Preparation of Epoxidized Rubber Using a Reactive Processing Technique. I. Synthesis and Characterization of Epoxidized Polybutadiene Rubber

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ABSTRACT: The epoxidation of high *cis*-butadiene rubbers (BR) with monoperoxy phthalic acid was successfully performed in reactive processing equipment of the HAKKE mixer at room temperature. The effects of such reaction conditions as the concentration of peroxy acid and reaction time on the epoxidation level and the efficiency of monoperoxy phthalic acid were investigated. The structure of epoxidized BR was characterized by ^{1}H NMR and Fourier transform infrared spectrometer. Differential scanning calorimeter analysis revealed that the glass transition temperature of epoxidized BR had a progressive increase with epoxidation level. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2987–2992, 2001

Key words: epoxidation; high *cis*-butadiene rubber; reactive processing; monoperoxy phthalic acid

INTRODUCTION

Chemical modification is a powerful tool for obtaining polymers with new properties and therefore for increasing the scope of their applications. Chemical reactions on unsaturated rubber have attracted considerable academic and industrial interest because of the technological importance of the parent material and the reactivity of the available double bonds.[1] The introduction of epoxy group along the polymeric chain by the epoxidation reaction of double bonds is one of the most promising methods of modifying polydiene rubbers.[2] However, up to now, almost all the epoxidation of rubbers has been performed either in solution[3] or in latex,[4] and these systems have disadvantages of high cost and complex operation.

In recent years, solventless reactive processing has been increasingly used in manufacturing rubber products.[5,6] This situation prompted us to explore the feasibility of applying this technology to the epoxidation of rubbers. If possible, what requirements does it need? What similarities and differences are there between it and the conventional epoxidation process? To shed light on these problems, we made efforts to arrange the experiments carefully. This report is the first example of epoxidation reaction of rubber in reactive processing equipment, i.e., the epoxidation reaction of high *cis*-butadiene rubber (BR) with monoperoxy phthalic acid (MPPA).

EXPERIMENTAL

Materials

High *cis*-BR (*cis* content, 96–98%), was supplied by Shanghai Gaoqiao Petrochemical Co., Ltd. in

Table I   Experimental Conditions for Epoxidation of BR with MPPA

Sample	1	2	3	4
$[=]_{CH0}$,[a] mol/100 g BR	1.85	1.85	1.85	1.85
$[OO]_{CH0}$,[a] mol/100 g BR	0.068	0.137	0.275	0.412
$[OO]_{CH0}/[=]_{CH0}$, mol %	3.7	7.4	14.8	22.3
Reaction times (min)	3, 6, 9, 15, 20, 25, 30	3, 6, 9, 12, 15, 20, 25	3, 6, 9, 12, 15, 18, 25	3, 6, 9, 12, 15

[a] $[=]_{CH0}$: initial molar amount of unsaturated double bonds in BR; $[OO]_{CH0}$: initial molar amount of MPPA.

China, and extracted with acetone to remove antioxidants just before use.

Phthalic anhydride, hydrogen peroxide (30% aqueous solution) and other chemicals were purchased from commercial sources, and used as received.

MPPA was synthesized from phthalic anhydride and hydrogen peroxide following the method described by Payne.[7]

Epoxidation of Polybutadiene Rubber

The epoxidized polybutadiene rubber (EBR) was prepared by reactive mixing of BR and MPPA in the mixer of a HAAKE RC-90 Rheometer at a roll rate of 20 rpm for a predetermined time at room temperature. The resulting product was dissolved in chloroform and precipitated in methanol not less than two times, and then dried under vacuum at 40°C.

Characterization of Epoxidized Polybutadiene Rubber

^{1}H NMR spectra were obtained from a Brucker DRX 500 spectrometer. Samples were determined at 25°C in CDCl$_3$ using TMS (tetramethylsilane) as internal standard.

Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer Paragon 1000 infrared spectrometer in KBr pellet.

Glass transition temperature (T_g) was determined using differential scanning calorimeter (DSC-SP; Rheometric Scientific Co.) equipped with a liquid nitrogen subambient cooling accessory and using nitrogen as purge gas. Samples (ca. 10 mg) were pretreated at 100°C for 2 min, quenched rapidly to −150°C, and scanned upwards at 10°C/min. Quoted T_g values are the onset temperature as computed with Rheometric Scientific™ 6.4.0 software.

The oxirane contents were analyzed according to Jay's method.[8] The degree of conversion of dou-

ble bonds to epoxy groups was calculated according to the following formula:

Epoxidation level % = the epoxy group content (in mol/100 g rubber)/the content of butadiene units containing double bonds (in mol/100 g rubber) × 100%

RESULTS AND DISCUSSION

Our primary intention is to develop new polymeric materials through reactive blending of epoxidized diene rubber with other substances. If epoxidizing and blending procedures can be completed within the same equipment, such operation is undoubtedly the simplest, and the entire process is also the cheapest in comparison with the operations used for epoxidation of rubbers in solution and latex. Following this idea, reactive processing becomes the route of choice.

Synthesis and Characterization of Epoxidized BR

The currently established method for rubber epoxidation of BR invariably involves reactions of double bonds with organic peroxy acids.[9] In our experiment, we chose MPPA as an epoxidizing reagent for its easy preparation, stability, and solid state at room temperature.

The epoxidation of BR with MPPA was performed in the HAAKE internal mixer under the experimental conditions shown in Table I. The principle of the reaction can be illustrated by Scheme 1. The reaction products were isolated
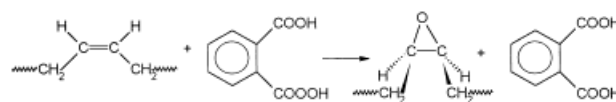
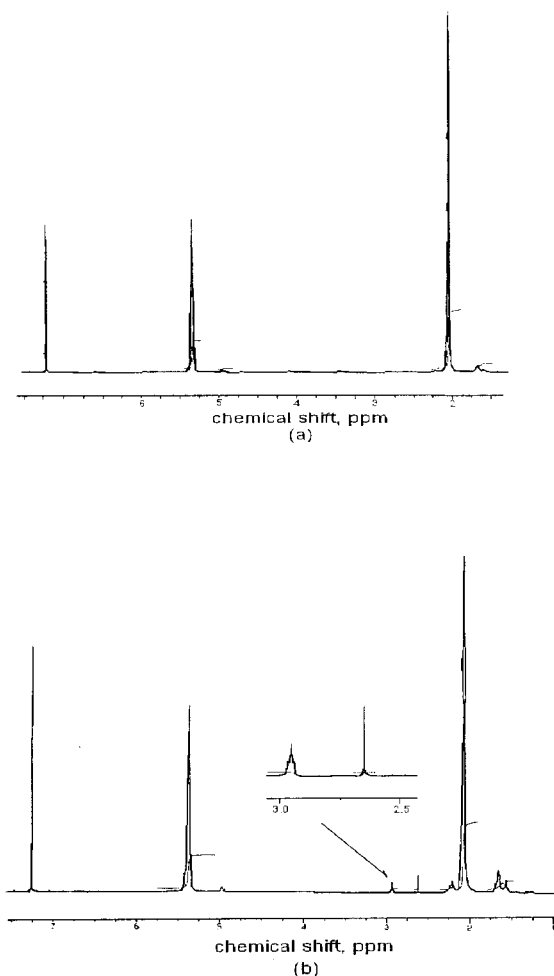**Scheme 1** The epoxidation reaction of BR with MPPA.

Figure 1 ^{1}H NMR spectra of sample 1 before (a) and after (b) epoxidation (reaction time 6 min).

Figure 2 FTIR spectra of sample 1 at different reaction times.

and purified before characterization (yield of the epoxidized BR >90%).

Figure 1 shows ^{1}H NMR spectra for BR and the reaction product (sample 1, reaction time, 6 min). It can be seen that there are obvious differences between them. In the spectrum of the parent BR [Fig. 1(a)], there are two doublets centered at δ = 5.0 and 5.24 ppm derived from olefinic resonances of substituted methine protons of the double bonds in BR. In the spectrum of the product [Fig. 1(b)], some new proton signals at δ = 2.65 and 2.95 ppm appear, which can be attributed to protons attached to epoxy groups,[10] indicating that the double bonds in BR have been converted into epoxy groups.

The FTIR spectrum of sample 1 at different reaction times is shown in Figure 2. The absorption band at 735 cm^{-1} is characteristic of the C—H out-of-plane deformation of *cis*-alkene. The
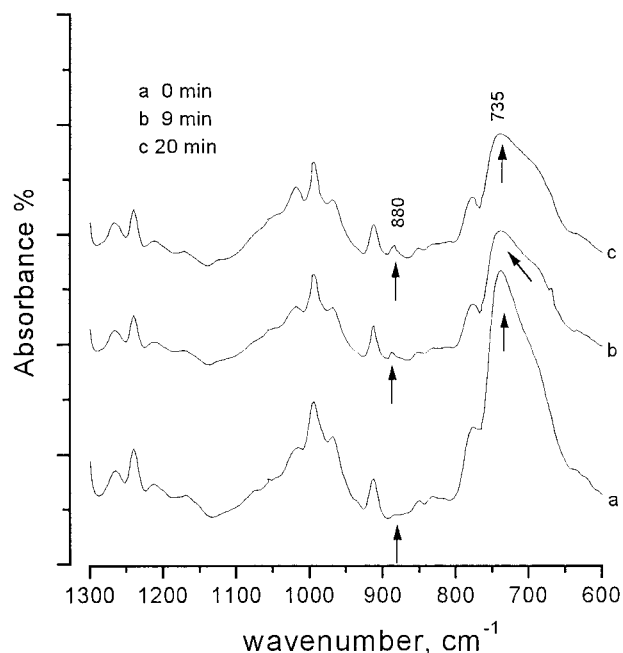
oxirane ring absorption is visible at 880 cm^{-1} (b,c). As the reaction proceeds, the double bond in BR is consumed and this can be reflected in the changes of shape and intensity of absorption at 735 cm^{-1} and the gradual increase in the intensity of the absorption at 880 cm^{-1}.

For describing the epoxidation reaction quantitatively, a reliable analysis method for measuring epoxy groups should be established. Several kinds of analytic techniques, such as direct chemical titration, NMR and DSC were successfully used for this end.[11] Direct titration of the oxirane with HBr gave good results, especially at low levels of epoxidation (<10%).[12] NMR gives not only the structure information of materials but also epoxy contents calculated by the ratio of the integrated areas of the olefinic and epoxy methine protons. Alternatively, DSC method is an indirect

Table II Epoxide Content of EBR Measured by Different Techniques (mol %)

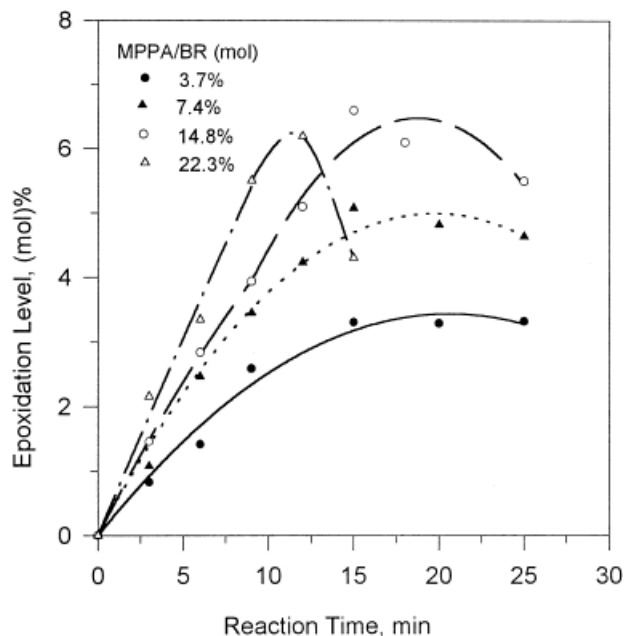| MPPA/Double Bond in BR (mol %)[a]	Titration Method	^{1}H NMR	DSC
3.7	1.42	1.71	1.99
7.4	2.45	2.92	3.1

[a] Reaction time 6 min.

Figure 3 Dependence of epoxidation level on reaction time at different MPPA/BR ratios.

approach, which requires an independent calibration curve of T_g versus epoxy content. Table II lists our results obtained from the three methods for comparison. We prefer to adopt the direct titration because of its accuracy at low levels of epoxidation and availability in our laboratory.

Effect of Reagent Ratio

To find suitable conditions for the epoxidation of BR with MPPA by reactive processing technique, various molar ratios of MPPA to BR were used. The results are given in Figure 3.

As shown in Figure 3, the epoxidation level sharply increases with increasing reaction time during the initial period of reaction, and then begins to fall off after reaching a maximum. Moreover, this trend becomes more obvious at the higher MPPA/BR ratios.

Figure 4 depicts the plot of efficiency of MPPA (efficiency % = the conversion of MPPA (in mol/100 g rubber)/the initial amount of MPPA (in mol/100 g rubber)) and maximum epoxidation level versus MPPA/BR, respectively. It was found from Figure 4 that as far as epoxidation level, there is an optimum MPPA/BR molar ratio, which is about 14 mol %, and that the reaction efficiency of MPPA decreases rapidly with increasing MPPA/BR molar ratios. These phenomena may
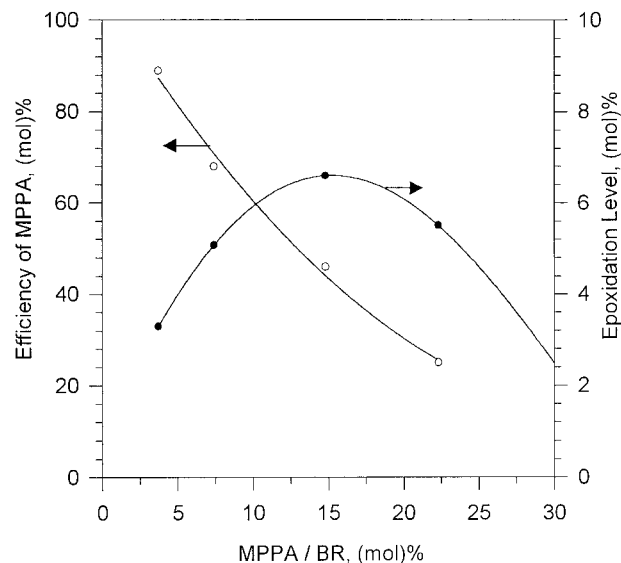

Figure 4 Effect of MPPA/BR ratio on efficiency of MPPA and epoxidation level.

be attributed to secondary reactions of the adjacent epoxy groups which were converted into ether on the conditions of high acidity, as can be demonstrated by the obvious appearance of absorption bands at 3445 cm^{-1} in Figures 5(c) and (d).[13]
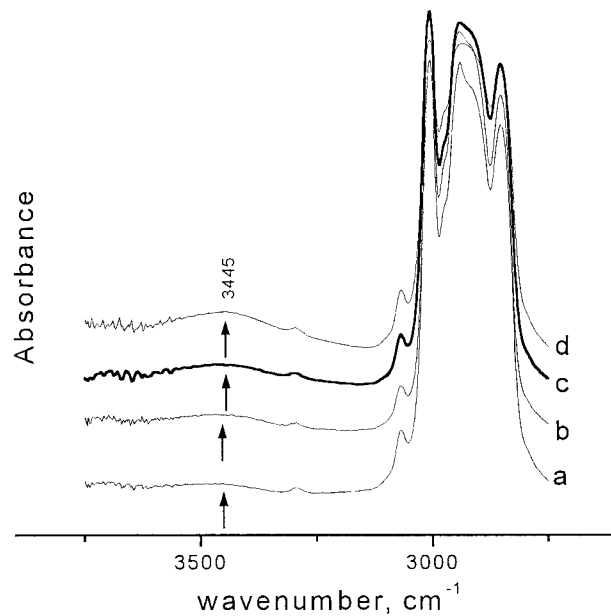

Figure 5 FTIR spectra of epoxidized BR at different MPPA/BR ratios (mol %) (a, 3.7; b, 7.4; c, 14.8; d, 22.3) and reaction time (a, 20 min; b, 20 min; c, 18 min; d, 15 min).
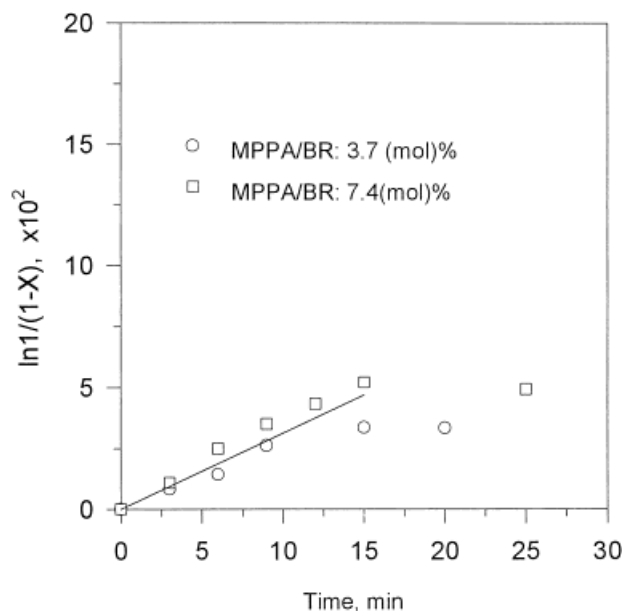
Figure 6   Plot of $\ln 1/(1-X)$ versus reaction time for eq. (3).

In contrast, at the lower peroxy acid concentration of 3.7 (mol)% and 7.4 (mol)% as shown in Figure 5(a) and (b), nearly no characteristic absorption peaks of hydroxyl group at about 3445 cm^{-1} can be seen in the FTIR spectra. The NMR spectra (Fig. 1) in which there is no peak of hydroxy resonance at about 3.4 ppm manifests that no ring opening reaction occurs at the given MPPA/BR ratio. These facts support the conclusion that there will be no significant side reaction under the conditions of MPPA/BR not more than 7.4 mol % and reaction time not more than 20 min.

Kinetics Analysis

Generally speaking, the epoxidation reaction in solution or latex system is based on a second-order reaction mechanism.[14] Similarly, the epoxidation reaction in rubber matrix may be expressed as:

$$-\frac{d[=]_{CH}}{dt} = \frac{dX}{dt} = k[=]_{CH}[OO]_{CH} \quad (1)$$

where $[=]_{CH}$, $[OO]_{CH}$, and X represent the molar amounts of unsaturated double bonds, MPPA, and epoxy units formed in the rubber, respectively. Because of the complexity of the reaction in reactive processing equipment, exact kinetics

analysis is rather difficult. Nevertheless, at a low concentration of peroxy acid, the amount of unsaturated double bonds is in large excess of MPPA (10 ~ 30 times in excess), and the decrease in $[=]_{CH}$ could be practically neglected, i.e., $[=]_{CH}$ is considered as a constant. Accordingly, the reaction could be viewed as a pseudo-first-order reaction. Equation (1) could be simplified as the following rate equation:

$$\frac{dX}{dt} = k'[OO]_{CH} \quad (2)$$

Moreover, at a low concentration of peroxy acid, there is evidently no crucial amount of side reactions as well, and the conversion of MPPA is equal to the amount of epoxy groups formed, X, in mol. The relationship $[OO]_{CH} = [OO]_{CH0} - X$ is applied in eq. (2) and then integrating eq. (2) from 0 to t gives eq. (3):

$$\ln \frac{1}{1-X} = k't \quad (3)$$

The apparent rate constant, k', can be obtained from, and equals the slope of a plot of $\ln 1/(1-X)$ versus t as shown in Figure 6. The plot is initially a straight line, but diverges from linearity after 15 min. This deviation might be attributable to the effect of an epoxide group on the reactivity of
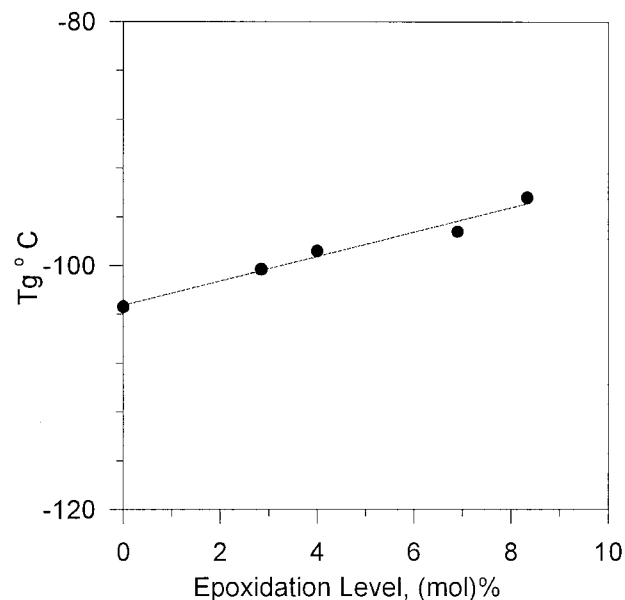

Figure 7   Influence of epoxidation level on the T_g of epoxidized BR.
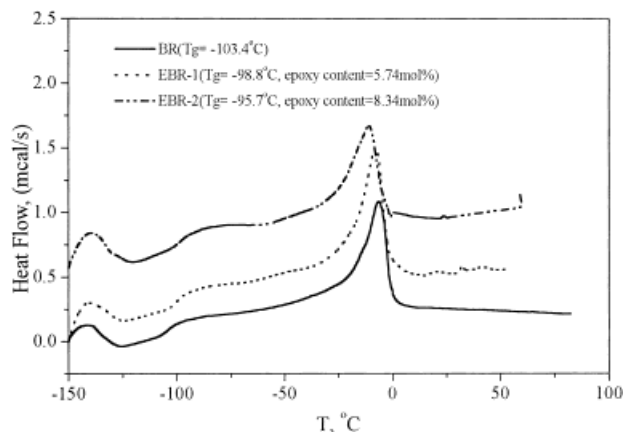
Figure 8 DSC scans of BR and EBR with different epoxidation levels.

adjacent unreacted unsaturated groups. The initial linearity of the plot confirms that the epoxidation reaction is pseudo-first-order and the apparent rate constant, k', calculated from the straight line is 3.13×10^{-3} min^{-1}.

Thermal Analysis

Main-chain modification of polydienes inevitably leads to high T_g values because of lowered rotational freedom of the modified repeating unit.[15] This foundational fact has been proved again in our experiment. Thermal analytic data show that the epoxidation indeed results in a progressive increase in T_g of the EBR with increasing epoxidation levels (Fig. 7).

Figure 8 is the DSC scans of BR and EBR with different modification levels. It can be seen that both EBR only show one T_g. This indicates that the distribution of epoxy groups along the BR main chain is random because of the absence of distinct T_g phenomenon in the modified rubber. This may imply that MPPA can be rapidly mixed with BR to give uniform epoxidation of BR.

CONCLUSION

High *cis*-butadiene rubber with low epoxidation levels (<10 mol %) have been successfully prepared by epoxidation of BR with MPPA in reactive processing equipment of the HAAKE mixer. At low concentration of peroxy acid, an apparent epoxidation of BR and few side reactions are evidenced by the FTIR and ^{1}H NMR spectra. Kinetic investigation indicates that the epoxidation reaction follows pseudo-first-order mechanism and the apparent rate constant is 3.13×10^{-3} min^{-1} at the reaction time not more 15 min. DSC analysis shows that the EBR has only one T_g, which increases with increasing epoxidation levels.

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