Peroxide Modification of Poly(butylene adipate-*co*-succinate)

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ABSTRACT: We attempted to introduce crosslinking into poly(butylene adipate-*co*-succinate) (PBAS) to improve the properties, such as the mechanical strength and elasticity, by a simple addition of dicumyl peroxide (DCP). Prior to curing, the thermal stability of PBAS was investigated. Above 170°C PBAS was severely degraded, and the degradation could not be successfully stabilized by an antioxidant. The PBAS was effectively crosslinked by DCP, and the gel fraction increased as the DCP content increased. A major structure of the crosslinked PBAS was an ester and aliphatic group. The tensile strength and elongation of PBAS were improved with an increasing content of DCP, but there was little affect on the tear strength. The biodegradability of crosslinked PBAS was not seriously deteriorated. A higher degree of crosslinking gave a lower heat of crystallization and heat of fusion. However, the melt crystallization temperatures of the crosslinked PBAS were higher than that of PBAS. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 637–645, 2001

Key words: poly(butylene adipate-*co*-succinate); organic peroxide; crosslinking; biodegradability; crystallization

INTRODUCTION

The three main strategies available for the management of plastic waste are incineration, recycling, and putting it in a landfill.[1] In recent years the utility of biodegradable polymers has received much attention because of their potential impact upon the complex issue of plastics waste management.[2,3] Aliphatic polyester is one of the most promising structural materials for biodegradable or compostable fibers, films, sheets, bottles, injection-molded products, and foamed sheets. However, commercial use of high molecular weight aliphatic polyesters has been limited to polyesters produced by microorganisms,[4] ring-opening polymerization of lactones,[5] and ring-opening polyaddition of cyclic dimers.[6] This approach is necessary because of the inherent difficulty in synthesizing high molecular weight aliphatic polyesters through the polycondensation of diols and dicarboxylic acids.[7] Because polycondensation alone does not produce polyesters with properties that make them suitable for practical use as biodegradable plastics, it is necessary to further increase the molecular weight. This can be accomplished through one of two methods: a polycondensation reaction with a multifunctional group such as trimethylolpropane, pentaerythritol, and diepoxide, or a coupling reaction of polyesters end groups with a compound that possesses two of the

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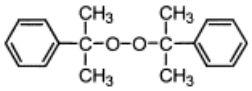


Scheme 1 The chemical structures of PBAS and DCP.

more reactive functional groups in a molecule. The initial use of an organic peroxide[8] as a crosslinking agent was reported for the first time by Ostromislenski in 1915 for the vulcanization of natural rubber. Since around 1950 the interest in the industrial use of peroxides as crosslinking agents has been increasing, partly as a result of the introduction of saturated rubbers such as ethylene-propylene monomer and silicone rubber, which cannot be vulcanized with the usual sulfur systems. Parallel to their application in elastomers, interest is being shown in the use of peroxides for the crosslinking of thermoplastics, the aim being to improve the latter's dimensional stability at elevated temperatures and their chemical resistance. Up to now, however, the crosslinking of saturated aliphatic polyesters has not been reported. In this study we attempted to introduce crosslinking into poly(butylene adipate-*co*-succinate) (PBAS) to improve properties such as the mechanical strength and elasticity by the simple addition of dicumyl peroxide (DCP).

EXPERIMENTAL

Materials

The PBAS used in the experiment was from a sample of SG2109 provided by SK Chemicals Co., Ltd. To minimize the moisture effects and hydrolysis, the PBAS was dried in a vacuum oven at 70°C for 12 h before use. A primary antioxidant (Irganox 1010) and secondary antioxidant (Irgafos 168) were supplied by Ciba Specialty Chemicals Inc. The DCP was from Nippon Oil & Fats Co., Ltd. Chloroform and 1,1,2,2,-tetrachloroethane were from Aldrich Chemical Co. All chemicals were used without further purification. Scheme 1 shows the chemical structure of the PBAS and DCP.

Thermal Stability

The thermal stability of PBAS was investigated to establish a processing temperature. The PBAS was placed in a convection oven at four different temperatures, and the change in the reduced viscosity of the PBAS was measured with respect to the oven residence time. The reduced viscosity of the polymers was measured by using an Ubbelohde viscometer in 1,1,2,2,-tetrachloroethane solvent at 0.05 g PBAS/10 mL solvent at 25°C.

Crosslinking Behavior

Crosslinked PBAS was prepared by simple mixing of DCP into PBAS in a Brabender plasticorder (PLE331) equipped with a cam-type rotor (model W50). The PBAS was melted at 150°C for 3 min, then the DCP was added. A rotor speed of 40 rpm was used, and the mixing torque change was recorded from the instant when the DCP was added. The crosslinked samples were extracted by chloroform using a Soxhlet extractor. The polymers were weighed and then extracted for 24 h. Prior to the final weighing, the samples were dried in a vacuum at 70°C for 24 h. The gel fraction was calculated as the weight of the dried extracted samples divided by the original sample weight. The solid-state ^{13}C-NMR spectra of the PBAS and extraction residual of PBAS cured by 4 phr DCP were obtained using a Varian Unity Inova 300WB.

Mechanical Properties

The PBAS was compounded with DCP in a Brabender Plasticorder at 115°C and subsequently compression molded into a sheet (0.25 ± 0.02 mm thickness) using a hydrodynamic press at 150°C. Tensile and tear tests were performed on an Instron model 4465. We used KS procedures for measuring the tensile strength, elongation at break, and tear strength (KS M 3503) of PBAS and DCP cured PBAS.

Thermal Properties

Thermogravimetric analysis (TGA) was administered to 10×1 mg samples under a nitrogen flow at a heating rate of 10°C/min on a Perkin–Elmer thermal analysis instrument (TGA 7). The calorimetric measurements were carried out on a Perkin–Elmer Pyris 1 differential scanning calorimeter (DSC) operating under a nitrogen flow. The samples were first heated at a rate of 10°C/min from 30 to 120°C and held at this temperature for 5 min to allow the complete melting of the crystallites. Then the samples were cooled at a rate of 10°C/min from 130 to 0°C. The values of the crystallization temperature T_c and enthalpy of crys-

tallization ΔH_c were calculated during these cooling runs. The samples were then heated to 120°C at 10°C/min and the results of the melting temperature T_m and enthalpy of melting ΔH_f referring to these traces were reported.

Enzymatic Degradation

Compression molded films of poly(ethylene terephthalate) (PET), PBAS, and crosslinked PBAS were degraded at 37°C in phosphate buffer solution (pH 7). Film samples (45 ± 2 μm thickness, 6.2-mm diameter) were introduced into small bottles containing 2 mL of buffer, and then 4 μL of a solution of lipase from *Rhizopus arrhizus* (200 U) was added. The enzymatic hydrolysis was carried out for 48 h. After filtration (0.2-μm membrane filter), a small amount of 1*N* hydrochloric acid was dropped onto the filtrate. The water-soluble total organic carbon (TOC) concentration in the filtrate was measured as an indication of the biodegradability with a Shimadzu 500 TOC analyzer. As controls, the TOC value for the enzyme itself was measured under the same condition. The TOC data were the average of three measurements and were corrected appropriately with the blank levels.

RESULTS AND DISCUSSION

Thermal Stability

If a polymer is thermally degraded in the course of processing, the mechanical properties of the end products will be deteriorated. Thus, it is important to measure the thermal stability of a polymer and set up the processing temperature window. Figure 1 shows the change in the reduced viscosity of PBAS as a function of the oven residence time.

At 170°C there was little change in the reduced viscosity of PBAS, but above 170°C the reduced viscosity was decreased as the oven residence time increased and the higher the temperature, the higher was the slope. This meant that polymer degradation rapidly occurred above 170°C. An antioxidant could not entirely stabilize the degradation. This result may have been due to the following. Scheme 2 shows the three decomposition modes of the polyester.[8] Hydrolytic degradation of polyester is due to water, and the carboxylic acid group formed on the hydrolysis of the ester group catalyzes the degradation reaction. In this study the PBAS was dried in a vacuum oven

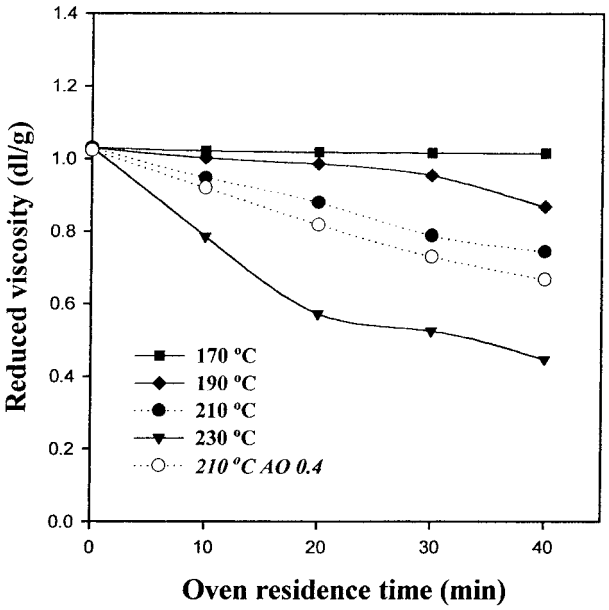
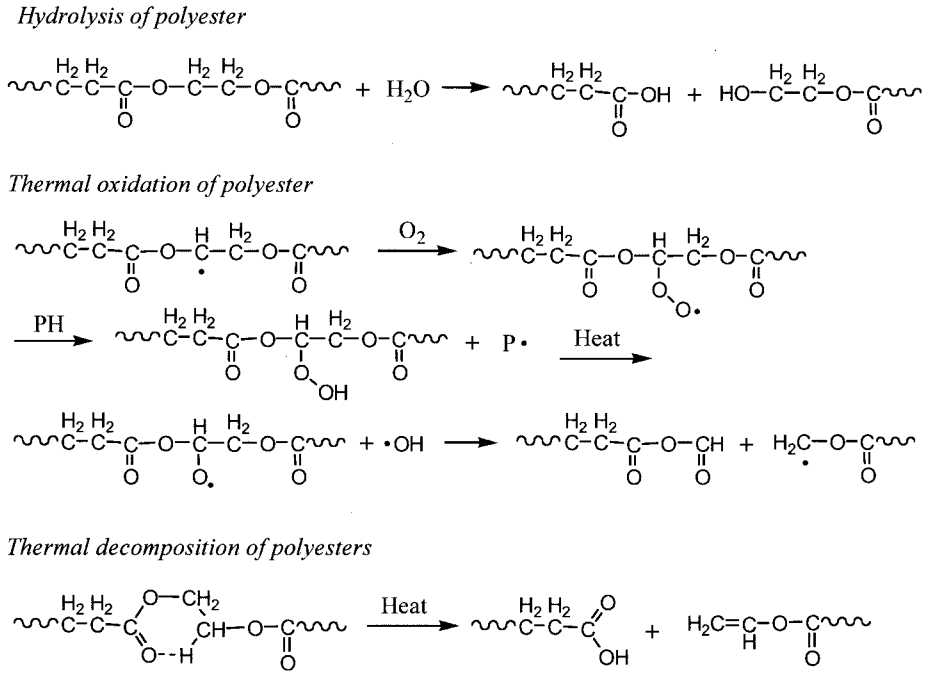


Figure 1 The change in the reduced viscosity of PBAS with respect to the oven residence time. AO 0.4, PBAS with 0.2 phr primary antioxidant and 0.2 phr secondary antioxidant.

at 70°C for 12 h before use, and so hydrolytic degradation could be disregarded.

A second degradation route is by the oxidation mechanism developed originally by Bolland and Gee.[9,10] It is generally assumed that primary radicals are formed through the action of heat or through the combined actions of heat and mechanical stress. The fixation of an oxygen molecule onto a carbon atom centered free radical is generally a very fast reaction if the concentration of oxygen in the polymer is sufficient. It rapidly transforms alkyl radicals (P·) into peroxy radicals (PO_2 ·). A primary antioxidant stabilizes alkyl radicals and peroxy radicals and inhibits the propagation reaction. A secondary antioxidant decomposes hydroperoxides without intermediate formation of free radicals. Commonly, primary and secondary antioxidants are mixed and used for their synergistic effect. However, in this study the PBAS was severely degraded at 210°C and degradation could not be successfully stabilized by an antioxidant. This was because thermal decomposition is concerned with degradation. As shown in Scheme 2, Plage and Schulten[11] reported that polyester forms a six-membered cyclic transition state and β hydrogen is transferred to oxygen to yield carboxylic and vinyl end groups. That is to say, although the PBAS in this experiment was degraded through thermal oxidation



Scheme 2 The hydrolytic, thermal, and thermooxidative degradation of polyester.

and thermal decomposition, antioxidants were only involved in the thermal oxidation. Thus, they could not entirely stabilize the degradation. Consequently, the processing temperature of PBAS should not be over 170°C.

Crosslinking Behavior

In order to be suitable for technical applications, a peroxide crosslinking agent must fulfill a number of conditions.[8] There are a number of major requirements. It must be safe to handle during transportation, storage, and processing. The nature of its decomposition products must be such that rapid crosslinking takes place at the desired temperature without a tendency to premature crosslinking (prevulcanization, scorch). It should react in such a way that crosslinking is the only modification to the polymer that occurs. According to the chemical structure, organic peroxides can be subdivided into hydroperoxides (ROOH), alkyl peroxides (R_1OOR_2), peroxyesters ($R_1O{=}COOR_2$), and diacyl peroxides ($R_1O{=}COOC{=}OR_2$). They have various decomposition temperatures and the range commences at a temperature below 0°C and finishes at nearly 200°C. DCP is one of the alkyl peroxides and its decomposition temperature is approximately 170°C. For polymers melting at 100–120°C, DCP is the most suitable.[12] Figure 2 shows the change in the Plasticorder torque with time when DCP was added to the PBAS.

A slight decline in the beginning was due to melting of the solid DCP. After 30–40 s the torque was rapidly increased and the higher the DCP content, the higher were the torque values. This meant that PBAS was effectively crosslinked by the simple addition of the organic peroxide

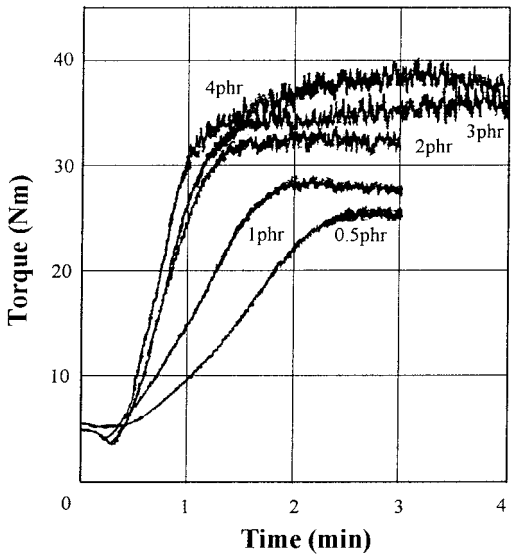


Figure 2 Brabender plastograms for PBAS as a function of the DCP content (150°C, 40 rpm).

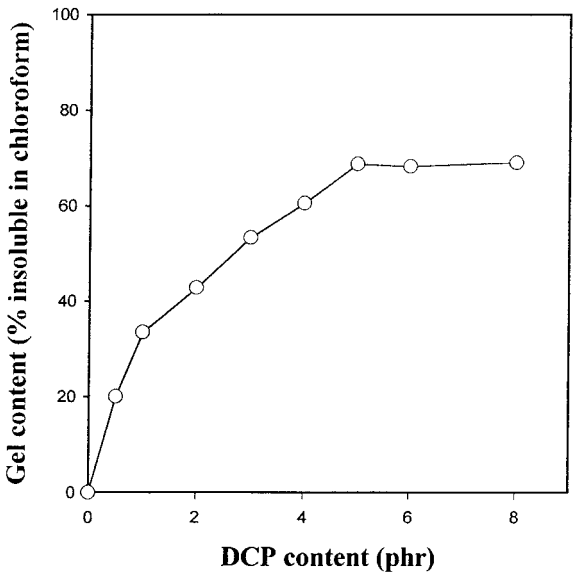
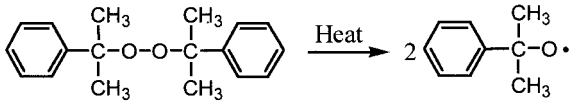


Figure 3 The effect of the DCP content on the gel percent of PBAS crosslinked in a Brabender plasticorder at 150°C.

DCP. The gel fraction of crosslinked PBAS with respect to the DCP content is shown in Figure 3.

The gel fraction was increased as the content of DCP increased, and the range was 20–69%. Above 5 phr no change was seen. Takashima and Nakayama[13] reported that the gel content of polyethylene (PE) crosslinked by 2 phr DCP at 140–180°C and then extracted by xylene was 80–90%. Comparing our results with Takashima and Nakayama's report, the PBAS showed a relatively lower gel content than PE. The possible justifications are as follows. First, PBAS may have fewer crosslinking sites than PE. The crosslinking reactions by DCP are as follows[14]:



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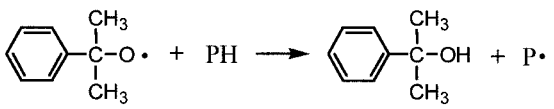

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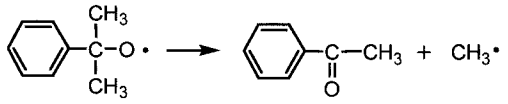

(3)

$$CH_3\cdot + PH \rightarrow CH_4 + P\cdot \quad (4)$$

$$2P\cdot \rightarrow P{-}P \quad \text{(crosslinking)} \quad (5)$$

DCP cleaves thermally to produce two cumyloxy radicals [reaction (1)] that abstract hydrogen atoms from the polymer chains [reaction (2)], and a cumyloxy radical can also lead to the formation of a methyl radical and a phenylmethyl ketone [reaction (3)]. The methyl radical is likewise able to abstract hydrogen [reaction (4)]. Then these polymer radicals couple to crosslink. Considering this crosslinking mechanism, it was anticipated that PBAS had a lower content of the methylene group in the main chain than PE. These relatively few crosslinking sites made it difficult to crosslink. Second, the polymer–solvent solubility parameter deference could be involved. This difference was one of the possible reasons for the gel content gap between DCP cured PE and PBAS.

On the other hand, a major attraction of aliphatic polyesters is their biodegradability and this comes from ester groups in the polymer main chain. If the ester groups of PBAS were broken down in the course of crosslinking, the biodegradability would be deteriorated. Figure 4 shows solid-state ^{13}CNMR spectra of PBAS and an extraction residual of PBAS cured by 4 phr DCP (EXXPBAS4d). The ester group carbon resonance at 173.7 ppm in spectrum a and those in spectra b–e at 28.6, 66.1, 25.9, and 34.8 ppm, respectively, were obtained.[15] However, there was no trace of resonance at 95–100 ppm. This result may explain that the basic structure of crosslinked PBAS consisted mainly of ester and aliphatic groups.

Mechanical Properties

One of the main purposes of this study was to improve the mechanical strength of aliphatic polyesters produced by crosslinking. Hence, we compared the tensile and tear properties of crosslinked PBAS with that of the unreacted polymer. Table I shows the tensile strength, elongation, and tear strength of PBAS and PBAS cured by DCP with respect to the DCP content. As we can see in the table, the higher DCP content caused the higher tensile strength and elongation. Nielsen[16] and Flory[17] illustrated the effect of molecular weight on the tensile strength of polymers as following equation:

$$\sigma_b = A - B/M_n$$

where M_n is the number-average molecular weight and A and B are constants. At very low molecular weights, the tensile stress to break (σ_b)

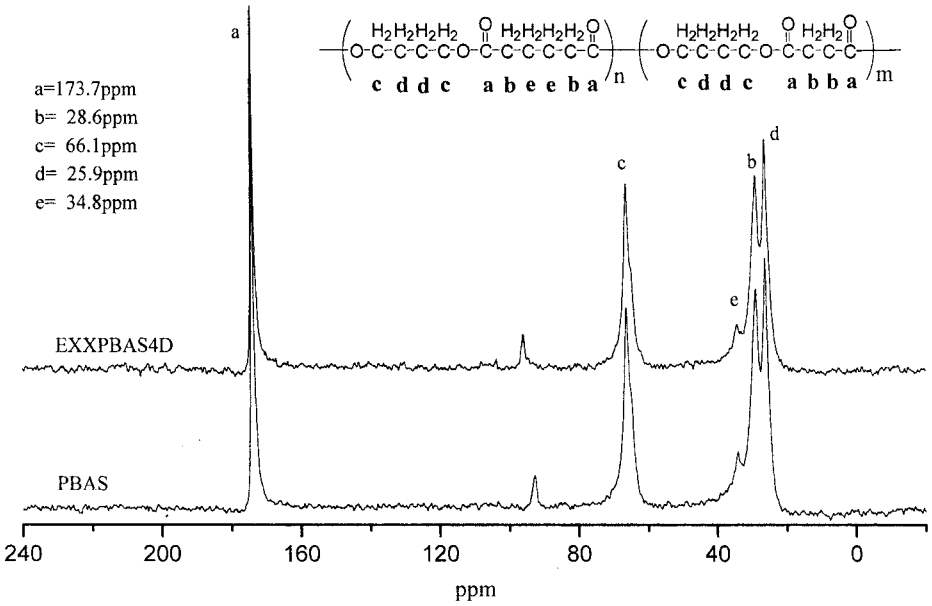

Figure 4 Solid-state ^{13}C-NMR spectra of PBAS and an extraction residual of PBAS cured by 4 phr DCP (EXXPBAS4D).

was near zero. As the molecular weight increased the tensile strength rapidly increased, then gradually leveled off. Because a major point of weakness on the molecular scale is the chain ends, which do not transmit the covalent bond strength, it is predicted that the tensile strength also reaches an asymptotic value at infinite molecular weight. In our study the number of chain ends was not reduced because the molecular weight of the polymer was increased by crosslinking, not by polymerization. However, supposing that two polymer chains of the same molecular weight are crosslinked by DCP to produce one crosslinking point, a molecule is made and the far off end to end distance is increased, although the number of chain ends is four. As a result, the number-average molecular weight is double what it was before. Accordingly, it is supposed that the molecular weight augmentation by curing enhanced the tensile properties. On the other hand, the tear strength was not affected by crosslinking.[18] We guessed that the tear strength of a polymer mainly depends on the basic chemical structure of the polymer, not the molecular weight or crosslinking.[18]

Thermal Properties

The thermal properties such as the crystallization, melting, and thermal degradation temperatures of the polymer would give useful information for processing and service temperatures.

Table I Mechanical Properties of PBAS and Crosslinked PBAS with Respect to DCP Content

Materials	Tensile Strength (kgf/cm^2)	Elongation (%)	Tear Strength (kgf/cm)
PBAS	179	275	181
PBAS + 0.5 phr DCP	183	254	181
PBAS + 1 phr DCP	237	368	180
PBAS + 2 phr DCP	231	412	184
PBAS + 3 phr DCP	235	458	186
PBAS + 4 phr DCP	243	528	191
PBAS + 5 phr DCP	256	486	194

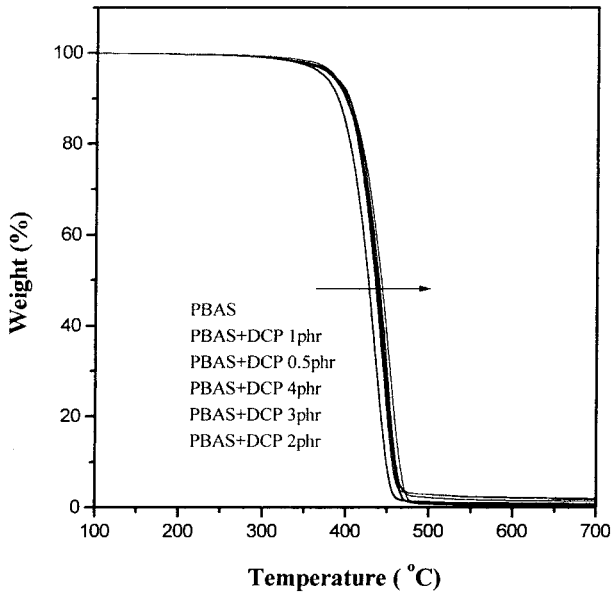

Figure 5 TGA thermograms of PBAS and crosslinked PBAS.

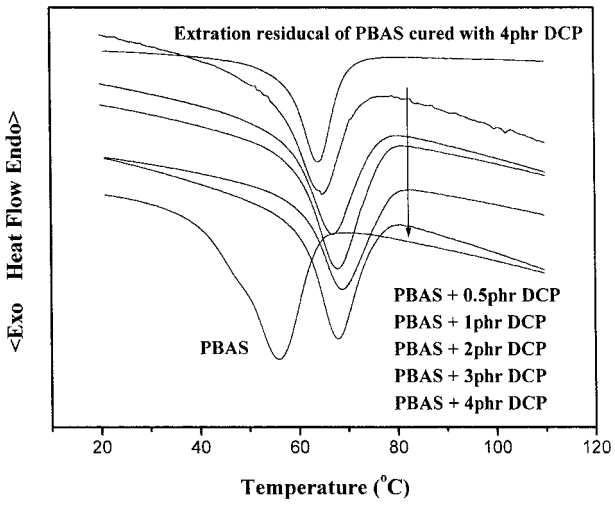

Figure 6 DSC thermograms for cooling runs of PBAS and PBAS cured by DCP.

Therefore, the polyester was studied with thermogravimetric (TGA) and differential scanning calorimetric (DSC) analysis. Figure 5 shows TGA thermograms of PBAS and crosslinked PBAS. The degradation temperature (temperature of maximum weight loss rate) for the PBAS was 435°C. The DCP content appeared to have a slight enhancing effect. The degradation temperature of the crosslinked PBAS was in the 440–450°C range.

Plage and Schulten[11] proposed that polyester forms a six-membered cyclic transition state and the β hydrogen is transferred to oxygen to yield carboxylic and vinyl end groups. If this scission is continued, PBAS may be degraded to butadiene, adipic acid, and succinic acid. Assuming the polyester was degraded like their assumption, the molecular weight and vaporizing temperature of the degradation products of crosslinked PBAS would be expected to be higher than that of PBAS. On that account, we think that the degradation temperature of the crosslinked PBAS shifted to a slightly higher temperature range.

Figures 6 and 7 show DSC thermograms for cooling and heating runs of PBAS and PBAS cured by DCP, respectively. The T_c and ΔH_c are summarized in Table II.

It is general knowledge that the crystallinity of a polymer is decreased with the introduction of crosslinking. Albertsson and Eklund[19] studied the copolymerization of adipic anhydride with 1,2,7,8-diepoxyoctane (DEO) as a curing agent. The percent gel fraction of the crosslinked copolyesters increased to 95 wt % with increasing the amount of DEO to 20 mol %, and these crosslinked polymers showed crystallinity. However, no crystallinity could be detected at DEO contents over 20 mol %. In our work the crystallinity was present in both the crosslinked PBAS and the extracted sample. This indicated that the crosslinking density of PBAS cured by DCP was low and polymer chains had enough mobility to crystallize.

Although the crystallization temperature of PBAS was 55.9°C, that of crosslinked PBAS

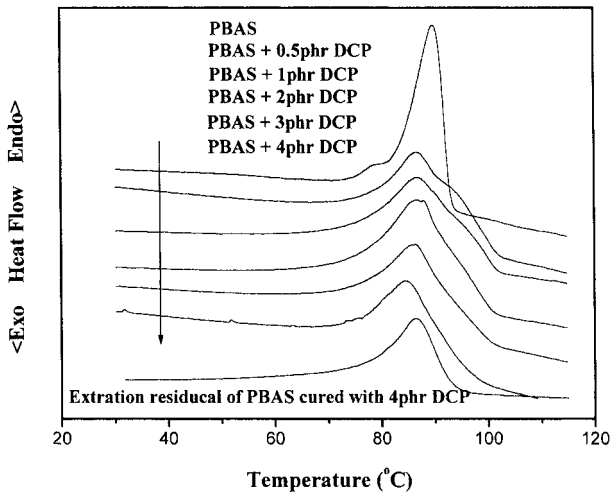

Figure 7 DSC thermograms for heating runs of PBAS and PBAS cured by DCP.

Table II Thermal Properties of PBAS and Crosslinked PBAS

		PBAS					
Material	PBAS	0.5 phr DCP	1 phr DCP	2 phr DCP	3 phr DCP	4 phr DCP	4DEX[a]
T_c (°C)	55.9	67.9	68.7	67.8	66.8	64.8	63.9
ΔH_c (J/G)	−59.3	−49.2	−46.2	−45.2	−49.4	−49.7	−38.5
T_m (°C)	89.9	86.9	87.0	86.3	86.5	85.0	86.6
ΔH_f (J/g)	48.8	51.7	46.6	44.6	42.5	39.1	42.1

[a] The extraction residual of PBAS cured with 4 phr DCP.

jumped to 68.7°C with increasing DCP content up to 1 phr and then gradually decreased in the cooling run. The crystallization temperature of crosslinked PBAS probably increased because of some substances acting as nucleating agents. Jensen[8] insisted that so-called spontaneous nucleation (i.e., nucleation without the intentional introduction of a nucleating agent) is generally believed to be due to a foreign substance such as catalyst residues, oxidatively degraded polymer, or other processing-determined impurities whose physicochemical nature is relatively unknown. The nucleating agent should be wetted or absorbed by the polymer and should be homogeneously dispersed in the polymer in as fine a form as possible. Based on this work, it may be possible that a by-product of the curing reaction or crosslinking point could act as an impurity that could initiate crystallization. In the meantime, the melting temperature and heat of fusion of the crosslinked PBAS was lower than that of PBAS in the heating scan. This intimated that the size and perfectness of the cured PBAS crystals were relatively low because crosslinks restricted chain motions.

Biodegradability

In the present work we investigated the effect of crosslinking on the enzymatic degradation behavior. Accelerated degradation was carried out with PBAS of various contents of the DCP curing agent. The biodegradability of these polymers was evaluated by measurement of the TOC values and comparing them with PET (Fig. 8).

Biodegradability of polyesters is highly dependent on the glass-transition temperature, crystallinity,[20–25] and the balance between hydrophilic and hydrophobic groups[26–29] in the backbone. PET shows low biodegradability because of its high glass-transition temperature and low chain mobility attributable to the rigid aromatic group. This is the reason why most of the biodegradable polyesters are aliphatic. As we can see in Figure 8, the biodegradability of PBAS was much higher than PET and that of crosslinked PBAS was similarly readily biodegraded. This was because the crosslinked PBAS still consisted of ester and aliphatic groups. A slight decrease in the TOC was observed at high DCP content, which was due to the increase in the molecular weight.

CONCLUSION

Above 170°C the PBAS was severely degraded and degradation could not be successfully stabi-

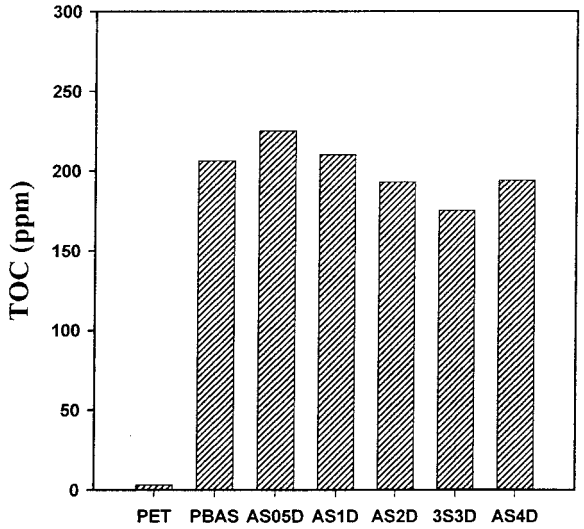

Figure 8 The change of the total organic carbon (TOC) in the enzymatic hydrolysis of PET, PBAS, and crosslinked PBAS. AS05D, PBAS cured with 0.5 phr DCP; AS1D, PBAS cured with 1 phr DCP; AS2D, PBAS cured with 2 phr DCP; AS3D, PBAS cured with 3 phr DCP; AS4D, PBAS cured with 4 phr DCP.

lized by an antioxidant. Thus, the processing temperature of PBAS should not be over 170°C. The PBAS was effectively crosslinked by DCP, the gel fraction increased as the DCP content increased, and the basic structure of the crosslinked PBAS was mainly ester and aliphatic groups. The tensile strength and elongation of PBAS were improved with increasing DCP content, but the tear strength was little affected. The degradation temperature of the crosslinked PBAS found by TGA measurement shifted to a slightly higher temperature range than PBAS. The crystallinity was present in both the extracted and nonextracted samples of crosslinked PBAS, and it could be due to low crosslinking density. The crystallization temperature of the crosslinked PBAS probably increased with the help of a substance produced in the course of crosslinking, which acted as nucleating agent. The enzymatic biodegradability of crosslinked PBAS was maintained.

REFERENCES

1. Amass, W.; Amass, A.; Tighe, B. Polym Int 1998, 47, 89.
2. Lenz, R. W. Adv Polym Sci 1993, 107, 1.
3. Mochizuki, M.; Mukai, K.; Yamada, K.; Ichise, N.; Murase, S.; Iwaya, Y. Macromolecules 1997, 30, 7403.
4. Doi, Y. Microbial Polyesters; VCH: New York, 1990.
5. Cox, E. F.; Hostettler, F.; Charleston, W. V. U.S. Pat. 3,021,309, 1962.
6. Schneider, A. K. U.S. Pat. 2,703,316, 1955.
7. Carothers, W. H.; Hill, J. W. J Am Chem Soc 1932, 54, 1579.
8. Hurnki, H. In Plastics Additives, 3rd ed.; Gachter, R., Muller, H., Eds.; Hanser: New York, 1990; p 22, 833, 873.
9. Bolland, J. L.; Gee, G. Trans Faraday Soc 1946, 42, 236.
10. Bolland, J. L. Trans Faraday Soc 1948, 44, 669.
11. Plage, B.; Schulten, H. R. Macromolecules 1990, 23, 2642.
12. Bruthun, B.; Zingsheim, P. In Handbook of Polymeric Foams and Foam Technology; Klempner, D., Frisch, K. C., Eds.; Hanser: New York, 1991; p 187.
13. Takashima, N.; Nakayama, Y. Kagaku Kogyo 1969, 20, 378.
14. Al-Malaika, S. Reactive Modifiers for Polymers, 1st ed.; Chapman & Hall: London, 1997; p 1.
15. Kurcok, P.; Dubois, P.; Sikorska, W.; Jedlinski, Z.; Jerome, R. Macromolecules 1997, 30, 5591.
16. Nielsen, L. E. Mechanical Properties of Polymers; Reinhold: New York, 1962; p 115.
17. Flory, P. J. J Am Chem Soc 1945, 67, 2048.
18. Sperling, L. H. Introduction to Physical Polymer Science; Wiley: New York, 1992.
19. Albertsson, A. C.; Eklund, M. J Polym Sci Part A Polym Chem 1996, 34, 1395.
20. Paszun, D.; Spychaj, T. Ind Eng Chem Res 1997, 36, 1373.
21. Allen, S.; Mohammadian, M.; Jones, K. Eur Polym J 1991, 27, 1373.
22. Otton, J.; Ratton, S. J Polym Sci Polym Chem Ed 1991, 29, 377.
23. Jacques, B.; Devaux, J.; Legras, R.; Nield, E. Polymer 1997, 38, 5367.
24. Cagiao, M.; Calleja, F.; Vanderdonckt, C.; Zachmann, H. Polymer 1993, 34, 2024.
25. Darwin, K.; Sebastian, M. Polym Int 1999, 48, 346.
26. Fields, R. D.; Rodriguez, F.; Firm, R. K. J Appl Polym Sci 1974, 18, 3571.
27. Diamond, M. J.; Feedman, B.; Garibaldi, J. A. J Int Biodegrad Bull 1975, 11, 127.
28. Bitritto, M. M.; Bell, J. P.; Brenckle, G. M.; Huang, S. J.; Knox, H. R. J Appl Polym Sci Appl Polym Symp 1979, 35, 405.
29. Mochizuki, M.; Hirano, M.; Kanmuri, Y.; Kudo, K.; Tokiwa, Y. J Appl Polym Sci 1995, 55, 289.