The Effect of Branching Structure on the Properties of Entangled or Non-covalently Crosslinked Polyisoprene

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INTRODUCTION

Natural rubber (NR) possesses excellent comprehensive properties such as high strength and toughness, crack resistance, anti-fatigue property and so on, which is widely used in various fields such as industry, agriculture, medical care and aerospace. The synthetic polyisoprene possesses similar main chain structure (e.g. molecular weight, stereoregularity) to NR, but its properties are still inferior to those of NR[1−4]. The main reason is ascribed to the nonrubber components in NR which formed natural net ties such as high strength and toughness, crack resistance, anti-fatigue property and so on, which is widely used in various fields such as industry, agriculture, medical care and aerospace. The synthetic polyisoprene possesses similar main chain structure (e.g. molecular weight, stereoregularity) to NR, but its properties are still inferior to those of NR[1−4]. The main reason is ascribed to the nonrubber components in NR which formed natural net network in polyisoprene matrix[5]. Both proteins at the ω-terminal and phospholipids at α-terminal formed branching structures by noncovalent bonding, which influence the entanglement or dynamic bonding between polyisoprene chains.[6]

In the last decades, many researches have been carried out to study the effects of the nonrubber components on NR network.[7−13] It has been proved that the branching structure in NR makes transient entanglements into permanent entanglements, which can accelerate the strain induced crystallization and stress upturn during the extension. Besides, the curing behavior, crosslinking density, and fatigue resistance of NR are better than those of purified NR as well as the isoprene rubber. The common method relied on removing nonrubber components hierarchically from NR to obtain deproteinized natural rubber (DPNR) and transesterified deproteinized natural rubber (TEDPNR).[14,15] Then the differences of the mechanical properties were compared to manifest the effect of the branching structure. However, the treatment of NR with lipase and phosphatase not only changed the topologies but also polyisoprene chain, which hindered the accurate evaluation of the effect of branching structure.[16] Moreover, the noncovalent bonding in the proteins or phospholipids also contribute to the mechanical properties, which is difficult to decouple with the effect of branching topology. Therefore, it is valuable to design artificial system to reveal the function of the branching structures unambiguously.

Herein, a polyisoprene-(polyisoprene-g-polyactide) block copolymer was designed and synthesized. PLA is a well-known polar plastic with glass transition temperature ($T_g$) around 60 °C, which will phase separate with polyisoprene and form discrete domains. At room temperature, the PLA phases stay at the frozen state and keep the branching structures stable. Therefore, it is ideal to use terminally hydroxyl functionalized polyisoprene to graft PLA and form branching structures. Epoxidation on polyisoprene part was also conducted and Fe$^{3+}$ was added to introduce coordination interaction between polyisoprene chains. The effect of branching cores was revealed by comparing with linear counterparts. The testing results proved that the branching structures...
would strengthen the interactions among the polyisoprene chains, and also improve the modulus and strength in both systems. Furthermore, branching structures showed more stable network than linear ones. Through the study of these model compounds, the function of branching structures could be verified, thus providing theoretical support for designing advanced synthetic rubbers.

**EXPERIMENTAL**

**Materials**

Neodymium neodecanoate \([\text{Nd(\text{VA})}_3]\) was purchased from Meryer and used as a hexane solution (solid content: 0.69 g/mL). Trisobutylaluminum \([\text{Al(i-Bu)}_3]\) (1.1 mol/L solution in toluene) and diisobutylaluminum chloride \([\text{Al(i-Bu)}_2\text{Cl}]\) (0.8 mol/L solution in heptanes) were purchased from Acros Chemical. Isoprene was purchased from Alfa and refluxed over CaH_2 for 2 h, and distilled prior to use. Iron(III) chloride and 1,8-diazabicyclo-[5.4.0]-7-undecene (DBU) were purchased from Adamas Meryer and used as a hexane solution (solid content: 0.69 g/mL). Triisobutylaluminium \([\text{Al(i-Bu)}_3]\) (1.1 mol/L solution in toluene) was purchased from Alfa and refluxed over CaH_2 for 18 h. Then Al(i-Bu)_2Cl (375 \(\mu\text{L}, 0.3 \text{ mmol}) was added into the ampoule and kept aging for 10 min at 50 °C before use. Isoprene (1.5 mol/L in hexane, 55 mL, 8.25 mmol) was placed in a flask and brought to a desired temperature. Then the performed catalyst solution was added into the flask via pipette. Polymerization was carried out at 50 °C for 4 h, then quenched by adding 2 mL of ethanol. The product was washed by aqueous solution of hydrochloric acid and methyl alcohol sequentially, and then dried in vacuum at 40 °C to give product (5.61 g, 93.1%). In-H-NMR (400 MHz, CDCl_3, ppm): 5.12 (t, 2H, \(-\text{CH}=-\)), 2.04 (m, 10H, \(-\text{CH}_2\text{C}=-\)), 1.67 (s, 3H, \(-\text{CH}_3\)).

**Synthesis of PI-OH**

Nd(\text{VA})_2 (197 \(\mu\text{L}, 0.15 \text{ mmol), Al(i-Bu)}_2 (2.73 mL, 3 \text{ mmol}) and isoprene (1 mol/L in hexane, 6 mL, 0.6 mmol) were injected into an ampoule via pipettes and aged at 50 °C for 10 min. Then Al(i-Bu)_2Cl (375 \(\mu\text{L}, 0.3 \text{ mmol}) was added into the ampoule and kept aging for 10 min at 50 °C before use. Isoprene (1.5 mol/L in hexane, 55 mL, 8.25 mmol) was placed in a flask and warmed to a desired temperature, then the performed catalyst solution was added into the flask via pipette. Polymerization was carried out at 50 °C for 4 h, then quenched by adding 2 mL of ethanol. The precipitated product was washed by aqueous solution of hydrochloric acid and methyl alcohol sequentially, and then dried in vacuum at 40 °C to give product (5.39 g, 88.2%). In-H-NMR (400 MHz, CDCl_3, ppm): 5.12 (t, 2H, \(-\text{CH}=-\)), 2.04 (m, 10H, \(-\text{CH}_2\text{C}=-\)), 1.67 (s, 3H, \(-\text{CH}_3\)), 1.20 (s, 6H, \(-\text{CH}_3\)). The molar ratio between hydroxyl monomer and isoprene is 35 versus 2034.

**Synthesis of PI-PLA (Epoxidized PI-PLA)**

PI-OH (2 g) was dissolved with CH_2Cl_2 (70 mL) in a three necked bottle. Then L-lactide (1 g, 6.94 mmol) and DBU (150 \(\mu\text{L}, 0.984 \text{ mmol}) were added sequentially. Ring-opening polymerization was carried out at 10 °C for 0.5 h. Then acetic acid (2 mL) was injected into the bottle to quench the polymerization. The polymer was washed by acetone and then dried in vacuum at 40 °C to give product (2.31 g, 76.3%). In-H-NMR (400 MHz, CDCl_3, ppm): 5.19–5.17 (m, 1H, \(-\text{CH}=-\)), 5.12 (t, 2H, \(-\text{CH}=-\)), 2.04 (m, 10H, \(-\text{CH}_2\text{C}=-\)), 1.83 (m, 2H, \(-\text{CH}_2\text{C}=-\)), 1.59–1.57 (m, 3H, \(-\text{CH}_3\)).

**Tensile measurements**

Tensile measurements were performed on a universal testing machine (INSTRON, America) at room temperature with a cross-head speed of 100 mm/min. The initial distance (18 mm) between the two clamps remained constant for each sample and the deformation rate was 0.1 s\(^{-1}\) during stretching. The specimen was a dumbbell shaped thin strip with central dimension of 35 mm x 2 mm x 0.5 mm.

**Synthesis of PI**

Nd(\text{VA})_2 (197 \(\mu\text{L}, 0.15 \text{ mmol), Al(i-Bu)}_2 (2.73 mL, 3 \text{ mmol}) and isoprene (1 mol/L in hexane, 6 mL, 0.6 mmol) were injected into an ampoule via pipettes and aged at 50 °C for 10 min. Then Al(i-Bu)_2Cl (375 \(\mu\text{L}, 0.3 \text{ mmol}) was added into the ampoule and kept aging for 10 min at 50 °C before use. Isoprene (1.5 mol/L in hexane, 55 mL, 8.25 mmol) was placed in a flask and kept aging for a desired temperature, then the performed catalyst solution was added into the flask via pipette. Polymerization was carried out at 50 °C for 4 h, then quenched by adding 2 mL of ethanol. The precipitated product was washed by aqueous solution of hydrochloric acid and methyl alcohol sequentially, and then dried in vacuum at 40 °C to give product (5.39 g, 88.2%). In-H-NMR (400 MHz, CDCl_3, ppm): 5.12 (t, 2H, \(-\text{CH}=-\)), 2.04 (m, 10H, \(-\text{CH}_2\text{C}=-\)), 1.67 (s, 3H, \(-\text{CH}_3\)), 1.20 (s, 6H, \(-\text{CH}_3\)). The molar ratio between hydroxyl monomer and isoprene is 35 versus 2034.

**Synthesis of EPI-PLA**

PI-PLA (2 g) was dissolved in a flask with cyclohexane (100 mL).
Hydrogen peroxide (7200 μL, 0.064 mol) and formic acid (2880 μL, 0.067 mol) were injected into the flask via pipettes when PI-PLA was absolutely dissolved. Then the reaction was kept at 30 °C for 1.5 h to obtain desired epoxidation degree of double bond. The reaction was quenched by saturated salt water and the solution was precipitated in methyl alcohol and dried in vacuum at 30 °C to give product (1.914 g, 95.7%). $^1$H-NMR (400 MHz, CDCl$_3$, δ ppm): 5.19–5.17 (m, 1H, –CH=), 5.12 (t, 2H, =CH–), 2.69 (s, 1H, –OCH–), 2.04 (m, 10H, –CH$_2$C–), 1.83 (m, 2H, –CH$_2$–), 1.67 (s, 3H, –CH$_3$), 1.59–1.57 (m, 3H, –CH$_3$). Epoxidized degree of EPI-PLA is 31%.

Synthesis of EPI-PLA-Fe$^{3+}$

EPI-PLA (3.1 g, ED=31%) was dissolved in chloroform before use. FeCl$_3$ (0.119 mol/L) in chloroform was injected into the EPI solution via a pipette (the molar ratio of ferric to epoxy is 1:9). After stirring for 10 min, the chloroform was removed by rotary evaporation and 50 mL of toluene was added into the flask. After stirring for 6 h, the solution was poured into polytetrafluoroethylene (PTFE) mould and dried.

Synthesis of EPI (Epoxidized PI)

PI (2 g) was dissolved in a flask with cyclohexane (100 mL). Hydrogen peroxide (7.20 mL, 0.067 mol) and formic acid (2.88 mL, 0.066 mol) were injected into the flask via pipettes. Then the reaction was kept at 30 °C for 1.5 h to obtain desired epoxidation degree of double bond. The reaction was quenched by saturated salt water and the polymer was precipitated in methyl alcohol and dried in vacuum at 30 °C to give product (1.922 g, 96.1%). $^1$H-NMR (400 MHz, CDCl$_3$, δ ppm): 5.12 (t, 2H, =CH–), 2.69 (s, 1H, –OCH–), 2.04 (m, 10H, –CH$_2$C–), 1.67 (s, 3H, –CH$_3$). Epoxidized degree of EPI is 31.5%.

RESULTS AND DISCUSSION

Synthesis

Terminally hydroxyl functionalized polyisoprene was synthesized by coordination copolymerization between isoprene and its polar monomer as shown in Scheme 1. Then the hydroxyl groups were used to initiate the ring-opening polymerization of L-lactide to generate a model compound PI-PLA. Pristine polyisoprene (PI) was prepared as a control polymer. Then epoxidation reactions were carried out on both PI-PLA and PI to generate EPI-PLA and EPI. The detailed synthetic procedures are described in experimental section.

$^1$H-NMR spectra of PI-OH, PI-PLA, EPI-PLA, and EPI are shown in Figs. 1(A)–1(D). The characteristic signals have been assigned according to their chemical structures, respectively. The hydroxyl content can be determined according to the methyl groups (1.20 ppm) adjacent to the hydroxyls, which can be calculated by the following formula:

$$\text{OH}\% = \frac{c}{[b + b']_{\text{PI-OH}}} \times 100 \% \quad (1)$$

where c represents the integral area of the methyl groups (six protons) adjacent to the hydroxy, and $b + b'$ represents the integral area of methylene groups on the main chain. By analysing the $^1$H-NMR spectrum (Fig. 1A), the hydroxyl content...
is calculated to be 1.7% related to isoprene unit, about 35 hydroxyl groups each chain. Then the length of PLA grafted onto polyisoprene was calculated. In 1H-NMR spectrum (Fig. 1B), the methyl and methenyl signals of PLA (−CH₂ 1.57−1.59 ppm; −CH 5.15−5.17 ppm) overlapped with those signals of polyisoprene (−CH₃ 1.68 ppm; −CH 5.12 ppm). Fortunately, the amount of methylene (−CH₂ 2.04 ppm) in polyisoprene chain is constant. Therefore, the PLA length can be calculated indirectly according to the increment of methylene protons by taking the methylene protons as reference. The PLA length was calculated by the following formula:

$$DP = \frac{(b + b' + b'')_{PLA} - (b + b')_{PI-OH}}{(a + a' + d + e)}$$

where \(b + b'\) is the integral area of methylene groups on PI-OH and \(b + b' + b''\) is the integral area of methylene groups on PI-PLA by normalizing the integral of methylene groups. \(a + a' + d + e\) is the integral area of the constant methylene (−CH₂ 2.04 ppm). The polymerization degree of PLA is about 4.34 lactide units each hydroxyl group.

Finally, epoxidized degrees of EPI and EPI-PLA were calculated according to the chemical shifts of methylene groups of 5.12 ppm and epoxide groups of 2.69 ppm. Based on this information, the epoxidized degree of EPI and EPI-PLA is calculated to be 31.5% and 31%, respectively.

**Formation of Branching Structure**

After synthesizing all samples, the branching structures of all PLA containing samples were investigated. According to the DSC curves in Fig. 2(a), the glass transition temperatures (\(T_g\)) of polyisoprene chains in PI and PI-PLA are at −62 °C. And there is another endothermic peak at 120 °C for PI-PLA which is ascribed to the melting of the polylactide phase.\(^{[18]}\) The terminal polylactide segments is immiscible with the polyisoprene chain, which will self-aggregate to form separated plastic phase. The TEM images (Figs. 2b and 2c) demonstrate that the polylactide phase still existed in EPI-PLA. TEM illustrated that the polylactide phase in EPI-PLA kept at 120 °C, which is about 20 °C higher than those of PI and PLA, respectively. This is ascribed to the increased polarity of epoxide groups on the main chains.\(^{[18]}\) The melting temperature of the polylactide phase in EPI-PLA kept at 120 °C, which illustrated that the polylactide phase still existed in EPI-PLA. TEM test confirmed that the branching structure was kept in EPI-PLA (Fig. S2 in the electronic supplementary information, ESI).

**Formation of Coordination Interactions**

After the formation of branching structures for EPI-PLA and EPI, the ferro ions were added to coordination with epoxide
groups. FTIR spectra of the model compounds are shown in Figs. 2(d) and 2(e). The band at 1756 cm\(^{-1}\) is assigned to the stretching vibration of C=O of polylactide. The bands at 873 and 1267 cm\(^{-1}\) are related to asymmetric and symmetric stretching vibration of epoxide groups, respectively. After the addition of Fe\(^{3+}\) ions, the disappearance of the band at 873 cm\(^{-1}\) indicates the association between the Fe\(^{3+}\) ions and the epoxide groups. Furthermore, the band at 1267 cm\(^{-1}\) shifted to 1213 cm\(^{-1}\), demonstrating the existence of Fe\(^{3+}\)―O coordination in EPI-Fe\(^{3+}\) and EPI-PLA-Fe\(^{3+}\). The Raman spectra (Fig. 2f) have been recorded to further demonstrate the Fe\(^{3+}\)―O coordination. The bands at 1020, 1450, 1670 cm\(^{-1}\) are assigned to the epoxide group, bending vibration of methylene and stretching vibration of double bond, respectively. After the addition of Fe\(^{3+}\) ions, the new bands emerging around 330 cm\(^{-1}\) are ascribed to the Fe\(^{3+}\)―O coordination in EPI-Fe\(^{3+}\) and EPI-PLA-Fe\(^{3+}\).[20] Due to the existence of Fe\(^{3+}\), the baselines of EPI-Fe\(^{3+}\) and EPI-PLA-Fe\(^{3+}\) are unsmoothened because of the fluorescence. All the above data convincingly verify the existence of Fe\(^{3+}\)―O coordination.

The Influence of Branching Structure on the Mechanical Properties

The stress-strain curves of PI and PI-PLA are shown in Fig. 3(a).

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The initial modulus and ultimate strength of PI-PLA are higher than those of PI. This is because the polylactide block of PI-PLA formed branching structure which anchored the chain and increased the chain entanglement. In contrast, the polyisoprene chain moved more freely and disentangled more rapidly under the external force.

In order to explore the effect of the branching structure on the noncovalent interactions, the Fe$^{3+}$-O coordination was incorporated into the polyisoprene chains. The mechanical properties of the coordination samples are promoted significantly due to increased crosslinking density. Both EPI-Fe$^{3+}$ and EPI-PLA-Fe$^{3+}$ performed the excellent extensibility and much higher strength and modulus compared to those of PI and PI-PLA. Moreover, the branching core also enhanced the mechanical properties. According to the stress-strain curves (Fig. 3b), the initial modulus and ultimate strength of EPI-PLA-Fe$^{3+}$ are higher than those of EPI-Fe$^{3+}$ due to the presence of branching core. Furthermore, the stress upturn phenomenon of EPI-PLA-Fe$^{3+}$ appears in advance compared to EPI-Fe$^{3+}$. A further calculation from stress-strain curves was conducted to disclose the relation between topological structure and modulus of the model compounds. Since the stress-strain curves behave typically nonlinear relations, Mooney-Rivlin laws were applied to describe the elastic behaviors. The Mooney reduced stress can be written by following forms:\(^7,\!2^{1}\)

\[ \sigma_{\text{red}} = \frac{\sigma}{\sigma - \alpha^2} = G_c + G_e f(\alpha), \alpha > 1 \]  

\[ f(\alpha) = \frac{1}{\alpha} \]  

where \(\sigma_{\text{red}}\) is the reduced stress, \(\sigma\) is the nominal stress and \(\alpha\) is the elongation ratio. \(G_c\) represents the elastic modulus, which is derived from the permanent cross-linking, \(G_e\) is the modulus due to the contribution of chain interactions. \(G_c\) and \(G_e\) can be determined from linear fits of \(\sigma_{\text{red}}\) vs. \(\alpha\) plots, respectively. The deformation range chosen for the linear fits is 0.4<\(\alpha<0.7\) to avoid the influence of stress upturn and guarantee finite deformation.

The reduced stress \(\sigma_{\text{red}}\) decreases in the low strain region because of the slippage or relaxation of coordination interplay. With further stretching, the \(\sigma_{\text{red}}\) increases due to the stress upturn. The fitting parameters \(G_c\) and \(G_e\) are presented in Fig. S3(b) (in ESI). The \(G_c\) values of EPI-Fe$^{3+}$ and EPI-PLA-Fe$^{3+}$ are both close to zero, which revealed the transient nature of noncovalent interactions. It is worth noting that \(G_e\) value of EPI-PLA-Fe$^{3+}$ is larger than that of EPI-Fe$^{3+}$, which means the Fe$^{3+}$-O coordination is stronger in EPI-PLA-Fe$^{3+}$ than that in EPI-Fe$^{3+}$. The difference is ascribed to the branching structure of the model compounds.

Dynamic mechanical analyses were performed to probe the network robustness and segmental motion. As shown in Figs. 3(c) and 3(d), the storage modulus (\(E'\)) of EPI-PLA-Fe$^{3+}$ is...
larger than that of EPI-Fe$^{3+}$, indicating the branching structure would increase the crosslinking density of the network. The reduced slope of modulus changes along the temperature increase also suggested a more thermally stable network for EPI-PLA-Fe$^{3+}$. The loss tangent peak \((\tan \delta)\) of EPI-PLA-Fe$^{3+}$ is at \(-2\) °C, which is \(5\) °C higher than the value of EPI-Fe$^{3+}$, demonstrating that the branching structure would retard the segment motion.

**The Influence of Branching Structure on the Rheological Behavior**

Frequency dependent rheological experiments were performed in a temperature range from 283.15 K to 363.15 K. The frequency dependent curves of PI-PLA and PI are shown in Figs. 4(a) and 4(b). The storage moduli \((G')\) represent the energy storage of the model compounds during the deformation and mainly reflect the elasticity. The loss moduli \((G'')\) represent the loss of energy and mainly reflect the viscosity. The relative magnitudes between \(G'\) and \(G''\) and the intersect value \((\delta)\) can reflect the relaxation rate of polymer chains. The \(f\) value of PI-PLA is smaller than that of PI at either 283.15 or 363.15 K, indicating that the polysoprene chains in PI-PLA are prone to entangle due to the branching structure, and the segmental motion is relatively slow under the shear force. From Figs. 4(c) and 4(d), more obvious changes in storage moduli were found due to the temperature dependent relaxation of reversible Fe$^{3+}$–O coordination in EPI-PLA-Fe$^{3+}$ or EPI-Fe$^{3+}$. And the storage moduli of EPI-PLA-Fe$^{3+}$ are almost an order higher than those of EPI-Fe$^{3+}$ either at 283.15 or 363.15 K, which is ascribed to enhanced entanglement and retarded chain relaxation due to the existence of the branching structure. It is worth noting that the storage modulus follows the time-temperature superposition principle quiet well and it is convenient to quantitatively reveal the influence of branching structure in EPI-PLA-Fe$^{3+}$ by comparing with EPI-Fe$^{3+}$.

Therefore, master curves were made by applying horizontal and vertical shift factors on the modulus curves at different temperatures, as shown in Fig. 5. The plot of horizontal shift factors as a function of temperature is shown in Fig. 5, which is fitted via the following Arrhenius equation:\(^{(5)}\)

\[
\ln (\sigma_f) = \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right)
\]

where \(E_a\) is the activation energy and \(R\) is the gas constant, \(T_{ref}\) is the reference temperature at 283.15 K. The activation energy of viscous transition for PI-PLA, PI, EPI-PLA-Fe$^{3+}$, and EPI-Fe$^{3+}$ were calculated to be 40.23, 38.01, 46.54, and 38.26 kJ/mol, respectively. It is found that branching structure caused even more energy difference of viscous transitions in coordination compounds. Considering a large family of dynamic crosslinking tools, this phenomenon may give guide to utilizing branching structures in other crosslinking systems of polysoprene.

![Fig. 4](https://doi.org/10.1007/s10118-020-2480-0)
CONCLUSIONS

In this work, two groups of model compounds with or without branching structures were precisely synthesized. Tensile measurements, DMA, frequency dependent rheological experiments were conducted to disclose the influence of branching structure on chain entanglements. Mooney-Rivlin law reveals that the branching structure would increase the chain entanglements. The rheological experiments show the network of EPI-PLA-Fe\(^{3+}\) (PI-PLA) is more stable than EPI-Fe\(^{3+}\) (PI) under shear force due to the branching structure. All the above results verified the contributions of branching structure to the chain entanglements and noncovalent interactions. The principle found here may promote the development of next generation high-performance polyisoprene.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge.
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