composites, CB/IR/LIP composites possessed higher mechanical properties, better aging resistance and long-term dimensional stability. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41485.

INTRODUCTION

In rubber industry aromatic, naphthenic hydrocarbon oil and paraffin are used as conventional oily plasticizers (COPs) to improve the processing characteristics and reduce energy consumption and cost of rubber materials.[1] However, COPs often migrate or volatilize from polymer matrix leading to serious environmental pollutions.[2] As a result, the researchers focus on the eco-friendly plasticizers,[3–5] which mainly include naturally occurring oils (NOOs) and polymeric plasticizers. NOOs, mainly coming from plants and animals, can improve the processability, the dispersion of CB and the abrasion resistance of rubber vulcanizates.[3,6] In the major cases, COPs and NOOs are low molecular and high boiling point liquids or some solid crystal substances. Because of the low molecular weight of COPs and NOOs, the molecules of COPs and NOOs may evaporate slowly, leading to the increase of hardness and modulus of the composites. Compared with the COPs and NOOs, the polymeric plasticizers own reactivity and low volatility during rubber vulcanization.[7–9] Then much attention has been focused on the research of polymeric plasticizers in recent years.[10–14] Li et al.[15] revealed that emulsion styrene-butadiene rubber compo-

sites filled with liquid isoprene plasticizer (LIP) have low rolling resistance, high wet grip, and high bound rubber content. Nakazono et al.[16,17] concluded that the miscibility of the polymeric plasticizers and rubber composite is important for maintaining the physical properties during the thermal aging process. However, it must be noted that the mechanism of polymeric plasticizers in polyisoprene rubber (IR) is not studied sufficiently yet.

In this work, LIP with appropriate molecular weight ($M_n \approx$ 50,000 g mol^{-1}) was prepared by anionic polymerization and used as a polymeric plasticizer. The effects of LIP and naphthenic oil (NPO) contents on the rheological properties, mechanical properties, thermal aging properties, dynamic mechanical properties, n-hexane extraction rates, and CB dispersion of CB/IR composites were investigated. The work was aimed at providing some theoretical basis and application basis for the use of polymeric plasticizers in the rubber industry.

EXPERIMENTAL

Materials

Liquid isoprene (LIP) was synthesized in our lab by anionic polymerization. Polyisoprene rubber (IR) was produced by

Table I. Structural Parameters of IR and LIP

	M_n (g mol^{-1})	Molecular weight distribution	cis-1,4 structure (%)	trans-1,4 structure (%)	-3,4 structure (%)
IR	333,000	3.07	92.81	3.39	3.79
LIP	48,000	1.23	71.29	21.73	6.98

Figure 1. Scheme of LIP polymerized reaction.

Qingdao Yikesi New Material, China. Carbon black (N234) was produced by Tianjin Haitun Carbon Black, China. Naphthenic oil (NPO) was produced by Nanjing Yangtze Petrochemical, China. The other rubber additives, such as zinc oxide, stearic acid, and sulfur, were commercial grades. The structural parameters of LIP and IR are listed in Table I.

Formulation for Rubber Compounds

IR 100.0, N234 50.0, zinc oxide 4.0, stearic acid 2.0, poly(1,2-dihydro-2,2,4 -trimethylquinoline)1.0, N-isopropyl-N'-phenyl-p-phenylenediamine 1.0, N-cyclohexyl- 2-benzothiazylsulfenamide 1.2, sulfur 2.25 (phr)[e]. [e]Parts-per-hundred rubber. Plasticizer contents are listed in Table II.
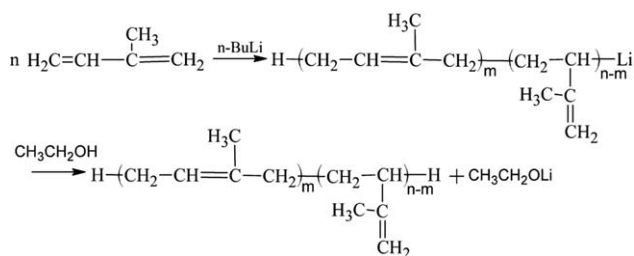
Specimen Preparation

Preparation of LIP. The purified isoprene and n-hexane were added into a 2L stainless reactor, which was purified with nitrogen gas and washed with living n-Butyllithium (n-BuLi) solution beforehand. The polymerization was initiated by butyl lithium, which had been calculated and prepared in advance. The temperature of the reactor was kept at 50°C for 2 h. At the end of the polyreaction, ethanol was added as termination agent. The polymer was dried in a vacuum oven at 50°C. At last, LIP was obtained after being dried to constant weight. The detailed conversion process is given elsewhere.[18] The reaction mechanism of LIP is shown in Figure 1.

Preparation of Rubber Compounds. Carbon black (CB) and other additives (except plasticizer and sulfur) were added into IR in turn and mixed by a $\Phi 360 \times 900$ mm^2 two-roll mill (Shanghai Rubber Machinery Works No. 1, Shanghai, China) to prepare a rubber masterbatch. Then the well-mixed rubber masterbatch was divided into several equal parts. Plasticizer and sulfur were added into each of the part in turn and mixed by a $\Phi 160 \times 320$ mm^2 two-roll mill. Finally the CB/IR/plasticizer compounds were sheeted, and the sheets were put aside for future use.

Preparation of Vulcanizates. The vulcanizing properties of the compounds were determined by a P3555B$_2$ Disc Vulkameter (Beijing Huanfeng Chemical Machinery Trial Plant, Beijing,

China). The composites were cured in an XLB-D350 × 350 plate vulcanization machine (Huzhou Dongfang Machinery, Zhejiang, China) at 145°C for the optimum cure time t_{90}. The hydraulic pressure was 15 MPa and the thickness of a composite sample was about 2 mm.

Characterization

The thermal stability of NPO and LIP was measured by Thermo gravimetric Analysis (TGA, Mettler Toledo TGA STAR system), with a heating ramp of 10°C min^{-1} in nitrogen atmospheres. In each case, 10 mg specimens were heated from room temperature to 600°C at the rate of 10°C min^{-1} under nitrogen flow.

The Mooney viscosity of the rubber compounds was measured according to ASTM D1646 (ML 100°C (1+4) min) by a M3810C viscometer (Beijing Huanfeng Chemical Industry, China).

The mixing properties of the compounds (A_{00}, A_{12}, and A_{22}) were measured by a Haake mixer (Haake, Germany). The software Haake Polysoft Os was utilized for controlling the mixing conditions and storing the data. IR, CB, and other ingredients (except sulfur) were added into the mixer in turn and mixed for 10 min at a rotating speed of 50 rpm. The original temperature of the mixer was 50°C.

The rheological properties were determined by an Instron 3211 Capillary Rheometer (Instron, UK). The diameter of the capillary was 0.12 cm, and the length/diameter ratio of the capillary was 40 : 1. The rheometer was set to run at piston speeds of 0.06, 0.20, 0.60, 2.00, 6.00, and 20.00 cm min^{-1}, a testing temperature of 90°C, and a preheat time of 2 min.

The mechanical properties were measured according to ASTM D412-06 by using a CMT4104 Electrical Tensile Tester (Shenzhen SANS Test Machine, China) at a crosshead speed of 500 mm min^{-1}. The hardness of the vulcanizates was measured with a rubber hardness apparatus produced by the 4th Chemical Industry Machine Factory, Shanghai, China.

The thermal aging properties were measured according to ASTM D573-04. The CB/IR composites were put in an oven (Tianjin Tianyu Experimental Device, China) at 100°C for 7 days. The percentage change of modulus at 100% elongation (P_m) was calculated by eq. (1):

$$P_m(\%) = (X_a - X_0)/X_0 \times 100, \quad (1)$$

where X_0 and X_a are the modulus at 100% elongation of the composites before and after the thermal aging, respectively.

The dynamic compression heat was determined according to ASTM D623-07 by a YS-25 Compression Heat Built-Up Tester
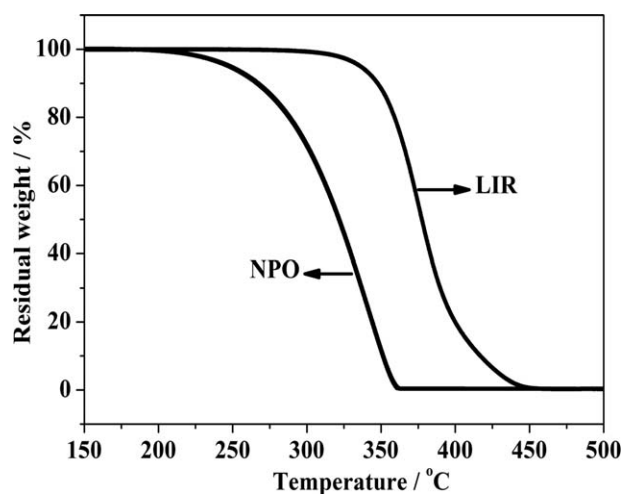
Table II. Plasticizer Content in CB/IR Compounds and Designations of Samples

Sample no.	A_{00}	A_{11}	A_{12}	A_{13}	A_{14}	A_{15}
NPO (phr)	0	3	5	7	10	15
Samples no.		A_{21}	A_{22}	A_{23}	A_{24}	A_{25}
LIP (phr)		3	5	7	10	15

Figure 2. Residual weight as a function of temperature for LIP and NPO.

(Shanghai Rubber Machinery Works, China) under the following testing conditions: the preheating time was 20 min, the compression time was 25 min, the frequency was 1800 min^{-1}, the stroke was 4.45 mm, and the load was 1 MPa.

The dynamic mechanical property (temperature sweep) was determined in a rectangular tension mode by VA3000 Dynamic Mechanical Thermal Analyzer, produced by 01dB-Metravib, France. The temperature was from $-90°C$ to $90°C$, the speed of temperature rise was $3°C$ min^{-1}, the frequency was 10 Hz and the strain amplitude was 0.1%.

The relaxation test was carried out according to ASTM D 674 standard. A relaxation test apparatus was designed and assembled for the purpose of testing the relaxation behavior of rubber materials. Relaxation curves for all samples were recorded at a strain $= 100\%$ at $30°C$.

The solvent extraction rates of the composites were determined by a Soxhlet apparatus at $80°C$. N-hexane was used as the solvent, and the extraction time was 72 h. The samples extracted were dried in a vacuum to constant weight (m_1) at $50°C$. The n-hexane extraction rate was calculated by eq. (2):

$$\text{Extraction rate (\%)} = (m_2 - m_1)/m_2 \times 100\%, \quad (2)$$

where m_2 is the weight of the sample before the extraction test.

The morphology of CB/IR/plasticizer composites was observed by a Tecnai G^{2}20 transmission electron microscope (FEI, USA) at an acceleration voltage of 200 kV. The thin sections were cut by a microtome at $-100°C$ and collected on copper grids.

RESULTS AND DISCUSSION

Thermal Stability

The thermal stabilities of LIP and NPO are shown in Figure 2. It is well-known that plasticizers are usually low molecular and high boiling point liquid or solid crystal substances. The boiling point or the pyrolysis temperature is important for the stability of plasticizers. As shown in Figure 2, the molecules of NPO begin to pyrolyze at $220°C$, and the pyrolysis is complete at $360°C$. However, the molecules of LIP begin to pyrolyze at $350°C$, and the pyrolysis is complete at $440°C$. The molecular

weight of NPO ranges from 250 to 450 g mol^{-1} which is lower than that of LIP. The intermolecular force of NPO is lower than that of LIP resulting in the lower boiling point of NPO. The pyrolysis temperature of LIP is higher than that of NPO, which is benefit to the thermal stability in long-term service.

Mixing Characteristics

The mixing characteristics of A_{00}, A_{12}, and A_{22} during processing are shown in Figure 3. The torque versus time curve of a rubber compound can display the mixing, dispersing, and homogenizing stages of filler particles and other additives. Figure 3 shows that LIP and NPO can decrease the hardness of the rubber compounds, and improve the dispersion of the CB nano-particles, indicating that the addition of LIP and/or NPO to IR can improve the mixing process. The torque of A_{22} is slightly higher than that of A_{12} due to the lower molecular weight of NPO. The temperatures of the three compounds all rise with increasing mixing time. Compared with those of A_{12} and A_{22}, the temperature rise of A_{00} is delayed more at the beginning of mixing, and then increases to a higher maximum, all because of the lower enwrapping effect of IR on CB and the higher internal friction between the IR molecules and the CB particles during dispersion. The addition of NPO and LIP to the CB/IR compounds can reduce the mixing energy consumption of the compounds and temperature rise; therefore, the rupture of the IR chains caused by shear heating decreases.

Rheological Properties

The rheological properties of the CB/IR/LIP (A_1 series) and CB/IR/NPO (A_2 series) compounds are shown in Figure 4. It is known that the Mooney viscosity and apparent viscosity are very important in the manufacturing of tyres, as an indicator of the processability of rubber composites. Figure 4(a) shows that the Mooney viscosity of the CB/IR composite decreases with increasing plasticizer content, indicating that LIP can be used as plasticizer to improve the processability of rubber composites. The plasticizing effect of LIP is lower than that of NPO. Figure 4(b) shows that the apparent viscosity (η_a) decreases and the shear stress (τ) increase with increasing shear rate ($\dot{\gamma}$), indicating that the three compounds are all shear-thinning non-
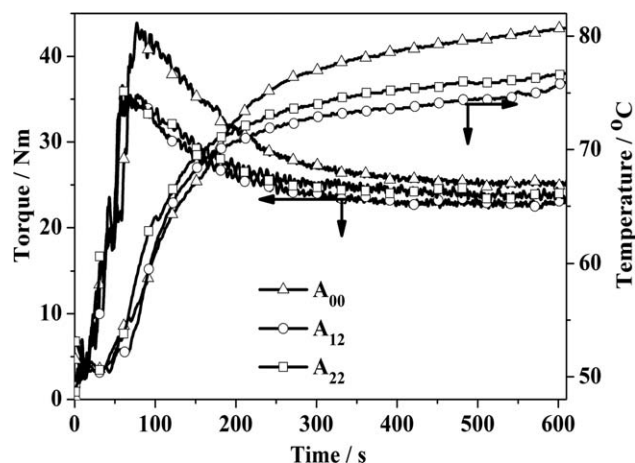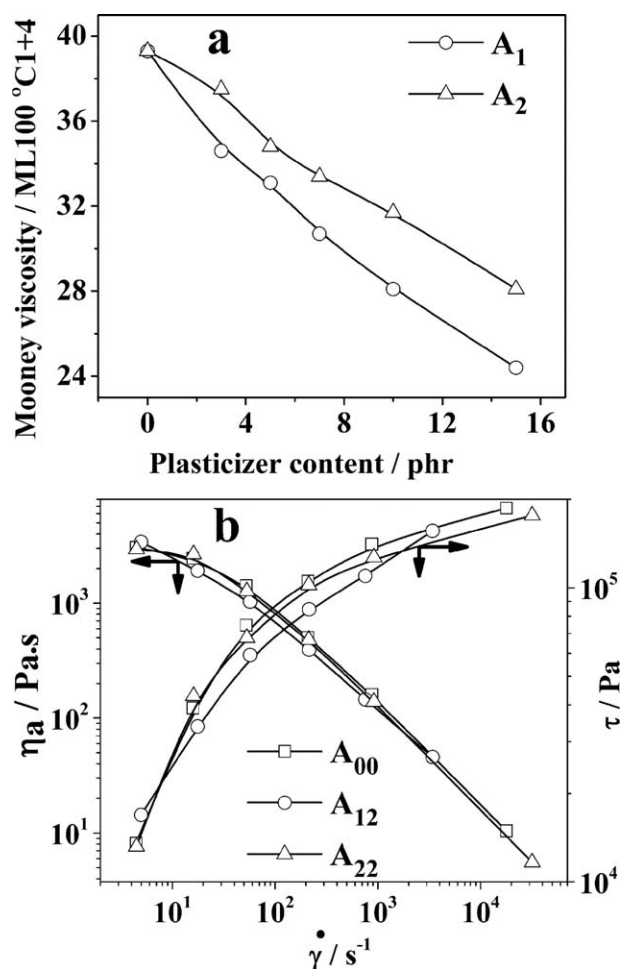

Figure 3. Torque vs. time and temperature vs. time curves of the three CB/IR composites.

Figure 4. Mooney viscosity (a) and capillary rheological properties (b) of CB/IR/LIP and CB/IR/NPO compounds.

Newtonian fluids. The order of η_a, together with τ, is $A_{00} > A_{22} > A_{12}$ at the same $\dot{\gamma}$, which is consistent with the results of Mooney viscosity. In fact, the molecular weight of

NPO is lower than that of LIP; therefore, the plasticizing effect of LIP is lower than that NPO.

Mechanical Properties

The mechanical properties of CB/IR/LIP and CB/IR/NPO are shown in Table III. Table III shows that with increasing plasticizer content, the hardness, tensile strength, modulus at 100% elongation, and compression heat build-up of the CB/IR/NPO and CB/IR/LIP composites decrease; however, the elongation at break increases. The hardness, tensile strength and tear strength of the CB/IR/LIP composites are higher than those of the CB/IR/NPO composites at the same plasticizer content because of the reactivity of LIP during vulcanization. The modulus at 100% elongation of CB/IR/LIP composites is larger than that of CB/IR/NPO composites, because NPO functioned as lubricant for CB/IR/NPO composites, which allows easier slippage and faster rearrangement of the macromolecules during tension. The P_m of CB/IR/NPO composites is larger than that of CB/IR/LIP composites due to the evaporation of NPO during aging. The molecular weight of LIP is much lower than that of IR, so the free chain ends in the crosslink network of the CB/IR/LIP composites are more numerous than those of the CB/IR/NPO composites, in which NPO only reduces the internal fraction between the rubber molecules and polymer-CB particles. Therefore, the compression heat build-up of the CB/IR/LIP composites is slightly higher than that of the CB/IR/NPO composites.

Stress Relaxation Characteristics

The data of relaxation test is used to predict the reduction of the stress in materials subject to constant deformation for long times. As shown in Figure 5, the stress and the equilibrium stress of CB/IR/NPO and CB/IR/LIP composites lower than those of CB/IR composite because of the plasticizing effect of NPO and LIP. The molecules of LIP become part of the network after vulcanization. NPO still exists as small molecules in rubber network after vulcanization and facilitates the rearrangement of the rubber molecular chains during relaxation. Compared with CB/IR/NPO composite, the CB/IR/LIP composite has lower stress relaxation in the initial stage, higher

Table III. Mechanical Properties of CB/IR/LIP and CB/IR/NPO Composites

Sample no.	Shore A hardness	Tensile strength (MPa)	Elongation at break (%)	Modulus at 100% (MPa)	Tear strength (kN m^{-1})	Compression heat build-up (°C)	P_m (%)
A_{00}	65	31.4	568	2.9	86	15.1	59.7
A_{11}	64	30.1	582	2.7	75	14.2	73.5
A_{12}	62	28.1	577	2.5	77	14.3	81.3
A_{13}	62	30.4	604	2.4	77	13.3	80.4
A_{14}	60	29.2	611	2.2	96	13.4	69.6
A_{15}	57	29.5	655	1.9	75	12.5	77.7
A_{21}	64	31.4	594	2.8	84	15.5	66.4
A_{22}	63	29.2	577	2.6	74	14.9	75.9
A_{23}	62	30.2	575	2.6	83	14.8	66.3
A_{24}	61	30.3	612	2.4	74	14.6	61.9
A_{25}	60	30.5	652	2.0	90	14.5	70.8
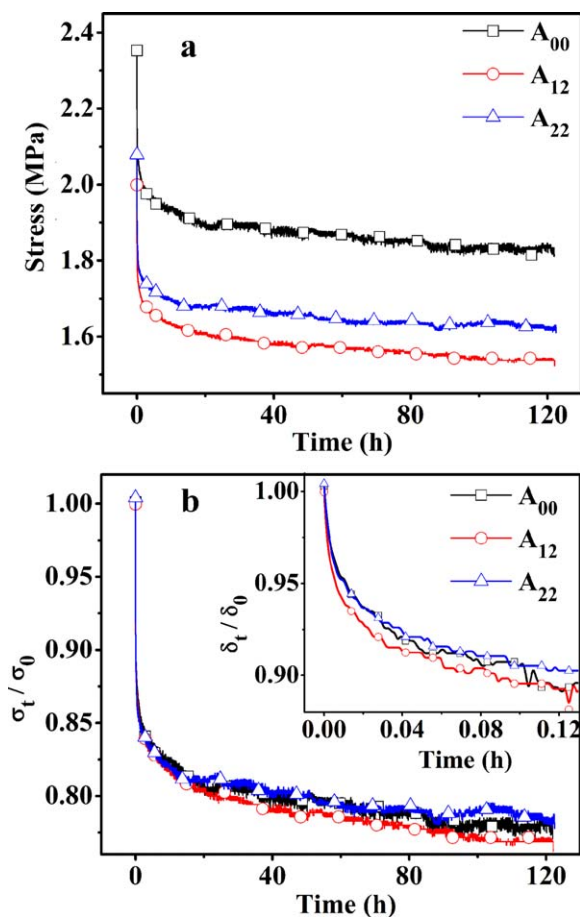
Figure 5. The variation of stress (a) and stress relaxation ratio σ_t/σ_0 (b) with time for the three CB/IR composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6. Temperature dependence of storage modulus G' (a) and loss factor tan δ (b) of the three CB/IR composites.
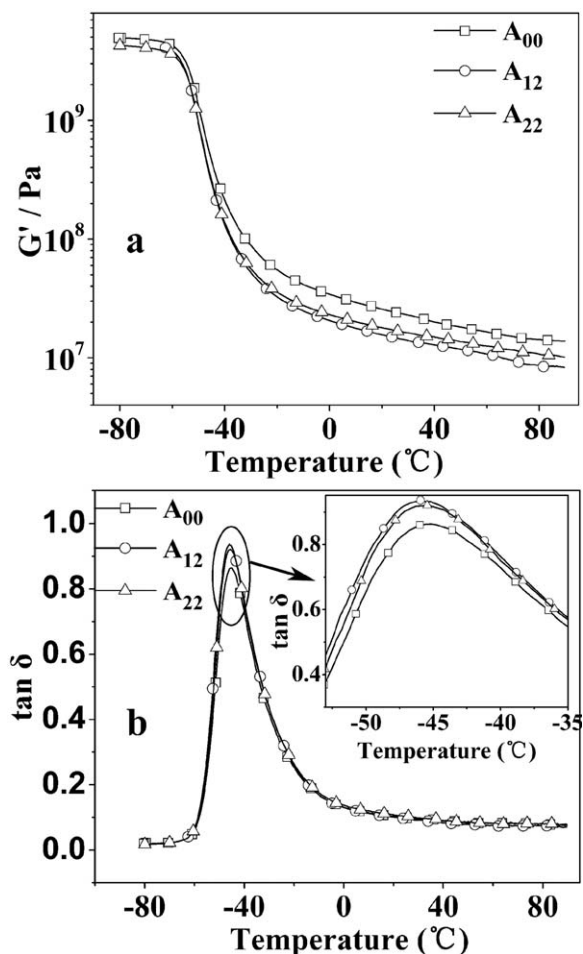
equilibrium stress and σ_t/σ_0 after long time relaxation. Therefore, the CB/IR/NPO composite has a lower dimensional changes and a better long-term dimensional stability.

Dynamic Mechanical Properties

The temperature dependence of dynamic mechanical viscoelasticity of A_{00}, A_{12}, and A_{22} is shown in Figure 6. From Figure 6, it can be seen that the storage modulus (G') and the loss factor (tan δ) peaks of CB/IR/NPO and CB/IR/LIP composites is higher than that of CB/IR composite, because NPO and LIP improve the mobility and reduce the rigidity of CB/IR composites. The G' of CB/IR/LIP composites is higher than that of CB/IR/NPO composites because NPO exists as small molecules and reduces the intermolecular force of the CB/IR composites. The addition of NPO and LIP does not change the glass–transition temperature (T_g) of CB/IR composites.
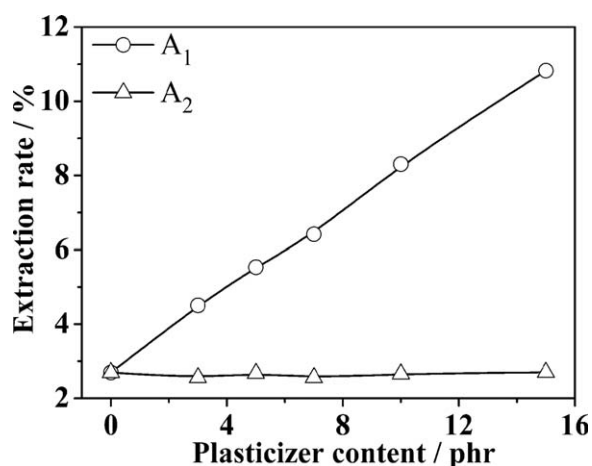
N-Hexane Extraction Rate

The effect of plasticizer content on the extraction rate of CB/IR composites is shown in Figure 7. As shown in Figure 7, the extraction rate of CB/IR/NPO composites increases linearly with the increase of NPO content due to the migration of NPO from the rubber composites. The extraction rate of CB/IR/LIP composites is constant at about 2.2% because of the migration of additives other than LIP. NPO exists as small molecules in rubber network after vulcanization; however, LIP can be vulcanized with IR and be part of the CB/IR composites upon vulcanization. NPO can migrate to the surface of CB/IR/NPO composites, leading to the increase of hardness and modulus of the

Figure 7. Extraction rate of CB/IR/LIP and CB/IR/NPO composites vs. plasticizer content.
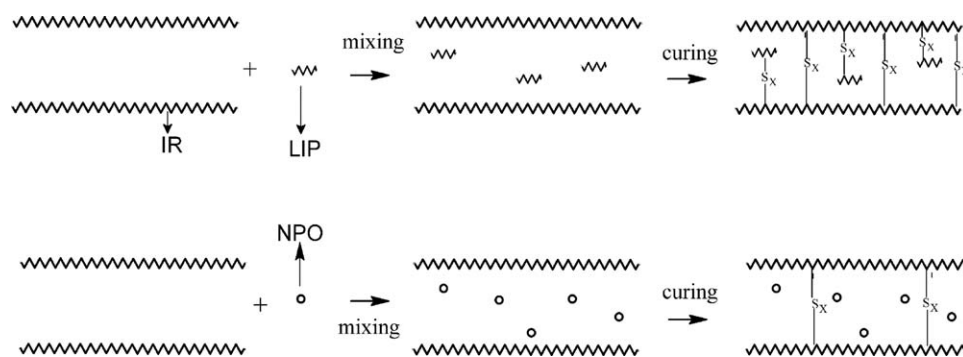
Figure 8. State of LIP and NPO in composites.

composites. The stability of CB/IR/LIP composites is better than that of CB/IR/NPO because of the reactivity and low volatility of LIP.

Based on the comprehensive performance, LIP and NPO show different effects on the mixing process and vulcanization of CB/IR compounds. LIP and NPO can both act as plasticizer during mixing; however, LIP can become part of the rubber network upon vulcanization. The state of LIP and NPO during mixing and vulcanization is illustrated in Figure 8.

Morphology of CB/IR Composites

The TEM images in Figure 9 show the CB dispersion in CB/IR composites. The dispersion of CB in the rubber matrix is one of the important factors in determining the comprehensive properties of the rubber composites. As shown clearly in Figure 9, CB particles in A_{12}.form obvious filler-network structure and 100–300 nm agglomeration. The dispersion of CB in A_{00} and A_{22} is better than that of A_{12}. During mixing the thermodynamic compatibility of plasticizers and rubber composites is important for the dispersion of plasticizer and ingredients. The
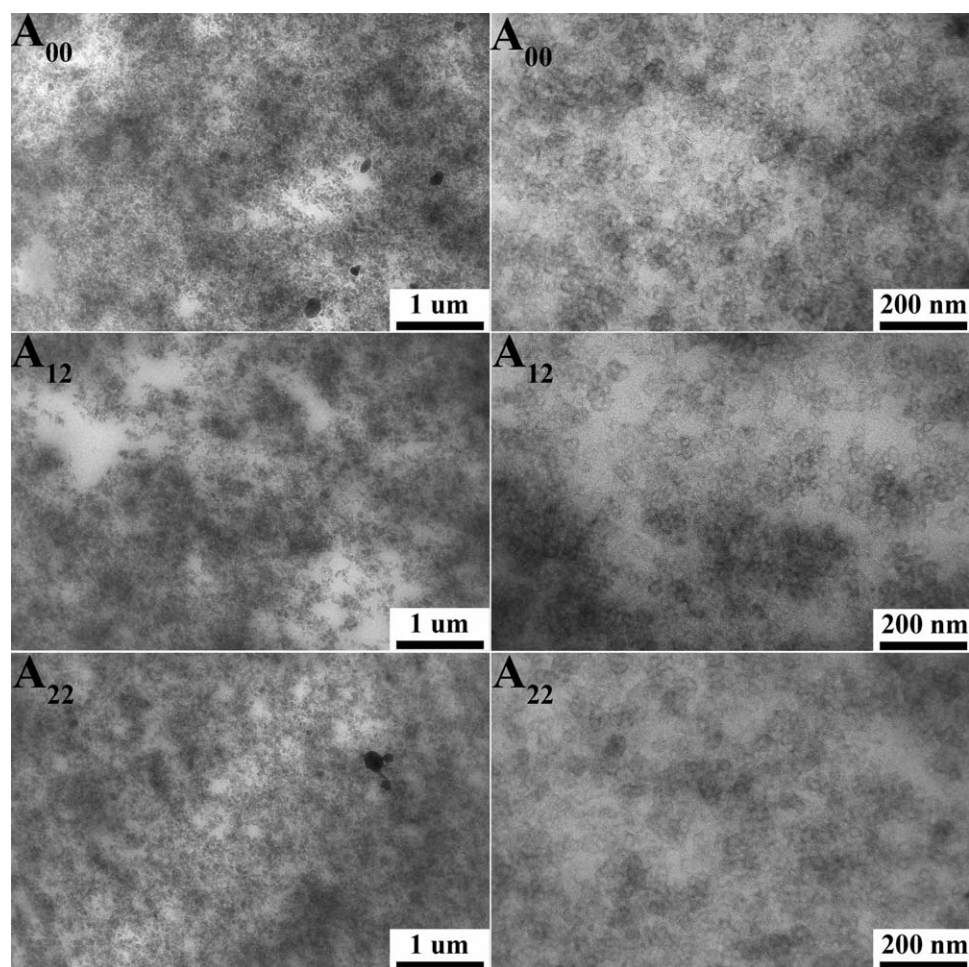

Figure 9. TEM photographs of the three CB/IR composites.

solubility parameters of NPO[19] and IR[20] are 7.0 and 8.2 (cal/cm³)$^{1/2}$. The solubility of LIP and IR is almost the same because the microstructure of LIP is similar to that of IR. According to the similar compatible principle, the compatibility of LIP and IR is better than that of NPO and IR. NPO mixes slowly into the CB/IR compound due to the inferior compatibility of NPO and IR. Moreover, the CB/IR/NPO compounds and the rotor slip during mixing, leading to an inferior mixing efficiency and CB dispersion. LIP can mix quickly into the CB/IR compound improving the processability and mixing efficiency.

CONCLUSIONS

In this work, LIP with appropriate molecular weight was synthesized by anionic polymerization. LIP could be used a polymeric plasticizer which was confirmed by mixing and rheological experiments. Compared with NPO, LIP improved the mixing efficiency and the dispersion of the CB particles of CB/IR composites. The CB/IR/LIP composites had lower extraction rates because LIP could covulcanize with the rubber matrix. The CB/IR/CB composites had better thermal aging properties and long-term dimensional stability than CB/IR/NPO composites due to the reactivity of LIP during vulcanization. Furthermore, the hardness, tensile strength, tear strength, modulus at 100% elongation and storage modulus of the CB/IR/LIP composites were higher than those of the CB/IR/NPO composites at the same plasticizer content. These results are of great importance to the practical application of LIP in rubber industry.

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