

In situ epoxidation of ethylene propylene diene rubber by performic acid

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In this paper, epoxidation of ethylene propylene diene rubber by *in situ* generated performic acid is discussed. The samples have been characterized by infra-red and ¹H-nuclear magnetic resonance analyses. Quantitative analysis of the reaction products is made possible by using the methyl deformation band at 1377 cm⁻¹ as internal standard. The conversion of double bonds increases rapidly within the first 1 h, then gradually, over 2 h, has only a slight increase. The maximum conversion ratio of double bonds is about 70%. The relative content of epoxy groups has a top value at about 7 h. The side reactions are also discussed.
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INTRODUCTION

Among many possibilities of chemical modifications of polyolefins, epoxidation is a simple and efficient method for introducing a new reactive group into the polymer backbone, leading to new and useful properties and wide use in a variety of applications, especially in polymer blending^{1–4}. Epoxidation of olefinic compounds using organic peracids has been extensively studied ever since oxiranes were prepared by reacting ethylenic compounds with perbenzoic acid. It has been shown that, using perbenzoic acid⁵, chloroperbenzoic acid⁶ and mono-perphthalic acid⁷, good yields of oxiranes were generally obtained. Performic acid is an extremely active organic peracid⁸, but, owing to its instability⁹, it has to be prepared *in situ*.

This paper presents a study of the epoxidation of ethylene propylene diene rubber (EPDM) by performic acid generated *in situ*. It is known that up to now there has been no paper dealing with this, though there are some papers on the chemical modification of ethylene propylene rubber by grafting various monomers¹⁰.

EXPERIMENTAL

Materials

EPDM (made in Japan, EPT 4045) has about 4 mol% of 5-ethylidene-2-norbornene (ENB) diene component, 35.9 mol% propylene (C₃) and a glass transition temperature (*T*_g) of -60°C. Formic acid (88%) hydrogen peroxide (30%) and all other solvents were reagent grade and used as supplied.

In situ epoxidation

EPDM rubber was first dissolved in toluene in a three-

necked glass flask equipped with a mechanical stirrer and thermometer, and maintained at 50°C in a water bath. Under continuous stirring, the EPDM solution was stepwise acidified with formic acid to pH 2–3, then hydrogen peroxide was slowly added dropwise for about 30 min. Fast introduction of this reagent will cause an excessive development of oxygen due to the decomposition of hydrogen peroxide at high temperature and is not recommended. Samples of reaction mixture were taken periodically, coagulated in acetone, thoroughly washed with distilled water, soaked in 1% (w/v) Na₂CO₃ aqueous solution for 24 h, and finally rinsed with distilled water again to ensure that any remaining acid had been removed. The epoxidized EPDM rubber (eEPDM) so obtained was dried to constant weight under vacuum at 40°C.

Characterization

Fourier transform infra-red (FTi.r.) spectra were recorded on a Bio-Rad FTS-7 FT i.r. spectrophotometer. The eEPDM obtained at different reaction times was dissolved in toluene to produce 5 wt% polymer solution. The thin films were cast on to a potassium bromide plate and laid in a dry atmosphere for five days, then dried in a vacuum oven at 40°C for three days. Sixteen scans at a resolution of 4 cm⁻¹ were signal-averaged. Proton nuclear magnetic resonance (¹H-n.m.r.) spectra were obtained by using a Unity-400 spectrometer with deuterated chloroform (CDCl₃) as solvent. Chemical shifts were reported in ppm relative to tetramethylsilane.

RESULTS AND DISCUSSION

Performic acid used for epoxidation of EPDM was generated *in situ*, then reacted with EPDM; as a result, double bonds of the diene component (ENB) in EPDM were transformed into epoxy groups. This reaction can

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be shown as follows:

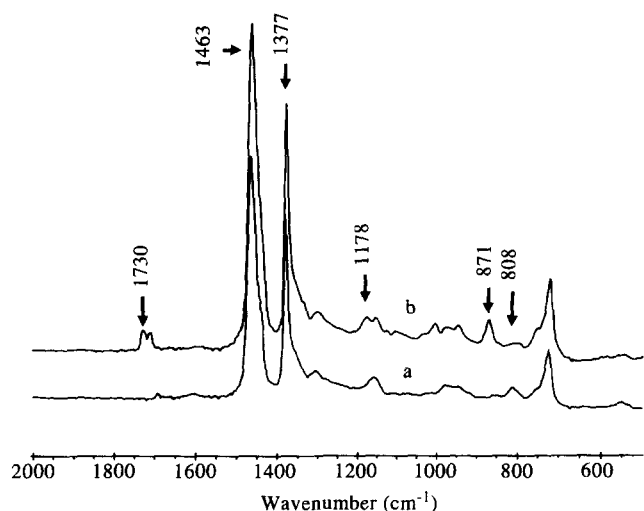
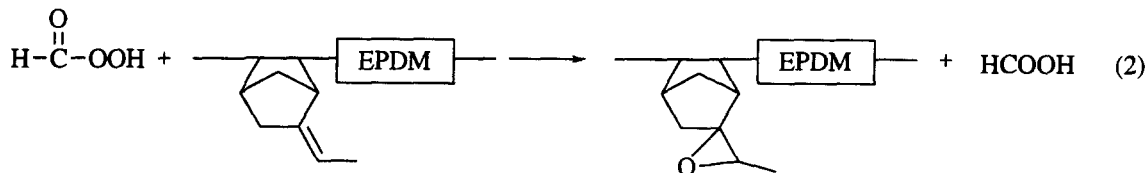
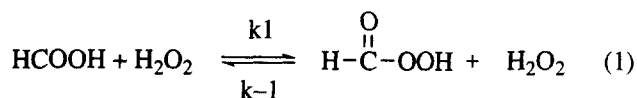


Figure 1 FT i.r. spectra of (a) EPDM and (b) eEPDM (7 h)

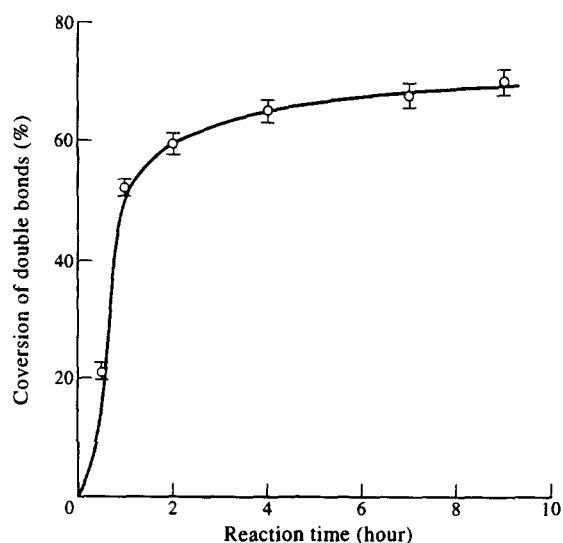


Figure 3 Conversion of double bonds versus reaction time of epoxidation

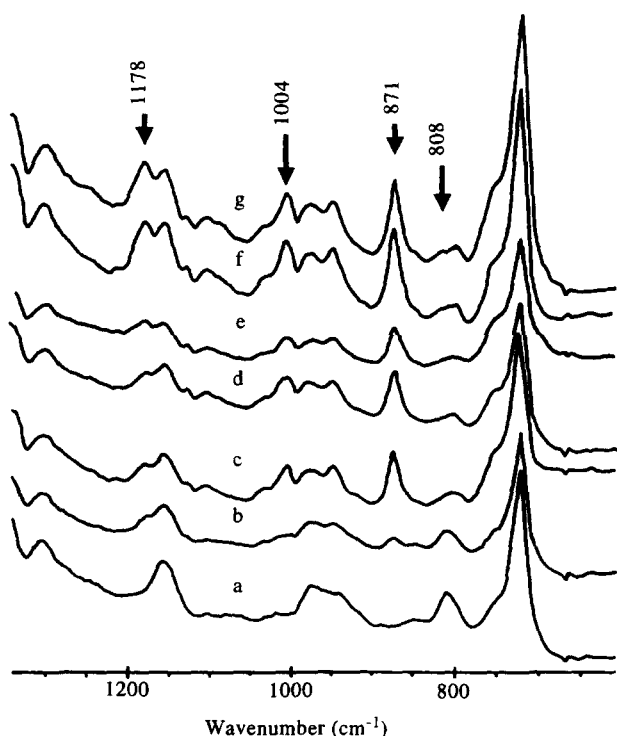


Figure 2 FT i.r. spectra of eEPDM at different reaction times: (a) 0 h; (b) 0.5 h; (c) 1 h; (d) 2 h; (e) 4 h; (f) 7 h; (g) 9 h

Figure 1 shows typical i.r. spectra for EPDM and eEPDM. It can be seen that there are obvious differences between them. The i.r. spectrum of eEPDM is characterized by the presence of specific epoxide band at 871 cm^{-1} (asymmetric epoxide ring stretching deformation vibration); meanwhile, the absorption intensity of 808 cm^{-1} , which was reported as the band of the double bond of the diene component in EPDM, is low compared with that of EPDM¹¹. Therefore, during epoxidation, double bonds of ENB can be transformed into epoxy functional groups, successfully introducing polar groups into the EPDM macromolecule backbone.

The i.r. spectra for eEPDM at different reaction times are shown in Figure 2. Relative changes of absorption intensity at 808 and 871 cm^{-1} are clearly seen. Quantitative analysis was determined by area measurement of the characterized absorption bands using the methyl deformation band at 1377 cm^{-1} as internal standard¹². The conversion of double bonds was calculated and shown in Figure 3. During the first 1 h, conversion of double bonds into epoxy groups increases rapidly, then gradually increases only slightly over 2 h. The maximum conversion of double bonds is about 70%, which is in agreement with that of previous studies dealing with epoxidation of a styrene-butadiene triblock copolymer¹³.

By comparing the absorption area at 871 cm^{-1} with

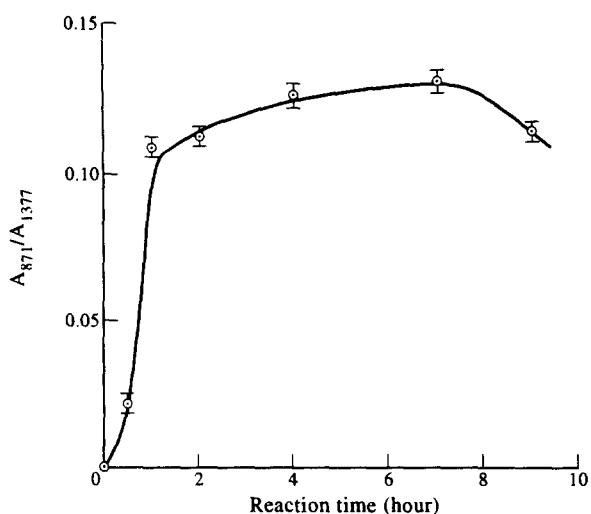
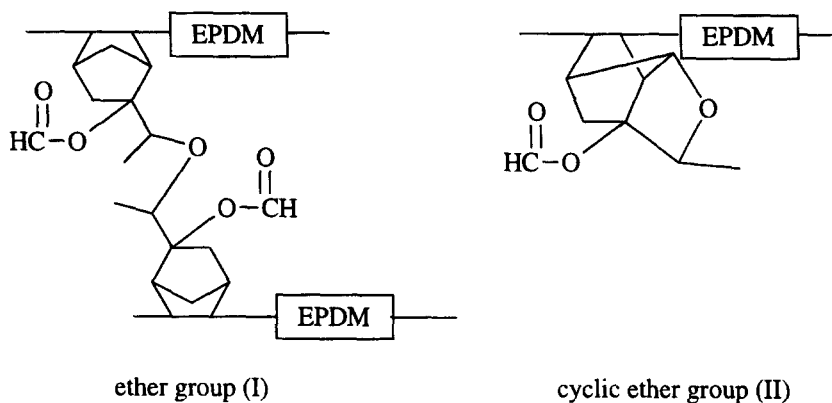


Figure 4 Relative content of epoxy groups in eEPDM versus reaction time of epoxidation

that at 1377 cm^{-1} , the relative content of epoxy groups at different reaction times can be obtained; Figure 4 shows the result. The curve is similar to that in Figure 3, but there exists a top ratio of epoxy groups at about 7 h and, beyond that time, the ratio is found to decrease. This phenomenon may be due to secondary reactions of epoxy groups. In conditions of high acidity of formic acid, epoxy groups would be acidolysed and converted into carbonyl ester, ether or cyclic ether groups, as can be demonstrated by the appearance of absorption bands at 1730 , 1178 and $1000\text{--}1100\text{ cm}^{-1}$ in Figures 1 and 2¹⁴. Side reactions soon occurred and increased with reaction time, as is confirmed by the i.r. spectra in Figure 2. Because the conversion of double bonds only increases slightly over 2 h, there must exist a maximum relative content of epoxy groups. The suggested structures of the ether group (I) and cyclic ether group (II) are¹⁵:



ether group (I)

cyclic ether group (II)

Typical $^1\text{H-n.m.r.}$ spectra of EPDM and eEPDM are shown in Figure 5. In the $^1\text{H-n.m.r.}$ spectrum of the parent polymer EPDM (Figure 5a), there are two doublets centred at $\delta = 5.01$ and 5.24 ppm derived from olefinic resonances of substituted methine protons of the diene component (ENB) in EPDM¹⁶. In the $^1\text{H-n.m.r.}$ spectrum of eEPDM (Figure 5b), some new proton signals at $\delta = 3.04$ and 3.09 ppm appear, which can be attributed to protons attached to epoxy groups and

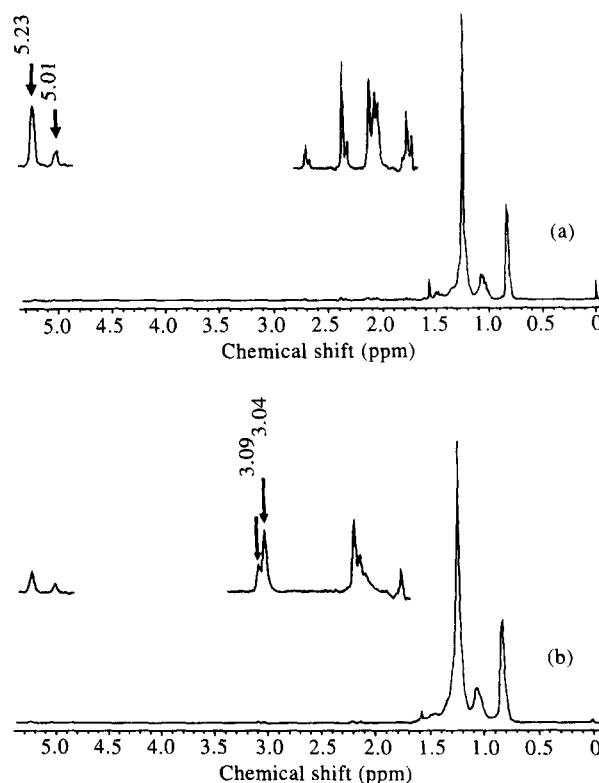


Figure 5 ^1H n.m.r. spectra of (a) EPDM and (b) eEPDM (7h)

prove that the double bonds have been converted into epoxy groups.

CONCLUSIONS

Epoxidation of EPDM can be performed by performic acid formed *in situ* successfully introducing polar groups

into the EPDM macromolecule backbone. The extent of epoxidation depends on reaction time. The maximum conversion ratio of double bonds is about 70% and a top relative content of epoxy groups exists at about 7 h due to secondary reactions of epoxy groups under the influence of formic acid. Epoxidation of EPDM will surely improve its reactivity. Epoxy groups in eEPDM become reactive sites for further modification and can be also used as cross-linking sites. Epoxy groups in eEPDM

are expected to improve the role of eEPDM greatly as an effective toughener because the increase in polarity and the probable reactive blending improve the compatibility of eEPDM with many polar polymers^{4,15}.

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