Fibers and Polymers 2002, Vol.3, No.3, 109-112

Epoxidized Polybutadiene as a Thermal Stabilizer for Poly(3-hydroxybutyrate). I. Effect of Epoxidation on the Thermal Properties of Polybutadiene

Ju Yol Choi[1], Jong Keun Lee[1], and Won Ho Park*

Department of Textile Engineering, School of Engineering, Chungnam National University, Taejon 305-764, Korea
[1]Department of Polymer Science and Engineering, Kumoh National University of Technology, Kumi, Kyungbuk 730-701, Korea

(Received August 12, 2002; Revised September 5, 2002; Accepted September 12, 2002)

Abstract: Polybutadiene (PB) was epoxidized to various extents with *m*-chloroperbenzoic acid (MCPBA) in homogeneous solution. The thermal properties of the epoxidized PBs were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). As a result of epoxidation the glass transition temperature (T_g) of PB increased by approximately 0.8 °C for each 1 mol% of epoxidation. The thermal decomposition of the epoxidised PBs occurred in two-step process, while that of PB exhibited apparent one-step degradation process.

Keywords: Polybutadiene, Epoxidation, Double bond, Glass transition temperature, Degradation

Introduction

The epoxidation of unsaturated polymers is an important reaction because epoxide groups can be used as reactive intermediates for further reactions such as crosslinking, the attachment of bioactive substances, and the introduction of ionizable groups.

Epoxidation reactions have been applied to natural rubber and other unsaturated elastomers[1-8], and many types of peracids, such as performic acid[2,3,6], peracetic acid[1,8], and *m*-chloroperbenzoic acid (MCPBA)[4,5,7], have been used for these reactions and for the epoxidation of low molecular weight unsaturated compounds[9-11]. For polymers, it is particularly important that the reaction occurs in a homogeneous phase without side reactions, especially the ring opening of the epoxide groups introduced and crosslinking. In this respect, MCPBA has the advantage over performic acid or peracetic acid because it do not induces the side reactions extensively even at high concentration.

In our recent studies[12,13], it was found that poly(3-hydroxyalkanoate)s (PHAs) with epoxide pendant groups have a higher thermal stability owing to crosslinking reactions of pendant epoxide groups with the carboxyl chain ends formed by fragmentation, during its thermal degradation. This suggests that end-group linking reactions using epoxide group could be applied effectively to repolymerize the thermally degraded polymer and then inhibit the rapid decrease in the molecular weight of poly(3-hydroxybutyrate) (PHB).

The aim of this study is to develop a polymeric thermal stabilizer containing epoxide groups for a representative microbial aliphatic polyester, PHB. For this, polybutadiene (PB) was epoxidized under the homogeneous condition using MCPBA, and its epoxidation yield (%) was determined by ^{1}H-NMR spectroscopy. The changes in thermal properties of the partially epoxidized PB (EPB) were investigated.

*Corresponding author: parkwh@cnu.ac.kr

Experimental

Materials

Polybutadiene (PB) (55 % *trans*-1,4, 36 % *cis*-1,4, and 9 % vinyl units) was purchased from Aldirich Co. (USA). *m*-Chloroperbenzoic acid (MCPBA) for the epoxidation was purified by washing the powder in a pH 7.4 phosphate buffer solution, filtering, and drying under vacuum for 2 days at 20 °C. Purity of MCPBA, which was determined by iodometric titration, was about 90 %. All other chemicals were used as received without further purification.

Epoxidation of PB

PB was epoxidized as following procedure. To a 100-m*l* vial containing 2.5 g PB dissolved in 50 m*l* chloroform was added 1.3 eq. parts (based on unsaturated groups in PB) of purified MCPBA with constant gentle stirring at 20 °C. After completion of the reaction, the solution was slowly poured into 500 m*l* cool methanol. The precipitate formed was washed with cool methanol twice and then dried *in vacuo* at 20 °C. The epoxidation yield (%) were determined by ^{1}H-NMR using the ratio of the resonance peak area of the hydrogen atoms in the oxirane (epoxy) groups at 2.8 ppm to those in the unsaturated groups at 4.9 ppm.

Polymer Characterization

^{1}H-NMR spectra were obtained with a Bruker AC-200 NMR spectrometer for polymer solutions in chloroform-*d*. The polymer concentration for ^{1}H-NMR spectroscopy was 10 mg/m*l*. The peaks were referenced to chloroform.

Differential scanning calorimetry was conducted using a TA Instrument 2910. The temperature scale of the instrument was calibrated with mercury and indium. Samples were

tested from −120 to 200 °C in a nitrogen atmosphere at a heating rate of 10 °C/min. The glass transition temperature (T_g) reported was taken as the inflection point. Thermogravimetric analysis was conducted using a TA Instrument 2950 in a nitrogen atmosphere from 30 to 700 °C at a heating rate of 20 °C/min. Maximum decomposition temperature was reported.

Results and Discussion

Epoxidation of PB

Epoxidation reactions were carried out with MCPBA because it is readily available, stable in solution at moderate temperature for prolonged periods, and reacts under mild conditions. As a result of the latter, the epoxidation of the unsaturated units in PB could be carried out quantitatively without side reactions in nonpolar solvents such as chloroform, xylene, toluene, and benzene. For this study PB samples with specific unsaturated unit contents were dissolved in chloroform at a concentration of 5 wt% and reacted with 1.3 eq. (based on the unsaturated unit content) of MCPBA at 20 °C for 20 min. The absence of significant amounts of side reactions was indicated by the observation that the polymers remained completely soluble after epoxidation. This observation indicates that crosslinking or ring-opening reaction of epoxide groups did not occurred to any extent to interfere with the rate measurements.

^{1}H-NMR spectroscopy was particularly useful for determining the degree of epoxidation (%), and it was obtained from the relative peak areas of the epoxide and olefinic hydrogen atoms. Figure 1 contains the 200 MHz ^{1}H-NMR spectrum of an epoxidized PB (EPB), as an example, after a partial epoxidation reaction with an epoxidation yield of 48 % at 20 °C. In comparison with the spectrum of the initial PB sample, the spectrum of EPB contained two new signals at 2.89 ppm and 2.74 ppm, which were assigned to the oxirane (epoxide) group. As these peaks increased in size with increasing epoxidation yield, two peaks at 4.88 ppm and 5.48 ppm in the initial PB sample, which corresponded to the unsaturated group, decreased. Spectral integration for the multiplet centered at 4.88 ppm and the multiplet centered at 2.89 ppm was used to determine the epoxidation yield in the products, and the yields as a function of reaction times for PB are shown in Figure 2. Epoxidation occurred rapidly up to 5 min, and thereafter proceeded gradually.

Polybutadiene used in this study had three types of double bonds, i.e., *cis*-1,4, *trans*-1,4, and vinyl-1,2 (pendant) type. It was expected that the reactivity of the double bonds to epoxidation strongly depends on their microstructure in PB[2,5]. It is possible to determine the 1,4-double bonds content of PB as the sum of *cis*/*trans* and also the 1,2-vinyl

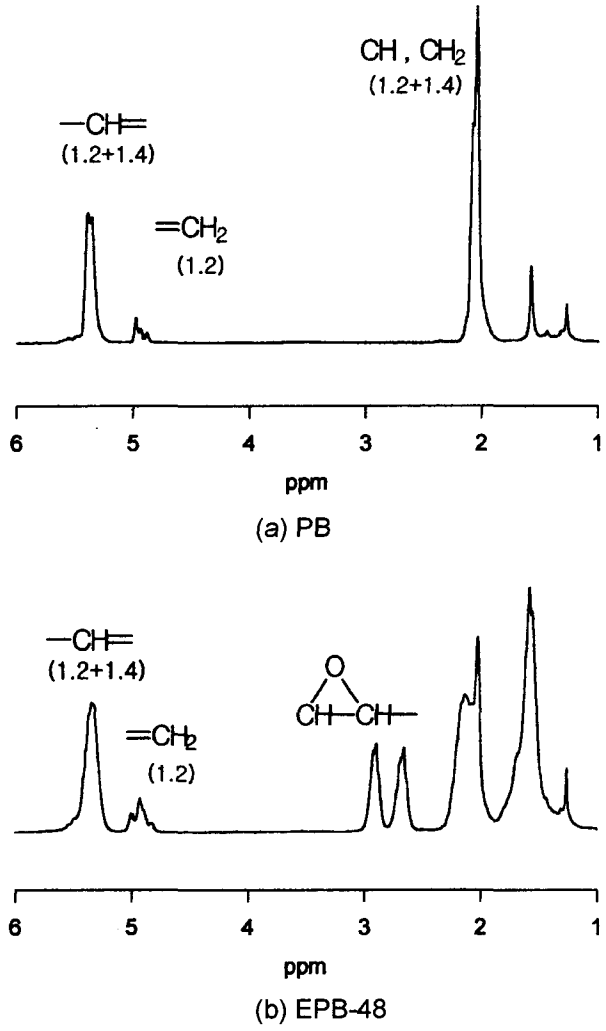

Figure 1. ^{1}H-NMR spectra of PB (a) and partially epoxidized PB (b) with an epoxidiation yield of 48 %.

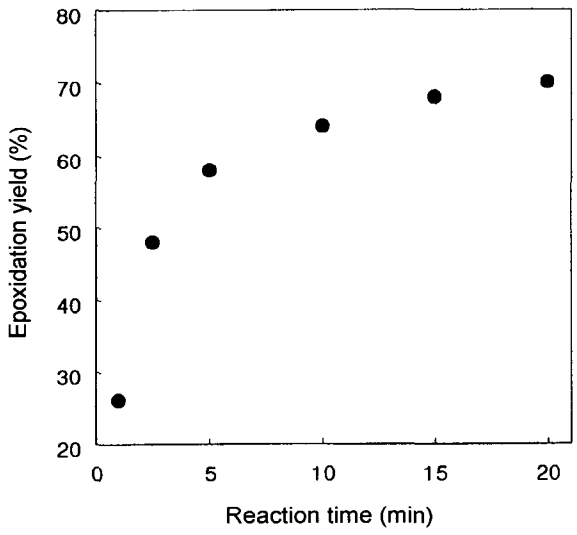

Figure 2. Epoxidation yield (%) as a function of reaction time.

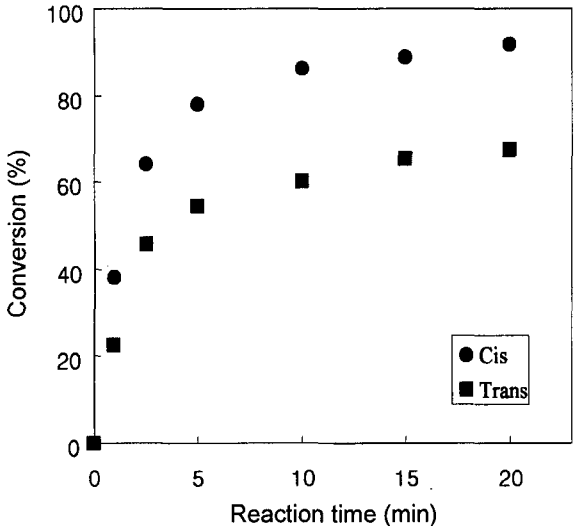

Figure 3. Conversion of *cis* and *trans* double bonds with reaction time.

content from ^{1}H-NMR spectrum, as shown in Figure 1(b). In addition, the relative content of *cis* and *trans* was able to calculated using two additional peaks by epoxide group at 2.89 ppm (*cis*) and 2.74 ppm (*trans*). Based on the initial content of three types of double bonds, the epoxidation yield (%) for *cis*- and *trans*-double bonds was obtained with the assumption that negligible amount of epoxidation of 1,2-vinyl units occurrs under this reaction conditions. Note that PB used in this study only has 1,2-vinyl units content of 9 mol% and the epoxidation does not occur in 1,2-vinyl units except for drastic conditions[14]. Figure 3 displays the conversion (%) of *cis* and *trans* double bonds with reaction time. Epoxidation reaction rapidly occurred within an initial 5 min, and thereafter gradually proceeded. The epoxidation of *cis* double bonds of PB was faster than that of *trans* double bonds. The conversion of *cis* double bonds reached at 92 % after 20 min, while that of *trans* double bonds was 67 % at that time. The difference in reactivity between *cis*- and *trans*-type might come from the difference in conformational stability to form an epoxide group. Therefore, the reactivity of double bonds in PB decreased in the following order; cis > trans ≫ vinyl.

Thermal Properties of Epoxidized PB (EPB)

The solubility of the EPBs in organic solvents, such as chloroform did not change, and the polymers remained in solution throughout the reaction. These observations indicate that crosslinking reactions did not occur to any significant extent during epoxidation.

The glass transition temperatures, T_g, increased with increasing degree of epoxidation. The increase in T_g as a result of epoxidation may be caused by the presence of the polar epoxide group, which gives more rigid backbone than

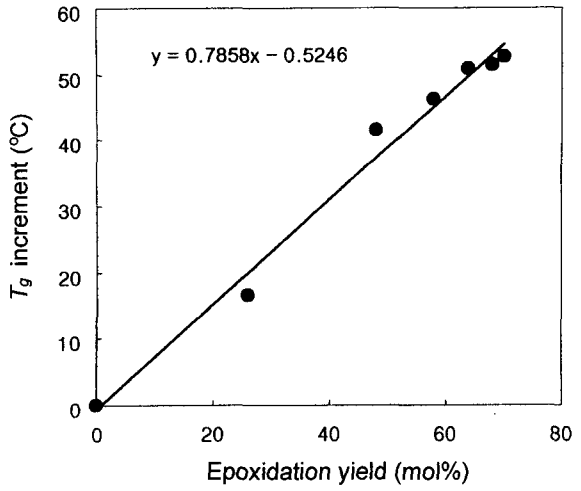

Figure 4. Incremental changes in T_g for partially epoxidized PBs as a function of epoxidation yield (%).

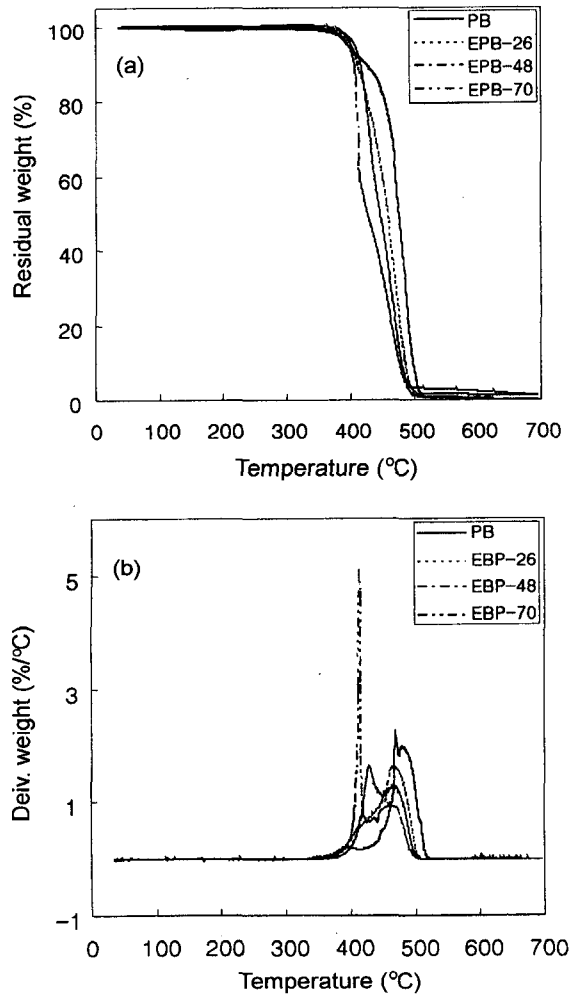

Figure 5. TGA (a) and DTG (b) thermograms of partially epoxidized PBs with different epoxidation yield.

the unsaturated group[15,16]. Figure 4 shows the plot of the T_g increment (°C) as function of the epoxide group content. A single, linear plot of the T_g increment was obtained for all of the EPB samples.

The epoxidation of natural rubber was also reported to cause an increase in T_g in a linear fashion, with a 1 °C increase for every 1 mol% of epoxidation[1,4]. For the EPB samples shown in Figure 4, the T_g increment for each 1 mol% of epoxidation was approximately 0.8 °C. This similarity can be attributed to the similar locations of the functional groups in these polymers.

The thermal degradation of the partially epoxidized PBs was also different from that of the PB. The TGA (a) and DTG (b) thermograms of the PB and EPB samples are shown in Figure 5. The TGA thermal degradation of PB proceeds by apparent one-step process with a maximum decomposition temperature (T_{max}) at 480 °C. On the other hand, the thermal degradation of partially epoxidized PBs proceeds by a two-step process and followed a considerably different pattern from PB, as shown clearly in Figure 5(b). From DTG thermograms of EPBs in Figure 5(b), it was noticeable that as the epoxide content of EPB samples increased from 26 % to 70 %, the new peak (T_{max1}) appeared and its area increased gradually in size without positional shift with decrease in the original peak (T_{max2}) area. Therefore, this strongly indicates that T_{max1} was directly related with the breakdown of epoxide group introduced. For the epoxidized natural rubber with epoxide groups of 50 mol%, the first degradation peak (T_{max1}) at ~380 °C has been reported to be associated with the breakdown of epoxide group and its decomposition[17].

Acknowledgment

This work was supported by Korean Research Foundation Grant (KRF-2000-041-E00432).

References

1. I. R. Gelling, *Rubber Chem. Technol.*, **58**, 86 (1985).
2. K. Maenz, H. Schutz, and D. Sardermann, *Eur. Polym. J.*, **29**, 855 (1993).
3. S. Roy, S. S. Namboodri, B. R. Maiti, and B. R. Gupta, *Polym. Eng. Sci.*, **33**, 92 (1993).
4. S. F. Thames and P. W. Poole, *J. Appl. Polym. Sci.*, **47**, 1255 (1993).
5. N. Vasanthan, *Polym. J.*, **26**, 1291 (1994).
6. Y. Kurusu, Y. Masuyama, and M. Miyamoto, *Polym. J.*, **26**, 1163 (1994).
7. J. E. Puskas and C. Wilds, *Rubber Chem. Tech.*, **67**, 329 (1994).
8. D. D. Sotiropoulou, K. G. Gravalos, and N. K. Kalfoglou, *J. Appl. Polym. Sci.*, **45**, 273 (1992).
9. J. Rabek Jr, L. Marshall, J. McManis, and R. Wolak, *J. Org. Chem.*, **51**, 1649 (1986).
10. A. M. Al-Ajlouni and J. H. Espenson, *J. Am. Chem. Soc.*, **117**, 9243 (1995).
11. N. N. Schwartz and J. H. Blumbers, *J. Org. Chem.*, **29**, 1976 (1964).
12. W. H. Park, R. W. Lenz, and S. Goodwin, *Macromolecules*, **31**, 1480 (1998).
13. W. H. Park, R. W. Lenz, and S. Goodwin, *Polym. Degrad. Stab.*, **63**, 287 (1999).
14. A. G. Magaritis and N. K. Kalfoglou, *Eur. Polym. J.*, **24**, 1043 (1988).
15. C. M. Roland, *Macromolecules*, **25**, 7031 (1992).
16. C. M. Roland, J. K. Kallitisis, and K. G. Gravalos, *Macromolecules*, **26**, 6474 (1993).
17. S. Mohanty, P. G. Mukunda, and G. B. Nando, *Polym. Degrad. Stab.*, **50**, 21 (1995).