

# Epoxidation of High *trans*-1,4-Polyisoprene and Its Properties

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Received 7 November 2006; accepted 5 September 2007

DOI 10.1002/app.27394

Published online 26 November 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A new organic-solvent-free water-phase suspension method was used to synthesize partially epoxidized high *trans*-1,4-polyisoprene (TPI) to improve its properties, including oil resistance and wet-skid resistance. The epoxidation was conducted in an aqueous peracetic acid solution and on the TPI granules prepared by a bulk precipitation method with supported titanium catalyst. The effects of the synthesis conditions, including reaction temperature, reaction time, and pH value, on the epoxy content were investigated. Epoxidized *trans*-1,4-polyisoprene (ETPI) with epoxy contents between 10 and 80%

were obtained within 4 h. Both the amorphous and crystalline regions of TPI were epoxidized. The crystallization properties decreased with increasing epoxy content. ETPIs possessed lower mechanical properties than TPI but could be enhanced by vulcanization. The oil resistance and wet-skid resistance were significantly improved after epoxidation. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2986–2993, 2008

**Key words:** kinetics (polym.); mechanical properties; microstructure; structure-property relations

## INTRODUCTION

High *trans*-1,4-polyisoprene (TPI) is a thermoplastic crystalline polymer that exhibits properties that are attractive for various applications. TPI has been widely used in medical materials, golf ball covers, electrical insulated materials, and shape-memory materials.<sup>1,2</sup> Vulcanized TPI shows robust properties at various crosslinking densities. Beyond a certain crosslinking density, TPI is an elastomer possessing excellent dynamic mechanical properties, including long fatigue life, good abrasion resistance, and low heat buildup.<sup>3,4</sup> These properties enable TPI to be an excellent candidate for high-performance tires.<sup>4</sup> For such an application, TPI should also impart other properties, including higher adhesiveness and wet-skid resistance. One of the effective approaches for improving these properties is to modify TPI to introduce polar groups into its backbone.

Epoxidation is one popular chemical modification method for polydiolefin rubbers. The epoxidized polydiolefin not only retains the structure and properties of polydiolefin but also enhances its properties, such as adhesiveness, wet-skid resistance, and abrasion resistance.<sup>5–7</sup> Epoxidation has been extensively applied to modify natural rubber. However, there are few reports on the epoxidation modification of TPI. A solution epoxidation method has been used for the epoxidation of TPI.<sup>8–10</sup> This method

uses organic solvents, such as benzene and chloroform, to dissolve TPI and organic peroxide acids, such as metachloroperbenzoic and performic acid. One of the disadvantages of this method is that a great amount of poisonous organic solvent is required, which is also costly both for the solvent itself and in solvent recycling. In addition, it is difficult to control the reaction conditions because of the high viscosity of the reaction system. In this study, a water-phase suspension reaction method was introduced to epoxidize TPI. This organic-solvent-free method could overcome the disadvantages of solution epoxidation method.<sup>11,12</sup> The effects of the reaction conditions on the structure and properties of epoxidized *trans*-1,4-polyisoprene (ETPI) were investigated.

## EXPERIMENTAL

### Materials

TPI was synthesized by bulk precipitation polymerization with supported titanium as a catalyst, as previously described.<sup>13,14</sup> The synthesized TPI was loose granules with an average particle size of 2 mm. TPI had a *trans*-1,4 structure content greater than 98%. Peracetic acid (12 ± 1 wt %) was made from hydrogen peroxide (35 wt %) and acetic acid (90 wt %) with a small amount of vitriol as a catalyst.

### Synthesis of ETPI

Peracetic acid was prepared according to ref. 15. The epoxidation of TPI was carried out in a three-necked

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flask equipped with a thermometer and an addition funnel. A certain volume of peracetic acid solution was adjusted to a certain pH value by sodium carbonate and was added to the flask. The TPI granules were then added to the peracetic acid solution under agitation by a high-speed agitator (Shanghai Jingmi Instrument Co., Ltd., Shanghai, China) at about 800 rpm to reach a uniform dispersion. After the reaction, the granules were filtered, washed with water to pH = 7, and dried in air to a constant weight. The filtered remnant liquid of peracetic acid could be regenerated by the addition of a certain amount of vitriol and hydrogen peroxide. The peracetic acid concentration change during the reaction was analyzed by titration to ensure that the desired epoxy content was obtained.

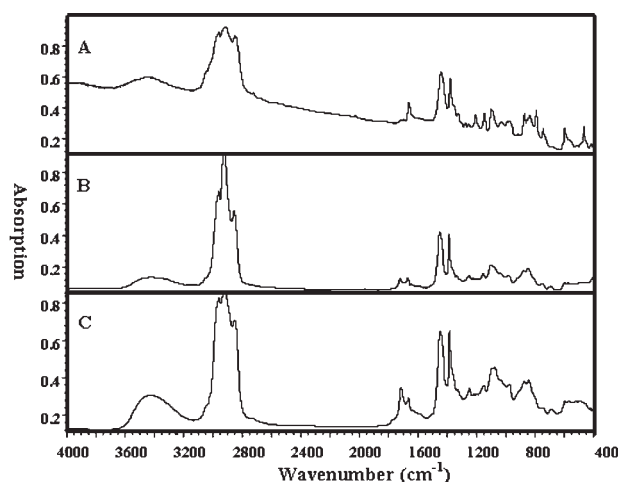
### Vulcanization

The rubbers (TPI, ETPI, NBR-34, and ENR-50) were mixed with vulcanizing agents on a two-roll mixing mill according to ASTM D 3182. The basic formulation used is given in Table I. The compounds were then compression-molded along the mill grain direction with an electrically heated hydraulic press (Qingdao Rubber Machine Factory, China) at 150°C with a force of 10 MPa.

### Characterization

Fourier transform infrared (FTIR) spectra were obtained with a Nicolet 450 infrared spectrometer (Thermo Nicolet Corporation, USA). <sup>1</sup>H-NMR spectra were recorded by a Bruker (Bruker Optics Co., Ltd., Germany) FT/AC-80 Fourier transform NMR spectrometer. Differential scanning calorimetry (DSC) was recorded with a Shimadzu (Shimadzu Co., Ltd., Japan) DSC-50 calorimeter. The sample was heated from -80 to 80°C at a heating rate of 20°C/min. Polarizing microscope photos were taken using a XPT-7 polarizing microscope camera (Shanghai Changfang Optic Instruments Co., Ltd., China).

The epoxy content of the product was calculated by the concentration change of peracetic acid during the reaction. The reaction liquid was extracted at the end of the reaction. The concentration of peracetic



**Figure 1** FTIR spectra of (A) TPI and (B,C) ETPI prepared at 13 and 25°C, respectively.

acid in the sample could be titrated by an iodometric method. The consumption of peracetic acid was then converted into epoxy content. For comparison, the epoxy content was also calculated from the <sup>1</sup>H-NMR spectra of the ETPIs. The epoxy content as measured by the two methods was consistent. Therefore, the measurement of epoxy content by peracetic acid concentration change was liable.

Tensile properties were tested at 25°C according to ISO 34 with dumbbell-shaped test pieces at a cross-head speed of 500 mm/min with a universal testing machine (Taiwan Yuken Co., Ltd., China).

Dynamic mechanical analysis (DMA) was conducted on a Netzsch DMA242 instrument (Netzsch Co., Ltd., Germany).

The specimen (20 × 5 × 1.6 mm<sup>3</sup>) was heated from -100 to 100°C at a heating rate of 38°C/min under a nitrogen stream. The applied frequency was controlled at 10 Hz.

An oil-resistance test was conducted according to ASTM D 471-98. The test specimens were immersed in ASTM #3 oil at 30°C for 24 h. The test specimens were then removed from the oil, wiped with tissue paper to remove excess oil from the surface, and weighed. The percentage mass swell was then calculated as follows:

$$\text{Swelling} = (W_2 - W_1)/W_1 \times 100\%$$

where  $W_1$  and  $W_2$  are the weight of the samples before and after immersion, respectively.

## RESULTS AND DISCUSSION

### Synthesis of ETPI

A new organic-solvent-free water-phase suspension reaction method was used to synthesize ETPI. This method could eliminate the necessity to recycle or-

**TABLE I**  
Compounding Recipe (Parts per Hundred Parts of Rubber by Weight)

Ingredient	TPI	ETPI	ENR-50	NBR-34
Carbon black N330	35	35	35	35
ZnO	5	5	5	5
Stearic acid	2	2	2	2
Sulfur	Various	Various	2	1.5
DTBMP <sup>a</sup>	1	1	1	1
DCBS <sup>b</sup>	1	1	1	1

<sup>a</sup> 2,6-Di-*tert*-butyl-4-methylphenol.

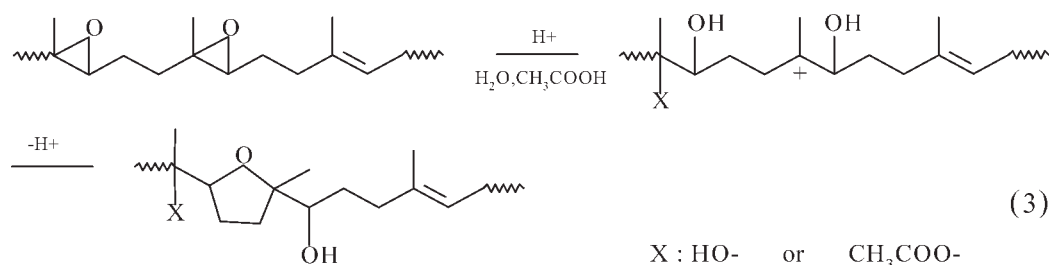
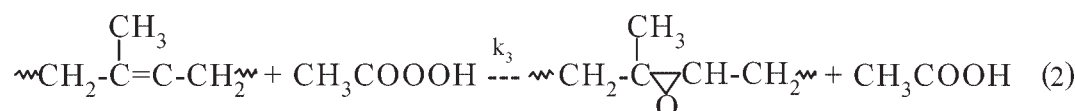
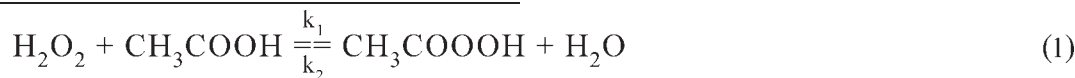
<sup>b</sup> *N*-Cyclohexyl-2-benzothiazole sulfenamide.

ganic solvents after synthesis. Successful epoxidation was confirmed by FTIR (Fig. 1) and  $^1\text{H-NMR}$  (Fig. 2) spectroscopy. Compared with TPI, ETPI showed characteristic absorptions of epoxy at 695, 874, and  $1250\text{ cm}^{-1}$ . ETPI retained the trans-1,4 structure of TPI, as evidenced by peaks at 1385 and  $2973\text{ cm}^{-1}$ . The absorptions at 1076, 1716, and  $3430\text{ cm}^{-1}$  were attributed to furyl, carbonyl, and hydroxy, respectively, in ETPI. The presence of these groups suggested that a side reaction occurred during the epox-

idation. Figure 3 shows the  $^1\text{H-NMR}$  spectra of TPI and ETPI. In addition to the characteristic peaks of TPI, ETPI also showed characteristic protons of epoxy groups at 2.68 ppm. These results verified that TPI was successfully epoxidized.

#### Effect of the reaction conditions

The reactions for the synthesis of ETPI can be represented as follows:



Among these reactions, reactions (1) and (2) are the main reactions, and reaction (3) is the side reaction. When epoxidation is conducted in strong acidic conditions, epoxy groups undergo a ring-opening reaction and yield hydroxyl groups [reaction (3)]. Gan et al.<sup>5</sup> showed that these hydroxyl groups decreased the mechanical properties of epoxidized polymers. Therefore, it is necessary to optimize the reaction conditions to reduce side reactions. The effects of the reaction temperature, reaction time, and pH value on the epoxy content were investigated.

**Reaction temperature.** The reaction temperature had a significant effect on the degree of epoxidation. The increase in reaction temperature favored the generation of epoxy groups. As shown in Figure 3, the epoxy content increased from 23 to 85% when the temperature rose from 0 to 25°C. However, the increase in reaction temperature also accelerated the side reaction. Figure 1(B,C) presents the FTIR spectra of ETPI prepared at reaction temperatures of 13 and 25°C. In addition to characteristic peaks of TPI and epoxy groups, the FTIR spectra also exhibited a carbonyl peak at  $1716\text{ cm}^{-1}$  and a hydroxyl peak at  $3430\text{ cm}^{-1}$  resulting from the ring-opening reaction of epoxy groups. The intensity of these two peaks were higher for ETPI prepared at the higher temperature [Fig. 1(C)], which indicated that the side

reaction was accelerated by the increase in reaction temperature.

**Reaction time.** Figure 4 shows the effect of the reaction time on the epoxy content. The increase in reaction time increased the epoxy content. Extending the reaction time could raise the reaction chance between peracetic acid and double bonds to yield more epoxy groups. However, an increase in reaction time could lead peracetic acid to decompose, which would slow down the reaction. Therefore, the reaction time

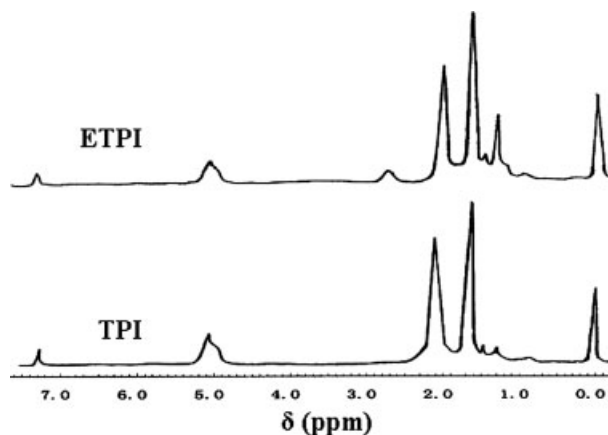
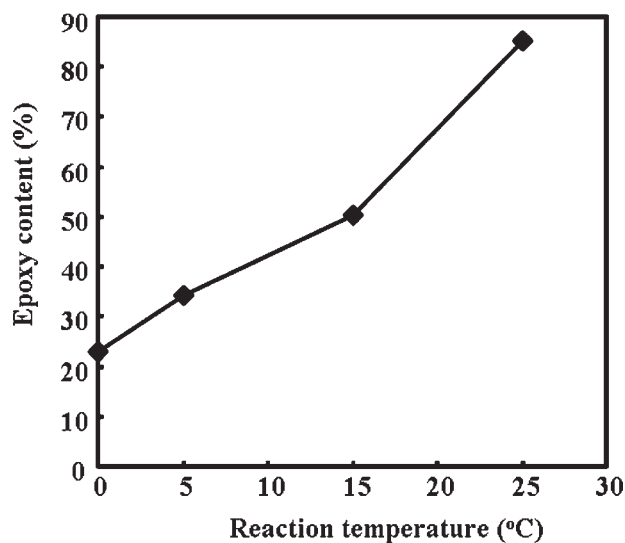


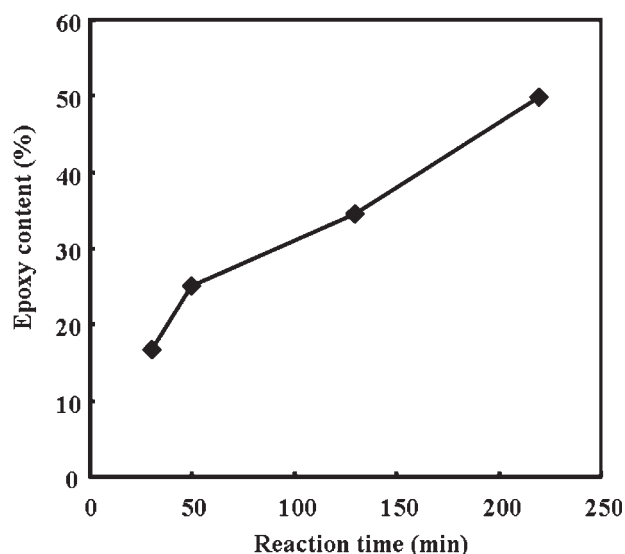
Figure 2  $^1\text{H-NMR}$  spectra of TPI and ETPI.



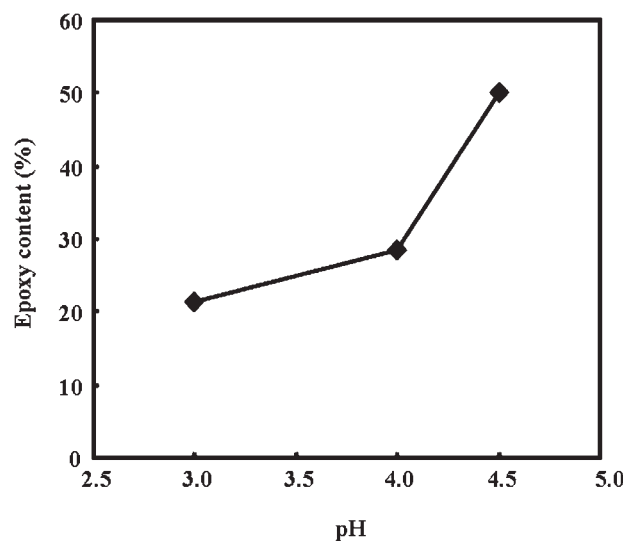
**Figure 3** Effect of the reaction temperature on the epoxy content (reaction time = 300 min, pH = 4.5).

should be controlled to obtain the desired epoxy content.

*pH value.* As shown in reactions (1) and (2), epoxy groups were produced in acidic conditions. The pH affected the epoxidation of the polymer and the ring-opening reaction of the epoxy groups. As shown in Figure 5, the drop in pH from 4.5 to 4.0 significantly decreased the epoxy content. A further decrease in pH slightly reduced the epoxy content. However, the decrease in pH increased the side reaction because the epoxy groups underwent a ring-opening reaction under acidic conditions.



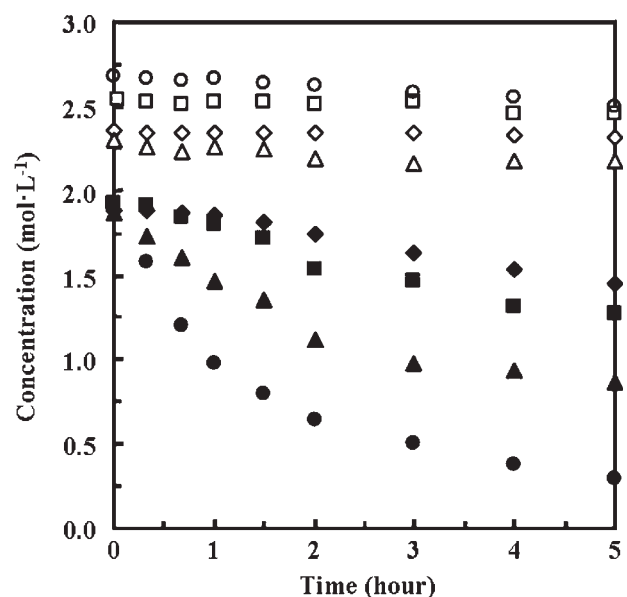
**Figure 4** Effect of the reaction time on the epoxy content (reaction temperature = 25°C, pH = 4.5).



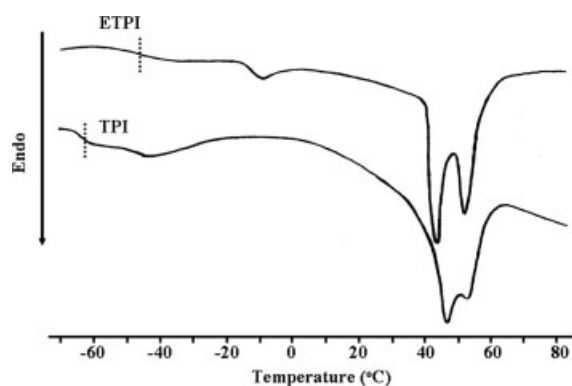
**Figure 5** Effect of the pH value on the epoxy content (reaction temperature = 15°C, reaction time = 220 min, pH = 4.5).

#### Reaction kinetics

The reaction kinetics of the epoxidation reaction were investigated and are shown in Figure 6. The concentration changes of peracetic acid and hydrogen peroxide during the reaction were monitored and were used as an index of reaction kinetics. As shown Figure 6, the concentration of peracetic acid decreased with time, whereas the concentration of hydrogen peroxide remained almost the same. This suggests that the reaction rate of reaction (2) was

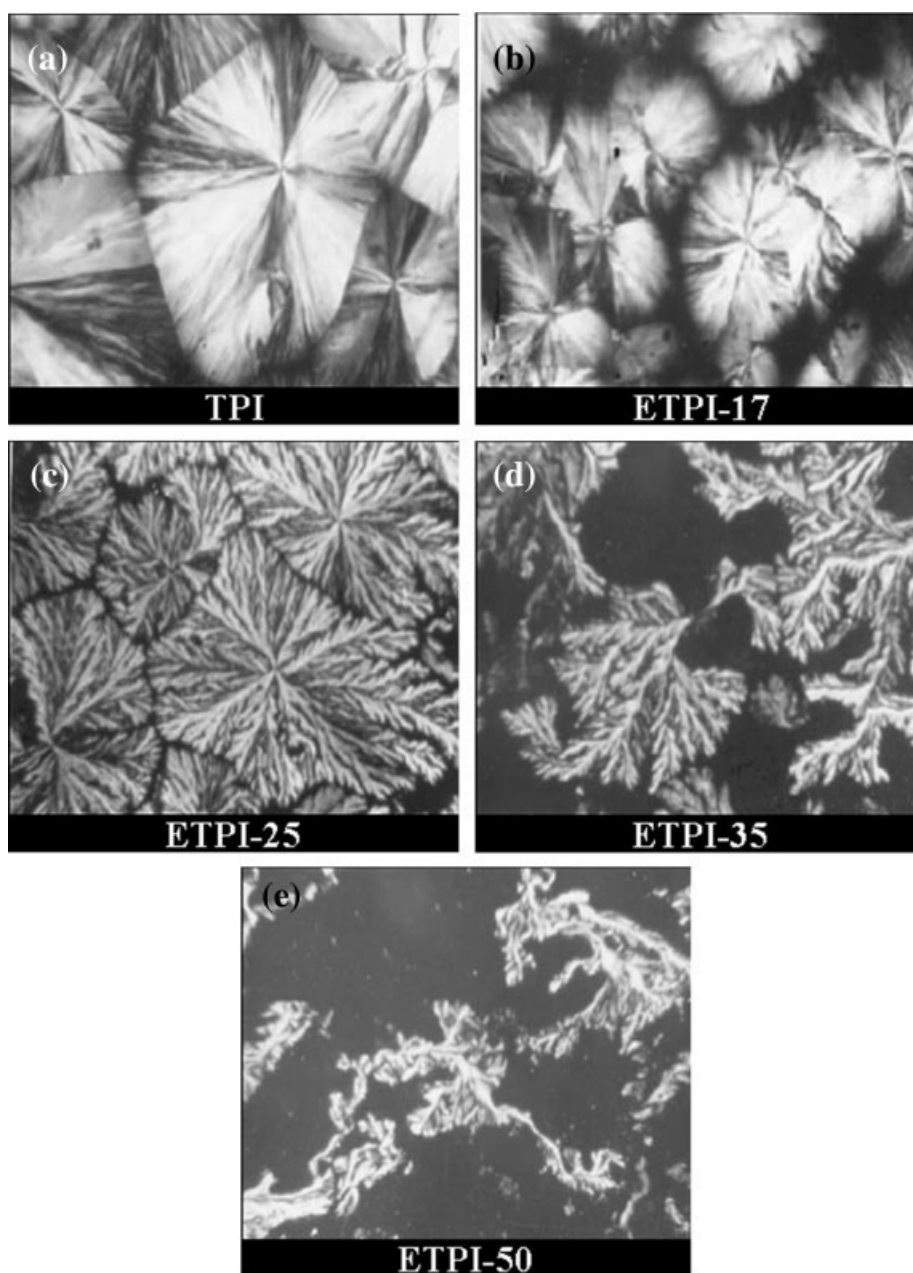


**Figure 6** Reaction kinetics of epoxidation at different temperatures (pH = 4.5): ( $\diamond$ ) 0, ( $\square$ ) 5, ( $\triangle$ ) 13, and ( $\circ$ ) 25°C for  $[\text{H}_2\text{O}_2]$  and ( $\blacklozenge$ ) 0, ( $\blacksquare$ ) 5, ( $\blacktriangle$ ) 13, and ( $\bullet$ ) 25°C for  $[\text{CH}_3\text{CO}_3\text{H}]$ .



**Figure 7** DSC curves of TPI and ETPI.

much greater than that of reaction (1). As a result, reaction (2) could be used to characterize the reaction kinetics. The reaction kinetics of different reaction temperatures were investigated. In general, the consumption of peracetic acid was accelerated when the reaction temperature increased (Fig. 6). This implicated that the epoxidation was accelerated. This was consistent with the results in Figure 3, where the epoxy content increased with reaction temperature. The epoxidation reaction in this system was a liquid–solid reaction. It was theoretically close to a zero-order reaction; that is, the reaction rate should have been related to the surface properties of the TPI granule, and the peracetic acid concentration



**Figure 8** Polarizing microscopy photographs of TPI and ETPI with different epoxy contents.

change should have been proportional to time. As shown in Figure 6, reactions at 0 and 5°C demonstrated characteristics of zero-order reactions because the peracetic acid concentration change was linear to time. For reactions at 15 and 25°C, the reaction kinetics exhibited two features, that is, a zero-order reaction at the beginning and a non-zero-order reaction at a later time. This phenomenon suggested that the reaction rate decreased at a later stage. In this epoxidation system, epoxidation occurred mainly on the surface of the granules and regions that reagents could diffuse into. Double bonds in the amorphous region reacted first followed by crystalline regions because the reactants could diffuse more easily into the less compact amorphous region. At lower temperatures, the reaction rate was relatively low, and double bonds in the amorphous region reacted progressively. In contrast, at higher temperatures, the initial reaction rate was high; this caused accessible double bonds in the amorphous region to be consumed in a shorter time, which prolonged the reaction time and led to an epoxidation of double bonds in the crystalline region. Because the reactants diffusion rate was low in the crystalline region, the reaction rate, therefore, decreased.

### Properties of ETPI

Thermal properties of ETPI

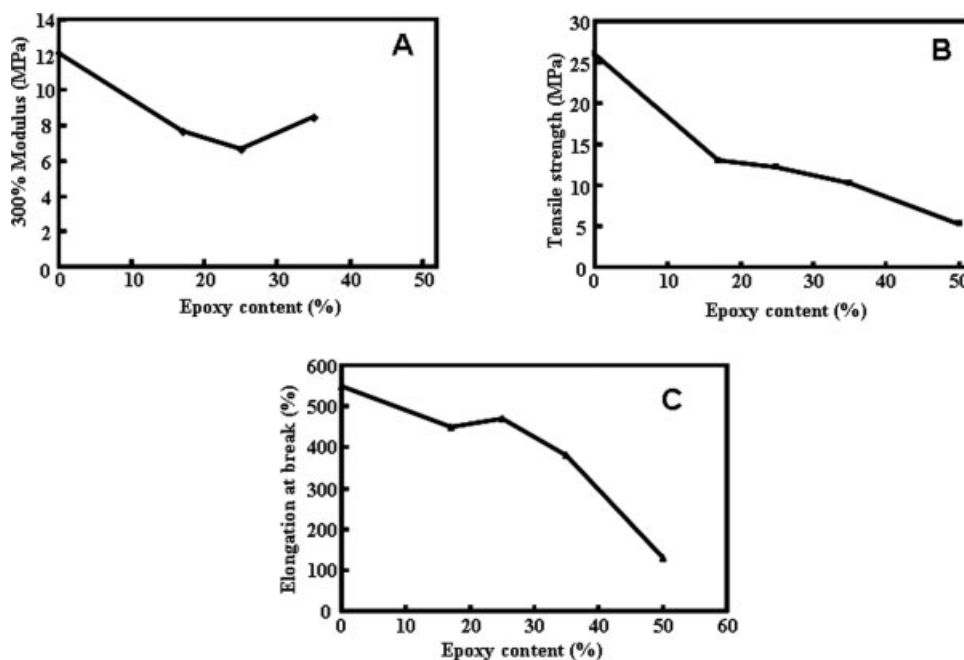
Figure 7 shows the DSC curves of TPI and ETPI. ETPI exhibited a higher glass-transition temperature

than TPI. This was due to the decrease in polymer chain flexibility and enhanced intermolecular interactions after the introduction of epoxy groups. Compared with TPI, ETPI possessed fewer double bonds because they participated in epoxidation, which therefore, decreased polymer chain flexibility. In addition, the introduction of polar epoxy groups increased intermolecular interactions and also decreased chain flexibility.

Both TPI and ETPI showed crystalline characteristics. TPI had double melting peaks at 47 and 53°C, which were related to the two TPI crystal forms,  $\beta$  and  $\alpha$ , respectively.<sup>3</sup> ETPI with an epoxy content of 21% also showed two melting peaks at 42 and 51°C, respectively. The melting-temperature decrease in ETPI revealed that the introduction of epoxy groups decreased polymer chain flexibility and hindered crystalline processes.

Figure 8 shows polarizing microscope pictures of ETPI with various epoxy contents. Epoxidation significantly affected the crystalline structure. With the increase in epoxy content, noncrystalline black specks in the rim and inside of the spherules increased, which indicated that the degree of crystalline decreased. This also implied that epoxidation could occur in the crystalline region.

ETPIs prepared by this method displayed a crystalline structure even when the epoxy content was 50%. This was contrary to the ETPI synthesized by a solution method where ETPI lost the ability to crystallize when the epoxy content was higher than 25%.<sup>10,16</sup> In the solution epoxidation method, TPI



**Figure 9** Mechanical properties of nonvulcanized ETPI (epoxy content = 17%): (A) 300% modulus, (B) tensile strength, and (C) elongation at break.

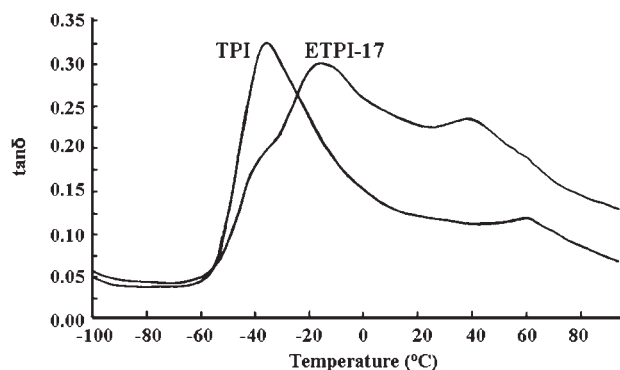


Figure 10 DMA of vulcanized TPI and ETPI.

was dissolved in an organic solvent, polymer chains had the same probability to be epoxidized, and epoxy groups distributed uniformly in the polymer chains; when the epoxy content was high, the interaction among epoxy groups greatly decreased the crystallization ability of ETPI. In contrast, in the water-phase suspension method, TPI granules were suspended in the reaction system, and only part of TPI was epoxidized because epoxidation occurred only on the surface and regions reagents could diffuse into; therefore, unreacted TPI still retained its crystalline structure. In addition, the reagents diffused more easily into the less compact amorphous region than the compact crystalline region; therefore, some crystalline regions still kept their crystalline structure.

### Mechanical properties of ETPI

Figure 9 shows the mechanical properties of TPI and ETPI with different epoxy contents. Compared with TPI, ETPIs showed reduced tensile strength, elongation at break, and 300% modulus. With the increase in epoxy content in ETPI, tensile strength and elongation at break decreased. For ETPIs, mechanical properties were mainly affected by the epoxy content and crystallinity. The increase in polar epoxy groups in the polymer chain enhanced intermolecular interactions, which should have theoretically increased the tensile strength and 300% modulus. Meanwhile, polymer crystallinity decreased with the increase in epoxy content, which should have decreased the tensile strength and 300% modulus. The results shown in Figure 9 indicate that the crystallinity predominantly affected the mechanical properties of ETPI.

### Properties of vulcanized ETPI

#### Mechanical properties

ETPIs were further vulcanized by a conventional sulfur vulcanization system. Figure 10 displays the mechanical properties of ETPI crosslinked with different sulfur content. In general, vulcanized ETPIs possessed decreased 300% modulus and deformation set compared to nonvulcanized ETPI. With the increase in sulfur content, the crosslinking density improved, which decreased the 300% modulus and deformation set. The tensile strength and elongation at break

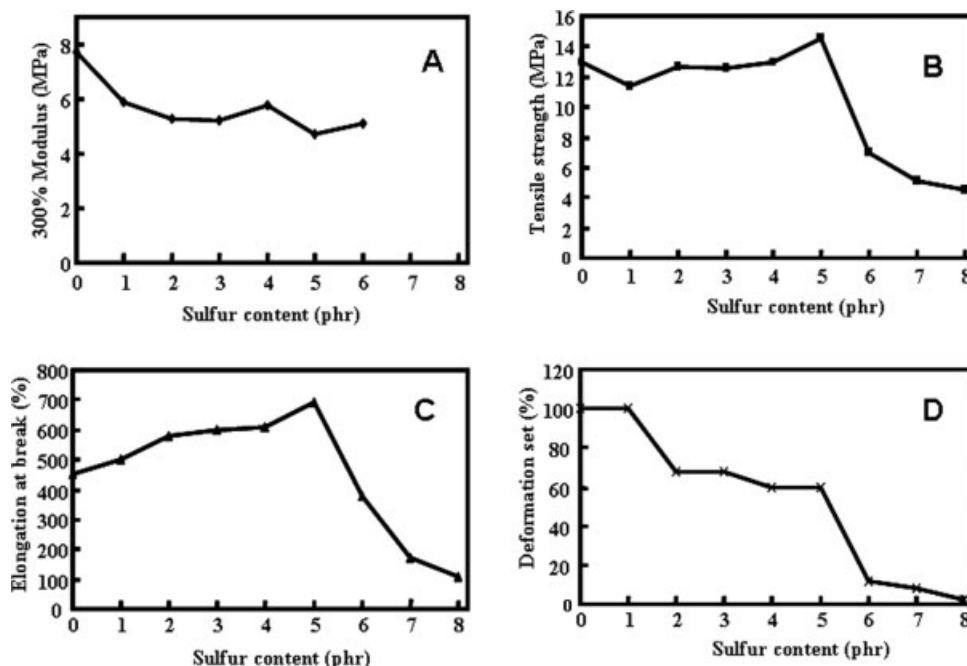
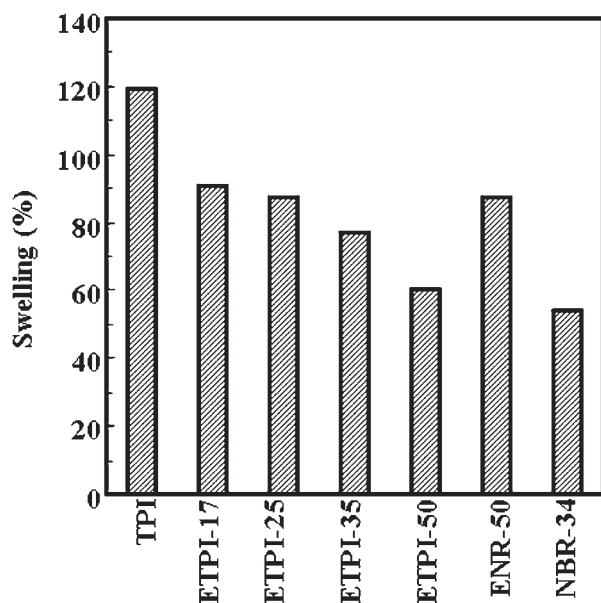


Figure 11 Mechanical properties of vulcanized ETPI (epoxy content = 17%): (A) 300% modulus, (B) tensile strength, (C) elongation at break, and (D) deformation set.



**Figure 12** Swelling ratio of vulcanized TPI, ETPI with different epoxy contents, ENR-50, and NBR-34 in oil. ETPI-X represents ETPI with an epoxy content of X%.

increased with sulfur content when it was lower than 5 phr. A further increase in sulfur content led to decreased tensile strength and elongation at break due to a high crosslinking density.

#### Viscoelastic properties

The viscoelasticity of ETPI was characterized by DMA. As shown in Figure 11, vulcanized ETPI showed a glass-transition temperature at  $-13.7^{\circ}\text{C}$  and a melting temperature at  $39.4^{\circ}\text{C}$ . TPI had a glass-transition temperature at  $-34.2^{\circ}\text{C}$  and a melting temperature at  $60^{\circ}\text{C}$ . ETPI possessed higher  $\tan \delta$  at 0, 60, and  $80^{\circ}\text{C}$  than TPI. This indicates that wet-skid resistance was significantly improved after epoxidation. However, rolling resistance and heat buildup also increased.

#### Oil-resistance properties

The oil resistance of ETPI with various epoxy contents was characterized by the swelling ratio in oil. For comparison, the oil resistance of ENR-50 and

NBR-34 were investigated. As shown in Figure 12, the vulcanized ETPIs had a significantly lower swelling ratio than TPI, which indicates that the epoxidation improved oil resistance remarkably. The ETPIs with epoxy contents of 17, 25, and 35% had oil resistances comparable to epoxidized ENR-50, whereas ETPI with an epoxy content 50% had an oil resistance similar to NBR-34. The oil resistance was related to the polarity of the polymer chain, whereby the oil resistance was expected to increase with polarity. The increase in epoxy content increased the polarity of ETPIs and, consequently, increased oil resistance.

## CONCLUSIONS

An organic-solvent-free water-phase suspension method was used to successfully synthesize partially epoxidized ETPI. ETPI with epoxy contents under 80% could be obtained within 4 h, depending on the reaction conditions. The ETPI increased the oil-resistance and wet-skid-resistance properties. ETPI can potentially be used for high-performance tires.

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