Modification of Poly(butylene succinate) with Peroxide: Crosslinking, Physical and Thermal Properties, and Biodegradation

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ABSTRACT: Prior to curing, we evaluated thermal stability of poly(butylene succinate) (PBS). Above 170°C, PBS was severely degraded and the degradation could not be successfully stabilized by an antioxidant. PBS was crosslinked effectively by DCP at 150°C, and the gel fraction was increased as DCP content increased. The major structure of crosslinked PBS is supposed to consist of an ester and an aliphatic group. The tensile strength and elongation of PBS were improved with increasing content of DCP, but tear strength was only slightly affected. The higher the crosslinking, the lower the heat of crystallization (ΔH_c) and heat of fusion (ΔH_f). However, the melt crystallization temperature (T_c) of crosslinked PBS was higher than that of PBS. The viscosity of crosslinked PBS increased and exhibited rubbery behavior as the content of curing agent increased. The biodegradability of crosslinked PBS did not seriously deteriorate. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1115–1124, 2001

Key words: poly(butylene succinate) (PBS); crosslinking; physical and thermal properties; biodegradation

INTRODUCTION

In the last quarter of the 20th century, plastic products gained universal use not only in food, clothing, and shelter, but also in the transportation, construction, medical, and leisure industries. Annual production of synthetic polymer is about thousands of millions tons[1] and synthetic plastics have been developed as durable substitute products. Recently, however, the extensive use of bioresistant synthetic polymers is considered to be one of the major causes of environmental pollution and there is growing demand for biodegradable plastics as a solution to problems concerning global environment and solid-waste management.

Although several polymers have been identified as degradable in model aqueous media or in animal bodies, at the moment the family of aliphatic polyesters appears to be the most attractive and promising.[2,3] 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] because of cost and their poor properties such as low melting point, low resistance to heat, tendency to hydrolyze, and mechanical strength.

Much of the investigative work has been generated because of the inherent difficulty in syn-

thesizing high molecular weight aliphatic polyesters through the polycondensation of diols and dicarboxylic acids.[7] Polycondensation alone, however, will not produce polyester with such properties that will make it suitable for practical use as a biodegradable plastic. It is necessary to further increase its molecular weight, which can be accomplished through (1) a polycondensation reaction with a multifunctional group such as trimethylolpropane, pentaerythritol, and diepoxide; or (2) a coupling reaction of polyester end groups with a compound that possesses two or more reactive functional groups in a molecule.[8–12] On the other hand, many researchers tried to introduce crosslinks into aliphatic polyesters to improve properties such as mechanical strength and elasticity. Han et al.[13] prepared biomedical materials by thermal crosslinking of unsaturated polyesters derived from a mixture of glycolic acid, lactide, fumaric acid, and maleic anhydride with radical initiator. Pramanick and Ray[14,15] synthesized crosslinked polyester from a mixture of glycerol, citric acid, and aspartic acid. Up to now, however, the crosslinking of saturated aliphatic polyesters has rarely been reported. In the present study, we introduced crosslinking into saturated aliphatic polyester, poly(butylene succinate) (PBS), to improve properties such as mechanical strength and elasticity by simple addition of an organic peroxide, dicumyl peroxide (DCP). Moreover, we investigated both the thermal properties and the biodegradation behavior of crosslinked PBS.

EXPERIMENTAL

Materials

PBS chips (SG1111) were kindly supplied by SK Chemicals (Korea). To minimize moisture effects and hydrolysis, PBS was dried in a vacuum oven at 80°C for 12 h before use. Primary antioxidant (Irganox 1010) and secondary antioxidant (Irgafos 168) were purchased from Ciba Specialty Chemicals (Summit, NJ). Dicumyl peroxide (DCP) was from Nippon Oil and Fats (Japan). Chloroform and 1,1,2,2,-tetrachloroethane were from Aldrich Chemicals (Milwaukee, WI). All chemicals were used without further purification.

Processing Temperature

To establish the processing temperature, the thermal stability of PBS was investigated. PBS

chips were placed in a convection oven at four different temperatures and change in the reduced viscosity of PBS was measured with respect to oven-residence time. Reduced viscosity of polymers was measured by using a Ubbelohde viscometer in 1,1,2,2,-tetrachloroethane solvent: 0.05 g PBS/10 mL solvent at 25°C. Gel permeation chromatography (GPC) was done on an HPLC (Waters 150cv; Waters Instruments, Rochester, MN) at 40°C with O-chlorophenol/chloroform (1 : 3 v/v) as solvent; molar mass is expressed as polystyrene-equivalent molar mass.

Crosslinking

PBS was crosslinked by simply mixing DCP in a Brabender Plasticorder (PLE331, Germany) equipped with a cam-type rotor (Model No. W50). PBS was first molten at 150°C for 3 min, after which DCP was added. A rotor speed of 40 rpm was used and mixing torque change was recorded from the instant when DCP was added. The crosslinked samples were weighed and extracted by chloroform for 24 h using a Soxhlet extractor. Prior to the final weighing, the samples were dried in a vacuum at 70°C for 24 h. Gel fraction was calculated as the weight of the dried extracted sample divided by the original sample weight. Solid-state ^{13}C–NMR spectra of the PBS and extraction residual of PBS cured by 4-phr DCP were obtained using a Varian Unity Inova 300WB (Varian Associates, Palo Alto, CA).

Mechanical Properties and Rheometric Dynamic Spectroscope Examination

PBS was mixed with DCP in a Brabender Plasticorder at 118°C and subsequently compression-molded into sheets (thickness 0.25 ± 0.02 mm for mechanical properties, 2 mm ± 0.1 for RDS) using hydrodynamic press (150°C). During the mixing, no change of torque was observed. Tensile and tear tests were performed on an Instron model 4465. Korean Industrial Standards procedures were used for measuring tensile strength, elongation at break, and tear strength (KS M 3503) of PBS and PBS cured by DCP. Viscoelastic properties of PBS and crosslinked PBS were performed on an RDS (Rheometrics Scientific, Piscataway, NJ) using parallel plate by frequency sweep. A frequency range of 0.16–100 rad/s and 2% strain were used.

DSC Measurement

The calorimetric measurements were carried out on a Perkin–Elmer Pyris 1 differential scanning

calorimeter (DSC; Perkin–Elmer, Palo Alto, CA) operating under 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. The samples were then cooled at a rate of 10°C/min from 130 to 0°C. The values of crystallization temperature T_c and enthalpy of crystallization ΔH_c were calculated during these cooling runs. The samples were then heated up to 120°C at 10°C/min and the results of melting temperature T_m and enthalpy of melting ΔH_f referred to these traces are reported.

Biodegradability

To evaluate biodegradability, two methods were applied: the enzymatic degradation [total organic carbon (TOC)] test and aerobic gas (CO_2) evolution test. For the enzymatic degradation test, compression-molded films (thickness 45 ± 2 μm, diameter 6.2 mm) of poly(ethylene terephthalate) (PET), PBS, and crosslinked PBS were introduced into small bottles containing 2 mL of phosphate-buffered solution (pH = 7) at 37°C and then added with 4 μL of solution of lipase from *Rhizopus arrhizus* (200 units). The enzymatic hydrolysis was carried out for 48 h. After filtration (0.2-μm membrane filter), a small amount of 1N hydrochloric acid was dropped onto the filtrate. The water-soluble TOC concentration in the filtrate was measured as an indication for the biodegradability with a Shimadzu 500 TOC analyzer (Shimadzu, Japan). As controls, the TOC value for the enzyme itself was measured under the same conditions. The TOC data were the average of two measurements and corrected appropriately with the blank levels. As another method, the aerobic gas evolution test was used and similar equipment was previously reported in the literature.[16] A powdered sample (10 g) was mixed with 190 g of compost. The entire experimental assembly was placed in a cultivation room at 50°C for 180 days. CO_2 evolved from the compost-containing sample and the blank test. The amount of CO_2 evolved was determined by titrating the remaining $Ba(OH)_2$. Percentage biodegradability was calculated from dividing the amount of CO_2 determined by the theoretical value.

RESULTS AND DISCUSSION

Thermal Stability

Virtually all polymeric materials, either of synthetic or natural origin, undergo thermal degra-
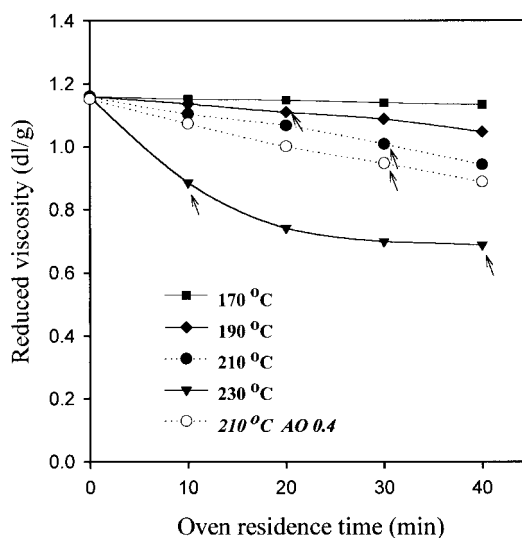

Figure 1 Change in reduced viscosity of PBS with respect to oven-residence time. AO 0.4, PBS + primary antioxidant 0.2 phr + secondary antioxidant 0.2 phr; arrow points, GPC measurement.

dation. Technically, it is important for manufacturers to evaluate thermal stability to establish processing conditions and service temperatures. Thus, prior to curing, we evaluated thermal stability of PBS to establish a processing temperature window.

Figure 1 shows the change in reduced viscosity of PBS as a function of oven-residence time. As shown in this figure, the reduced viscosity change of PBS with time can be neglected at 170°C. But as temperature increased, its reduced viscosity decreased with time, which means that PBS is degraded thermally over 170°C. One of the major mechanisms of thermal degradation is oxidation. The typical manifestations of oxidation are summarized by the term *aging phenomena*. Fundamentally, there are various means available to retard thermal oxidation. One of them is addition of stabilizing additives, antioxidants; addition of antioxidants is the most commonly used method of stabilization. In the case of PBS, however, as we can see in Figure 1 and Table I, antioxidant could not entirely prevent thermal degradation. The possible justification is as following. The three main decomposition modes of polyester—thermal, hydrolytic, and thermooxidative degradation—are shown in **Scheme 1** .[17]

The hydrolytic degradation of polyester is attributed to water. In this study, we dried PBS in a vacuum oven at 70°C for 12 h before use and so hydrolytic degradation may be disregarded. The

Table I   Change in Molecular Weights of PBS with Respect to Oven Aging

Sample	Oven Aging	η_{red}	M_n	M_w	PDI[a]
PBS	Non	1.159	18,750	119,750	6.39
PBS	190°C, 20 min	1.110	17,470	112,960	6.47
PBS	210°C, 30 min	1.008	14,290	86,850	6.08
PBS	230°C, 10 min	0.886	12,590	64,600	5.13
PBS	230°C, 40 min	0.688	11,680	54,810	4.69
PBS + AO 0.4[b]	190°C, 20 min	0.943	15,980	79,120	4.95

[a] Polydispersity index.
[b] PBS + primary antioxidant 0.2 phr + secondary antioxidant 0.2 phr.

oxidation mechanism was developed originally by Bolland and Gee.[18,19] 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 transforms alkyl radicals P· rapidly into peroxy radicals $PO_2^{\bullet}$. The primary antioxidant stabilizes alkyl radicals and peroxy radicals and inhibits the propagation reaction. The secondary antioxidant decomposes hydroperoxides without intermediate formation of free radicals. Commonly, primary and secondary antioxidants are mixed up and used for synergy effect. But, in this study, PBS was degraded severely at 210°C and degradation could not be suc-

cessfully stabilized by antioxidants, which is because thermal decomposition is concerned with degradation. As shown in **Scheme 1**, Plage and Schulten[20] reported that polyester forms a six-membered cyclic transition state and β hydrogen is transferred to oxygen to yield a carboxylic and vinyl end group. That is to say, whereas PBS in this experiment is degraded both through thermal oxidation and thermal decomposition, antioxidants are involved only in thermal oxidation; so, they could not entirely stabilize degradation. From these results, we could conclude that the processing temperature of PBS should not be over 170°C.
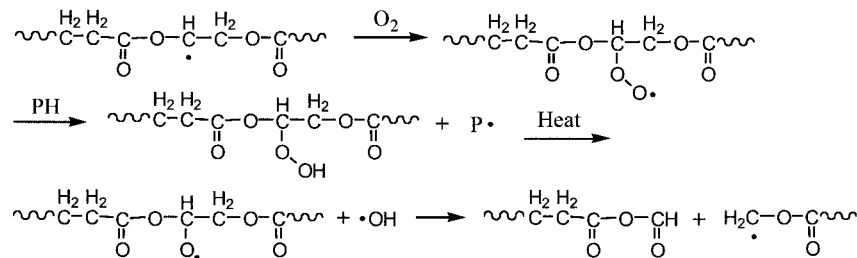
Crosslinking Behavior

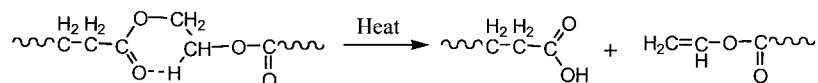The use of an organic peroxide as a crosslinking agent was first reported for the first time in 1915.
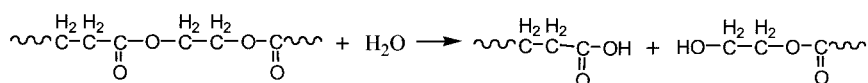
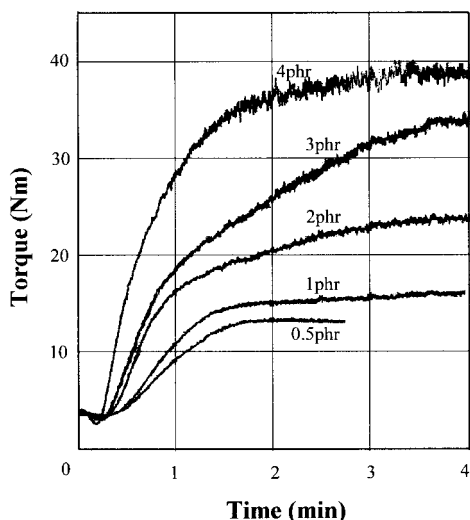**Scheme 1**   Hydrolytic, thermal, and thermooxidative degradation of polyester.

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

Since around 1950, 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 rubber (EPM) and silicone rubber, which cannot be vulcanized with the usual sulfur system. Up to now, however, the crosslinking of thermoplastics for technical applications has been mainly limited to polyethylene and its copolymers. In this study, we sought to introduce crosslinking to PBS, biodegradable saturated aliphatic polyester, by using organic peroxide.

To be suitable for technical applications, a peroxide crosslinking agent must fulfill a number of conditions.[17] One of the major requirements is that 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). Organic peroxides have various decomposition temperatures and the range commences at a temperature below 0°C and finishes at nearly 200°C. Dicumyl peroxide (DCP) is one of the alkyl peroxides and its decomposition range is approximately 170°C. Taking decomposition temperature into consideration, DCP might be the most suitable for polymers melting at 100–120°C.[21] Figure 2 shows the change in Plasticorder torque with time when DCP is added to PBS.

In the early stage, torque value was slightly decreased as DCP was added to PBS. It should be the result of melting of solid DCP. Then after 30–40 s, torque was rapidly increased, such that

the higher the DCP content, the higher the torque value. This means PBS is crosslinked effectively by simple addition of the organic peroxide DCP. The gel fraction of crosslinked PBS with respect to DCP content is shown in Figure 3.

Gel fraction was augmented as the content of DCP increased and at above 5 phr, a slight change was seen. Takshima and Nakayama[22] 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 those reported by Takshima, PBS shows relatively lower gel content than that of PE. The possible justifications are as follows. First, PBS may have fewer crosslinking sites than those of PE. The crosslinking reactions by DCP are as follows[23]: DCP cleaves thermally to produce two cumyloxy radicals (1), which abstract hydrogen atoms from polymer chains (2). A cumyloxy radical can also lead to the formation of a methyl radical and of phenylmethyl ketone (3). The methyl radical is likewise able to abstract hydrogen (4). These polymer radicals then couple to crosslink. Taking the crosslinking mechanism into consideration, it is supposed that PBS has a lower content of methylene group in the main chain than that of PE, such that relatively small crosslinking sites make it difficult to crosslink. Second, polymer–solvent solubility parameter deference could be concerned. That is to say, although Takshima used xylene as a Soxhlet extraction solvent for crosslinked PE, we used chlo-
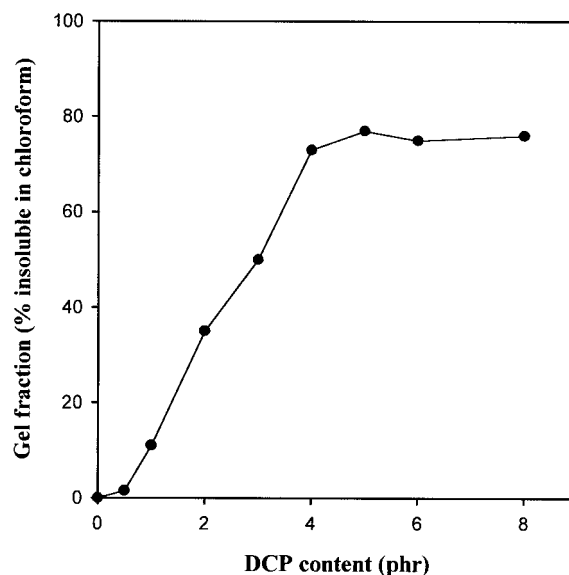

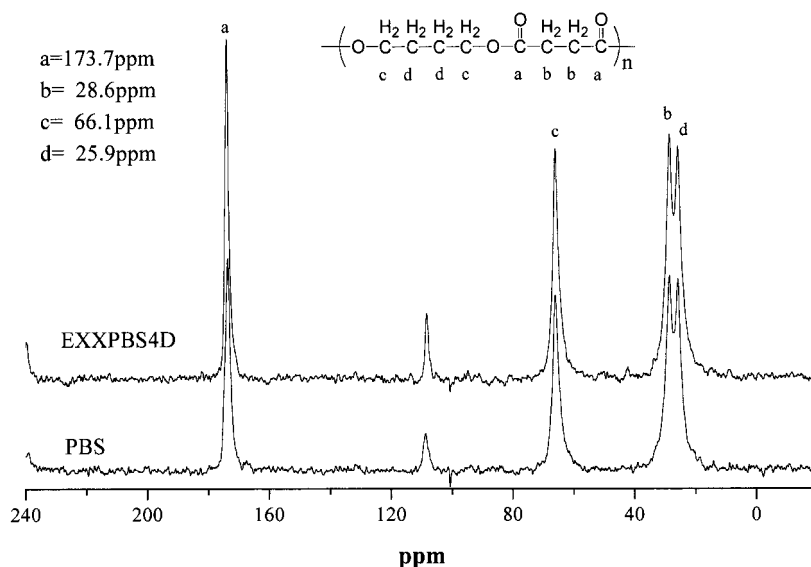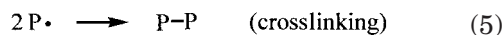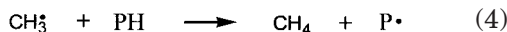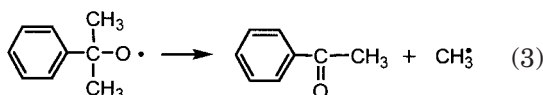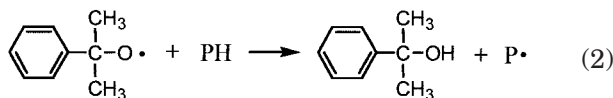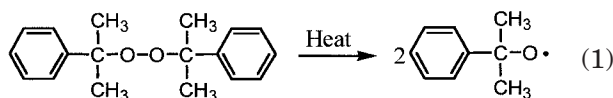**Figure 3** Gel fraction of crosslinked PBS with respect to DCP content.

Figure 4 Solid-state ^{13}C–NMR spectra of PBS and extraction residual of PBS cured by 4-phr DCP (EXXPBS4D).

roform for crosslinked PBS. Thus this difference may be one of the possible reasons for the gap in gel content between DCP-cured PE and PBS.

In the meantime, many investigators have been doing research on aliphatic polyesters because of its biodegradability, which results from ester and flexible aliphatic groups in the polymer main chain. By the way, if ester group of PBS were broken down in the course of crosslinking, biodegradability would be deteriorated. If a radical produced by decomposition of DCP attacks the ester group (C=O) in the PBS main chain, a carbon atom is placed between two oxygen atoms

(–O—C—O–); this carbon resonance at 95–100 ppm can be obtained.[24] So, we investigated solid-state ^{13}C–NMR spectra to identify the existence of this carbon atom. Figure 4 shows solid-state ^{13}C–NMR spectra of PBSD and the extraction residual of PBS cured by 4-phr DCP (EXXPBS4D).

The ester group carbon "a" resonance at 173.7 ppm, and carbon "b," carbon "c," and carbon "d" at 28.6, 66.1, and 25.9 ppm, respectively, were obtained. There was little difference between the two spectra and there was no trace of resonance at 95–100 ppm, which may imply that the basic structure of crosslinked PBS consists mainly of an ester and an aliphatic group and that we can anticipate that crosslinking may not deteriorate the biodegradability of PBS.

Mechanical Properties

One of the reasons for crosslinking PBS is to improve the mechanical strength of aliphatic polyester. Tensile strength, elongation, and tear strength of PBS and PBS cured by DCP are shown in Table II.

Tensile strength and elongation were enhanced with an increase of DCP content added to PBS. Nielsen[25] and Flory[26] illustrated that at very low molecular weights, the tensile stress to break, σ_b, is near zero and as the molecular weight increases, the tensile strength rapidly increases, then gradually levels off. A major point of weakness at the molecular scale is the chain end,

Table II Mechanical Properties of PBS and Crosslinked PBS

Material	Tensile Strength (kg$_f$/cm^2)	Elongation (%)	Tear Strength (kg$_f$/cm)
PBS	287	57	184
PBS + 0.5D[a]	280	77	181
PBS + 1D	304	87	214
PBS + 2D	316	152	192
PBS + 3D	307	192	182
PBS + 4D	339	252	206

[a] Content of DCP (phr).

which does not transmit the covalent bond strength; in the case of crosslinking of PBS in our study, the number of chain ends was not reduced because the molecular weight of polymer was increased, not polymerization but interchain crosslinking. However, supposing that two polymer chains of the same molecular weight are crosslinked 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, number-average molecular weight is double what it was before. Accordingly, it is supposed that molecular weight augmentation by curing enhanced the tensile properties. On the other hand, tear strength was not affected by crosslinking. We guess that tear strength of a polymer is concerned with breaking of main-chain covalent bonds. Therefore, it is supposed that tear strength depends mainly on the basic chemical structure of the polymer, not molecular weight or crosslinking.

Thermal and Viscoelastic Properties

DSC thermograms for both cooling and heating runs of PBS and PBS cured by DCP were investigated and crystalline temperature (T_c) and heat of crystallization (ΔH_c) values are summarized in Table III.

As can be seen in Table III, crystallinity was present in both crosslinked PBS and the extracted sample. Generally, it is known that the crystallinity of a polymer disappears with the introduction of crosslinking, although Albertsson and Eklund[27] did an interesting study, in which they obtained methylene segment crosslinks by copolymerizing adipic anhydride with 1,2,7,8-diepoxyoctane (DEO). The percentage gel fraction increased up to 95 wt % with an increasing amount of crosslinking agent, up to 20 mol % DEO, and these crosslinked polymers showed crystallinity. However, no crystallinity could be detected at DEO contents over 20 mol %. Taking their report into account, the crosslinking density of PBS cured by DCP is low, so that polymer chains have mobility to crystallize. Meanwhile, it is noteworthy to see the effect of crosslinking on crystallization temperature of PBS. Crystallization temperature of crosslinked PBS is higher than that of PBS. We surmise that the crystallization temperature of crosslinked PBS probably increased as a result of some substances acting as nucleating agents.

Table III Thermal Properties of PBS and Crosslinked PBS

Property	PBS	PBS + 0.5D[a]	1D	2D	3D	4D	4DEX[b]
T_c (°C)	79.6	89.8	92.4	93.8	93.2	93.4	92.3
ΔH_c (J/G)	−79.6	−81.9	−78.5	−76.7	−75.0	−71.1	−55.0
T_m (°C)	114.3	112.9	112.4	111.4	110.4	110.7	108.9
ΔH_f (J/G)	80.1	75.9	74.3	72.3	71.9	63.3	54.6

[a] Content of DCP (phr).
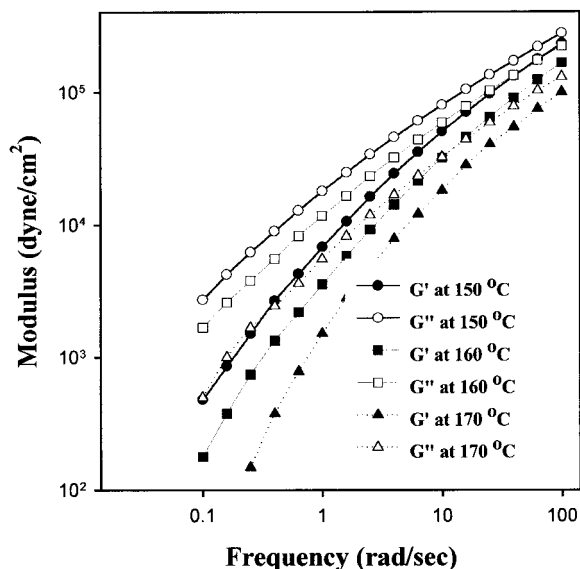[b] Extraction residual of PBS cured with 4-phr DCP.

Figure 5 Modulus change of PBS as a function of frequency at various temperatures.

Jensen[17] insisted that so-called spontaneous nucleation, that is, nucleation without an intentional introduction of a nucleating agent, is generally believed to be attributed to foreign substances such as catalyst residues, oxidatively degraded polymer, or other, processing-determined impurities about whose physicochemical nature very little is known. The nucleating agent should be wetted or absorbed by the polymer and it should be homogeneously dispersed in the polymer, in as fine a form as possible. Considering his insistence, it may be possible that a by-product of curing reaction or crosslinking point could act as an impurity that can initiate crystallization. In the meantime, the melting temperature and heat of fusion of crosslinked PBS were lower than that of PBS in the heating scan. This intimates that size and perfectness of cured PBS crystals are relatively low because crosslinks restrict chain motions.

Figure 5 shows storage modulus (G') and loss modulus (G'') change of PBS with frequency. G'' surpassed G' in most frequency ranges and the gap between G' and G'' was decreased with increasing frequency, which is the characteristically time-dependent viscoelastic behavior of thermoplastic polymer melts: the higher the strain rate, the higher the elasticity. In Table IV, crossover frequency in the G' and G'' of PBS and PBS cure by DCP is summarized. In the case of PBS cured by 0.5-phr DCP, G'' exceeded G' over 40 rad/s at 150°C. Crossover frequency shifted to

Table IV   Crossover Frequency in the G' and G'' of PBS Cured by DCP (Frequency Range: 0.16–100 rad/s)

Material	Temperature (°C)		
	150	160	170
PBS	Non	Non	Non
PBS + 0.5D[b]	40 rad/s	Non	Non
PBS + 1D	6.3 rad/s	100 rad/s	Non
PBS + 2D	All range[c]	All range	All range
PBS + 3D	All range	All range	All range
PBS + 4D	All range	All range	All range

[a] G'' surpassed G' in the all-frequency range.
[b] Content of DCP (phr).
[c] G' surpassed in the all-frequency range.

low frequency with increasing crosslinking and lower temperature. In the case of PBS cured with 2-phr DCP, G' surpassed G'' in the all-frequency range (Fig. 6).

This may be explained as follows. First, generally, the higher the molecular weight of a polymer, the higher the elasticity, because chain entanglement restricts chain slippage, which is irreversible deformation. Second, enhancement of entropy elasticity[28] by crosslinking could be considered like that in the rubber. On the other hand, the test procedure of melt strength usually used involves increasing the wind-up speed and noting
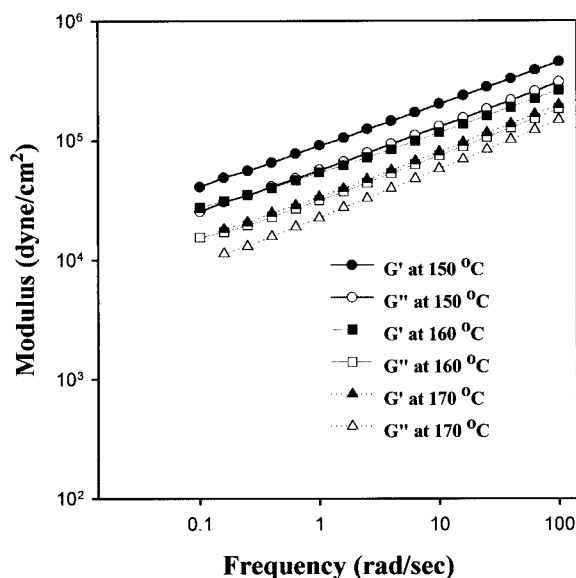

Figure 6 Modulus change of PBS cured with DCP (2-phr) as a function of frequency at various temperatures.

the force level when the filament breaks.[29] If melt strength of a polymer is not sufficient, it is difficult to process the polymer. Melt strength of a polymer depends on viscosity, G', and G''. Much investigative work has been generated because of the inherent difficulty in synthesizing high molecular weight aliphatic polyesters through the polycondensation of diols and dicarboxylic acids. One of the major purposes of this works was to improve the melt strength of aliphatic polyesters. Accordingly, RDS results suggest that simple addition of organic peroxide will be able to control viscoelastic properties of PBS without adding any functional group into the polymer main chain.

Biodegradability

The biodegradability of crosslinked PBS was evaluated by measurement of TOC values (Fig. 7) and the aerobic gas evolution test (Fig. 8).

As Figure 7 shows, TOC of PBS is much higher than that of PET, and that of crosslinked PBS is rarely deteriorated. Moreover, the percentage biodegradability measured by the aerobic gas evolution test of PBS cured with 2-phr DCP is almost equal to that of cellulose. This may be because crosslinked PBS still consists of an ester and an aliphatic group (as considered in Fig. 4). Biodegradability of polyesters is highly dependent on glass-transition temperature, crystallinity,[30–35] and balance between hydrophilic and hydropho-

Figure 8 Results of compost test for cellulose, PE, and PBS cured with 2-phr DCP (PBS2D).

bic groups[36–39] in the backbone. PET shows low biodegradability by reason of high glass-transition temperature and low chain mobility attributed to the rigid aromatic group. This is the reason that most of the biodegradable polyesters are aliphatic. Consequently, we may be able to say that crosslinking caused by organic peroxide exerts only a slight effect on the biodegradability of PBS, aliphatic polyester.

CONCLUSIONS

The processing temperature of PBS should not be over 170°C and antioxidants cannot entirely prevent thermal degradation. By simple addition of DCP, PBS was crosslinked effectively and gel fraction increased as DCP content increased. ^{13}C–NMR spectra revealed that the major structure of crosslinked PBS is still an ester and an aliphatic group. Crosslinking introduced to PBS enhanced tensile properties, although tear strength was only slightly affected by curing. Crosslinking density of PBS cured by DCP may be low so that polymer chains have mobility to crystallize. It is supposed that the crystallization temperature of crosslinked PBS increased for the help that a substance produced in the course of crosslinking acts as nucleating agent. Elasticity of crosslinked PBS was increased as content of the curing agent increased, which indicates that processibility of
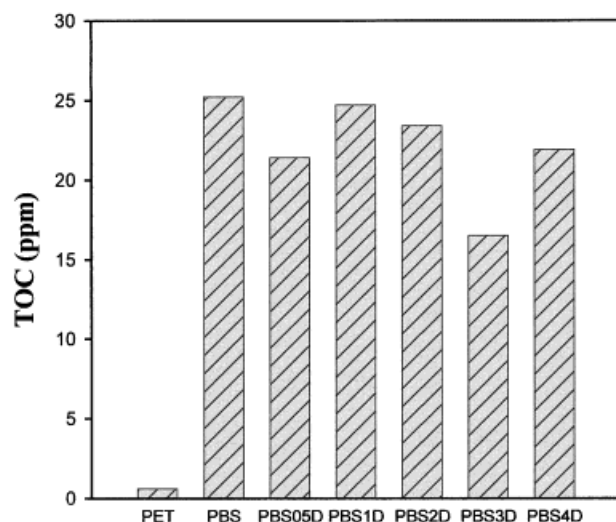

Figure 7 Change of TOC on enzymatic hydrolysis of PET, PBS, and DCP-cured PBS. PBS05D, PBS cured with 0.5-phr DCP; PBS1D, PBS cured with 1-phr DCP; PBS2D, PBS cured with 2-phr DCP; PBS3D, PBS cured with 3-phr DCP; PBS4, PBS cured with 4-phr DCP.
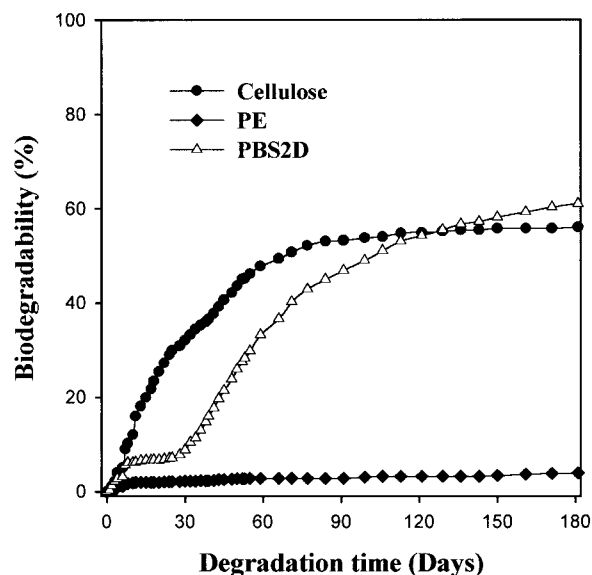
PBS can be regulated by simple addition of DCP. The biodegradability of crosslinked PBS was rarely deteriorated and similar to that of cellulose.

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