Epoxidized Polybutadiene as a Thermal Stabilizer for Poly(3-hydroxybutyrate). II. Thermal Stabilization of Poly(3-hydroxybutyrate) by Epoxidized Polybutadiene

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Abstract: Epoxidized polybutadiene (EPB) was prepared by polybutadiene (PB) with *m*-chloroperbenzoic acid (MCPBA) in homogeneous solution. EPB was blended with poly(3-hydroxybutyrate) (PHB) up to 30 wt% by solution-precipitation procedure. The thermal decomposition of PHB/EPB blends was studied by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and differential thermal analysis (DTA). The thermograms of PHB/EPB blends contained a two-step degradation process, while that of pure PHB sample exhibited only one-step degradation process. This degradation behavior of PHB/EPB blends, which have a higher thermal stability as measured by maximum decomposition temperature and residual weight, is probably due to crosslinking reactions of the epoxide groups in the EPB component with the carboxyl chain ends of PHB fragments during the degradation process, and the occurrence of such reactions can be assigned to the exothermic peaks in their DTA thermograms.

Keywords: Polybutadiene, Epoxidized polybutadiene, Poly(3-hydroxybutyrate), Thermal degradation, Residual weight

Introduction

Biodegradable poly(3-hydroxybutyrate) (PHB), which is biosynthesized by a wide variety of bacteria, has much potential in applications such as surgical suture, and degradable plastics. However, until now there is no large commercial product because PHB has the higher cost, narrow processability window and brittleness. In particular the thermal instability of PHB in the melt state prevents it from substituting the non-biodegradable polymeric materials in commercial products.

The chain scission rate of PHB at near melting point is well known to be too fast [1-3]. In principle, this problem might be overcome either by reducing the crystalline melting point to lower the processing temperature, or by adopting some means of reforming links in the fragmented polymer, e.g. by crosslinking. As an approach on the former, copolymerization of 3-hydroxybutyrate with either 3-hydroxyvalerate or 4-hydroxybutyrate using the bacterial fermentation method has been developed. However, it is difficult to utilize these copolymers for diverse applications because the fermentation medium is rather limited and costly. Another approach to reduce the chain scission rate of PHB is blending with various additives or crosslinkers, which can repolymerize thermally fragmented polymer chains. Accordingly, several attempts [4,5] to improve the melt stability of PHB have been made by the use of additives, including organic or inorganic compounds.

However, most of them were proven to be not effective because additives are able to yield the chain radicals capable of accelerating the polymer degradation as well as forming the crosslinks.

In our previous studies [6,7], it was found that poly(3-hydroxyalkanoates) (PHAs) with epoxide pendant groups have a higher thermal stability owing to crosslinking reactions of pendant epoxide groups with the carboxyl chain ends fragmented. 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 PHB.

The aim of this study is to develop a polymeric thermal stabilizer containing epoxide groups for a representative microbial aliphatic polyester, PHB. In a previous article [8], polybutadiene (PB) was epoxidized with *m*-chloroperbenzoic acid (MCPBA) in homogeneous solution, and the thermal properties of the epoxidized PB (EPB) were investigated. In this study, EPB with epoxide content of 43 mol% was blended up to 30 wt% with PHB. The thermal stability of PHB/EPB blends was invesigated by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and differential thermal analysis (DTA).

Experimental

Materials

PHB, in a powder form, was supplied from KOHAP Ltd. (Korea). Polybutadiene (PB) (55 % *trans*-1,4, 36 % *cis*-1,4, and 9 % vinyl units) was purchased from Aldrich Co. (USA).

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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 %. PB was epoxidized with MCPBA in homogeneous solution, as in the previous study [8]. All other chemicals were used as received without further purification.

Preparation of PHB/EPB Blends

We used EPB sample with a degree of epoxidation of 43 % for blending with PHB. PHB/EPB blends (100/0, 90/10, 80/20, 70/30, w/w) were prepared by coprecipitation from chloroform solution (2 wt%) with predetermined weight ratios. The resulting precipitates were dried under vacuum at 30 °C.

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/ml. 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. Differential thermal analysis (DTA) was conducted using a TG-DTA 2000S (MAC Science Co.) in a nitrogen atmosphere from 30 to 600 °C at a heating rate of 20 °C/min.

Results and Discussion

Epoxidation of PB

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. In this study PB samples with specific unsaturated unit contents were dissolved in chloroform at a concentration of 5 % and reacted with MCPBA at 20 °C for 30 min. The degree of epoxidation (%) was obtained from the relative peak areas of the epoxide and olefinic hydrogen atoms on ^{1}H-NMR spectrum [8].

Table 1 shows the degree of epoxidation (%) of MCPBA to the unsaturated (olefinic) group of PB for the molar ratio of 0.3 and 0.5 at 30 min. The degree of epoxidation (%) determined from NMR spectrum indicates that most, if not all, of MCPBA may have participated in the epoxidation reaction. This means that EPB with a desired epoxide content can be easily obtained by controlling the amounts of

Table 1. Degree of epoxidation (%) of MCPBA to the unsaturated group of PB for the molar ratio of 0.3 and 0.5

PB (mole)	MCPBA (mole)	Theoretical epoxidation (%)	Epoxidation (%) from NMR
1	0.3	30	26
1	0.5	50	43

Table 2. Thermal transition parameters of the PHB/EPB blends

PHB/ EPB	T_{g1} (°C)	T_{g2} (°C)	T_c (°C)	ΔH_c (J/g)[a]	T_m (°C)	ΔH_m (J/g)[a]
100/0	-	5	65	42	176	68
90/10	-	8	62	43	175	69
80/20	-51	8	65	45	176	73
70/30	-49	6	66	44	174	73

[a]Normalized values.

MCPBA added. For the large-scale synthesis of EPB, a suitable reaction condition was chosen at a molar ratio of 0.5 and reaction time of 30 min. All the subsequent results are for EPB sample reacted in this condition.

Miscibility of PHB/EPB Blends

Table 2 shows thermal transition parameters (T_g, T_m, and T_c) obtained from the second scanned DSC curves of PHB/EPB blends with the EPB content up to 30 wt%. EPB-43 has only a glass transition occurred at −49 °C, while from the second scan the DSC curve of PHB shows the glass transition (T_g = 5 °C), followed by cold crystallization (peak maximum at T_c = 65 °C) and melting (T_m = 176 °C). The glass transition temperatures of PHB and EPB components were almost constant independent of the blend composition, indicating the immiscibility of the two blend components in the range of blend compositions investigated. From the values reported in Table 2 it is evident that the presence of EPB would slightly affect the enthalpy of fusion of PHB, as well as the crystallization temperature and the enthalpy of crystallization.

TGA and DTA Study of PHB/EPB Blends

Figure 1(a) shows the TGA thermograms of PHB/EPB blends containing the EPB content up to 30 wt%. The thermal degradation of pure PHB proceeds by a one-step process with a maximum decomposition temperature at 302 °C. This thermal degradation at maximum decomposition temperature of approximately 300 °C is mainly associated with the ester cleavage of PHB component by *β*-elimination reaction. However, the thermal decomposition patterns of blends followed a considerably different pattern from the single-step reaction of the PHB, and as the EPB content in blends increased up to 30 wt%, their thermal stability as measured by first maximum decomposition temperature also
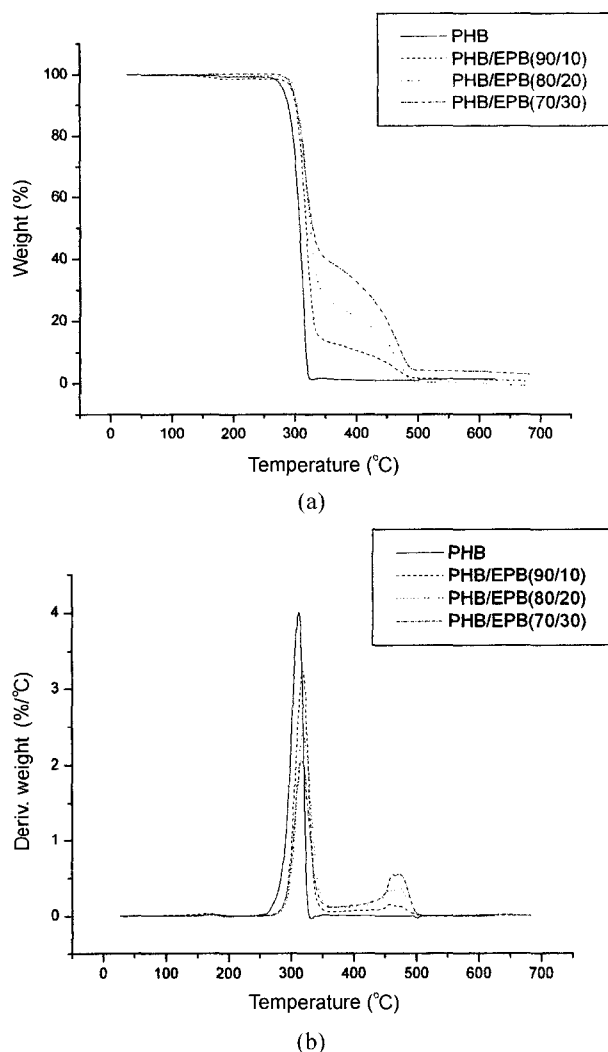
Figure 1. TGA (a) and DTG (b) thermograms of PHB/EPB blends.

Table 3. Initial and maximum decomposition temperatures evaluated from TGA and DTG thermogram of PHB/EPB Blends

PHB/EPB	$T_i (^\circ C)^{a)}$	$T_{max1} (^\circ C)$	$T_{max2} (^\circ C)$
100/0	282	312	-
90/10	296	318	458
80/20	302	318	456
70/30	298	316	462

$^{a)}$ Values determined at a 5 % weight loss on the TGA thermograms

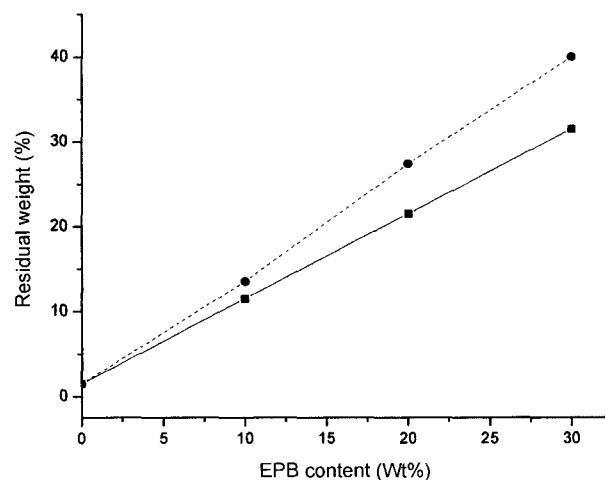**Figure 2.** Residual weight at 350 °C as a function of EPB content in blends: solid line, calculated; dotted line, observed.

increased from 302 °C to 318 °C. The thermograms for blends contained two separated degradation steps, or stages, with two maximum rate peaks as shown clearly in the corresponding DTG curves. Figure 1(b) shows the DTG thermograms of PHB/EPB blends with the EPB content. As the epoxide content of blends increased, the new second maximum decomposition peaks increased in size without positional change ($T_{max2} = 459 \pm 3$ °C), whereas the first ones shifted to higher temperature (302 °C to 318 °C) with decrease in the peak area. The initial and maximum degradation temperatures for PHB/EPB blends were summarized in Table 3.

The relationship between the EPB content in blends and residual weight (observed and calculated) at 350 °C, which was a temperature beyond maximum decomposition temperature of PHB, is shown in Figure 2. The calculated residual weights for PHB/EPB blends could be obtained by using the residual weight of pure PHB and EPB component.

As seen in Figure 2, the residual weight is directly related to the amounted of EPB in blends in a linear manner. It was noticeable that the observed residual weights (%) showed higher values up to ~10 % (for PHB/EPB, 70/30) than the calculated ones. This indicates that some parts of the epoxide groups in EPB may have participated in the thermal crosslinking reactions, as described below.
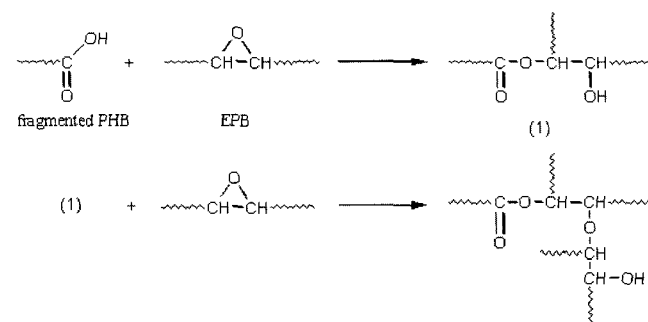
This retarded degradation indicates that the reactions between two polymers take place during the initial degradation process, and then PHB are more stabilized in blend. In order to investigate whether crosslinking reactions occurred
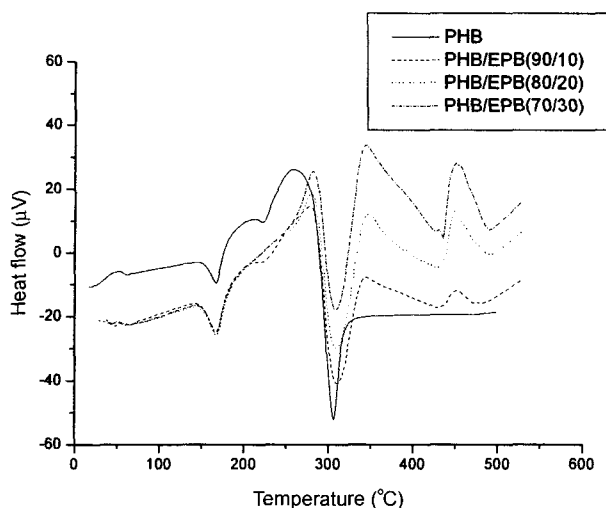
Figure 3. DTA thermograms for (a) pure PHB and (b) PHB/EPB (70/30) blends.

during the degradation of PHB/EPB blends, the DTA analyses were conducted up to 600 °C. Figure 3 shows the DTA thermograms for pure PHB and PHB/EPB blends. The DTA thermogram of blend sample shows an endothermic peak at 305 °C and one exothermic peak at 450 °C, in contrast to the DTA thermogram of pure PHB sample which showed only a single endothermic decomposition peak at 305 °C. The exothermic peak at 450 °C on the DTA thermogram also increased with the EPB content in blends. The exothermic peak following the endothermic decomposition peak can be partially ascribed to a thermal crosslinking reaction of the epoxide groups of EPB with carboxylic acid groups, which are formed by the random chain scission of PHB component, and with hydroxyl groups formed as a result of former reaction. The reaction of the epoxide groups of EPB with carboxylic acid groups leads to ester linkages, while that of epoxide groups with hydroxyl groups results in ether linkage. As reported for epoxy-rich/anhydride curing system [9,10], ester formation reaction is faster than ether formation.

The two polymers are immiscible in the composition range studied and the blends results in a biphasic structure. However, the PHB oligmers with carboxylic acid ends formed in the initial decomposition stage could diffuse from PHB phase to EPB one, due to the enhanced miscibility of the two polymer components caused by thermal degradation of PHB, and could react rapidly with the epoxide groups of EPB to form new interchain bonds, resulting in retarding the degradation of blend. Therefore, the second maximum peaks

on DTG thermogram (Figure 3) may be partially ascribed to decomposition of newly formed interchain bonds.

A similar type of melt reaction was proposed by Grassie and co-workers, who suggested that, in the initial stages of the thermal degradation of PHB, terminal hydroxyl end groups on original polymer chains can react with carboxylic acid groups formed by chain scission [2]. Reactions of this type during the thermal degradation of polymers have also been reported previously for hydroxy-terminated siloxanes [11-13] and polyamides [14], although the extent of this reaction would be limited due to a low concentration of terminal hydroxyl chain ends.

Acknowledgment

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