Preparation and Biodegradation of Hydroxyl Terminated Poly(fumaric acid-*co*-diethylene glycol) and Its Segmented Polyurethane

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ABSTRACT: Hydroxyl terminated poly(fumaric acid-*co*-diethylene glycol), poly(FA-*co*-DEG) was prepared by melt polycondensation. The resultant unsaturated aliphatic polyester was characterized by Fourier transform infrared (FTIR) spectroscopy, hydroxyl value, acid value, and intrinsic viscosity. Its enzymatic degradation and crosslinking behavior as well as the effect of crosslinking degree on enzymatic degradation were also investigated. The crosslinking degree and reduction of carbon–carbon double bonds revealed excellent self-crosslinking nature of poly(FA-*co*-DEG) at high temperature. The results of enzymatic degradation showed that poly(FA-*co*-DEG) has excellent biodegradability and that the biodegradation can be controlled by the crosslinking degree. Polyurethane was prepared by the reaction of poly(FA-*co*-DEG), 2,4-toluene diisocyanate (TDI), and 1,4-butanediol (BD). It was found that the biodegradation of the obtained polyurethane was slower than that of the original unsaturated aliphatic polyester poly(FA-*co*-DEG). The peeling strength of the polyurethane was very high, supporting better adhesion property with enhanced crosslinking. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2477–2484, 2011

Key words: hydroxyl terminated; unsaturated aliphatic polyesters; polycondensation; biodegradable; peeling strength; polyurethanes

INTRODUCTION

Over the past decades, the synthesis and properties of biodegradable polymers have been studied intensively. Aliphatic polyesters made from dicarboxylic acids and diols have been expected to be the most economically competitive biodegradable polymers.[1,2] However, only a few investigations have been reported on unsaturated aliphatic polyesters, especially on the biodegradation of chain-extended unsaturated aliphatic polyesters.[3,4]

Unsaturated aliphatic polyesters developed thus far are mainly based on the combination of propylene glycol or ethylene glycol and fumaric acid or maleic acid. They are applied to different fields, for example, biomedical area as bone substitutes, cements, drug delivery matrices, or cartilage repairing materials.[5–8] These unsaturated aliphatic polyesters can be crosslinked through their carbon–carbon double bonds when combined with appropriate vinyl monomers, such as styrene in the presence of a peroxide catalyst.[9,10] But they are not self-crosslinkable unless treated either at high temperature or over lengthy times.[5,11] Sometimes, the self-crosslinking character of their carbon–carbon double bonds is efficiently utilized for specific purposes, for example, pigment printing adhesives consisting of carbon–carbon double bonds. Their carbon–carbon double bonds are allowed to be crosslinked to improve the fastness of prints.

Polyurethanes (PU) are a versatile class of polymers that can be efficiently tailored to give a diverse range of products, such as foams, coatings, adhesives, fibers, rubbers, and thermoplastic elastomers.[12] Of special interest are polyurethane adhesives, which are used for producing laminates for food packaging and composite fabrics because of their flexibility and wide range of application temperature. However, the function of their laminates is limited to holding of polymer films because of their meager contribution to the overall barrier performance.

In the present study, a hydroxyl-terminated unsaturated aliphatic polyester, poly(FA-*co*-DEG), is prepared by melt polycondensation of fumaric acid (FA) and diethylene glycol (DEG) to investigate the relation between enzymatic degradation and crosslinking degree. The FA units can readily be crosslinked

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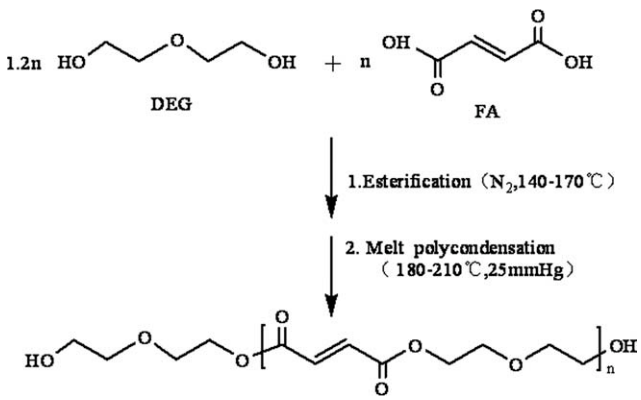


Scheme 1 Synthesis of hydroxyl terminated poly(FA-*co*-DEG).

by combination with appropriate vinyl monomers. A segmented polyurethane is also prepared from the synthesized hydroxyl terminated poly(FA-*co*-DEG), 1,4-butanediol (BD), and 2,4-toluene diisocyanate (TDI) to investigate the effect of the crosslinking on the peeling strength and enzymatic degradation.

EXPERIMENTAL

Materials

FA, succinic acid (SA), DEG, TDI, BD, tin (II) chloride dihydrate, and dibutyltin dilaurate were reagent grade products. Lipase type II (crude 70% protein, specific activity 71 IU mg^{-1}) from porcine pancreas was purchased from Sigma Chemical (St Louis, MO).

Synthesis of hydroxyl-terminated unsaturated aliphatic polyester polyesters

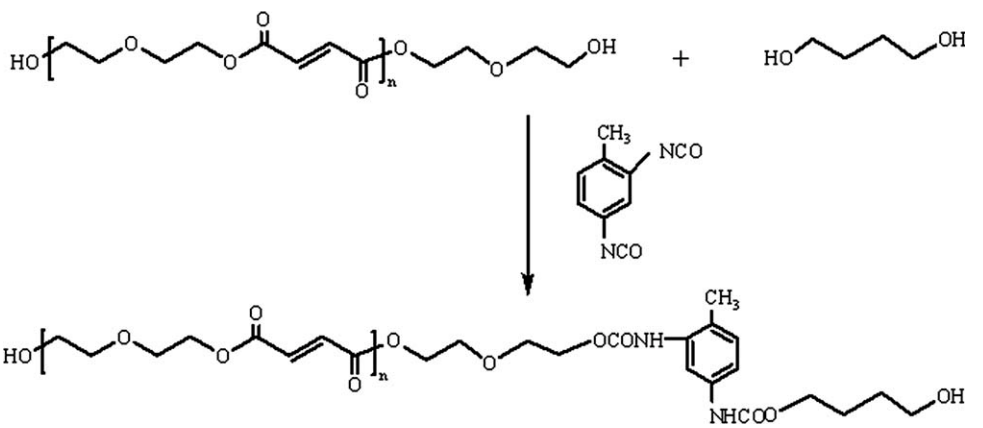
Hydroxyl-terminated unsaturated aliphatic polyester poly(FA-*co*-DEG) was prepared from FA and DEG by melt polycondensation according to Scheme 1.

The polycondensation was conducted in bulk with stirring in an oil bath using the following optimum conditions. FA (31.4 g, 0.27 mol) and DEG (30.7 mL, 0.32 mol) (DEG/FA = 1.2 in molar ratio) were placed in a round-bottom flask, then $SnCl_2$ (0.4 g, 0.3 mol %/monomer) was added under a nitrogen flow. The round-bottom flask was immersed in an oil bath for ~ 5 h at 150°C until more than 70% of the theoretical amount of by-product (water) was completely distilled out. Subsequently, the reaction mixture was gradually evacuated to ~ 25 mmHg and heated to 190°C for another 5 h. After cooling, the resultant crude product was dissolved in chloroform, and poured into methanol for re-precipitating the polyester. The precipitate was washed with methanol twice and with diethyl ether, and dried *in vacuo* for 3 days at ambient temperature. The chemical structure of the hydroxyl-terminated unsaturated aliphatic polyester of poly(FA-*co*-DEG) was confirmed by ^1H NMR spectrum. ^1H NMR ($CDCl_3$): δ = 3.6 (—COO—$CH_2CH_2OCH_2CH_2$OH), 3.8 (—COO—$CH_2CH_2OCH_2CH_2$OH, and —COO—$CH_2CH_2OCH_2CH_2OCH_2CH_2$OC O—), 4.4 (—COO—$CH_2CH_2OCH_2CH_2$OH, and —COO —$CH_2CH_2OCH_2CH_2$OCO—), 6.8 (—CO—CH=CH—C O—) ppm.

A saturated polyester poly(SA-*co*-DEG) was also prepared from SA and DEG likewise as a reference sample.

Synthesis of segmented polyurethane

Polyurethane was prepared from the synthesized hydroxyl-terminated unsaturated polyester poly(FA-*co*-DEG), BD, and TDI according to Scheme 2. The hydroxyl-terminated polyester poly(FA-*co*-DEG) (M_n = 2100, 40.0 g) was placed in a round-bottom flask containing the solvent (butanone 50 mL) and was dissolved with stirring. Then, TDI (4.2 g) and catalyst (dibutyltin dilaurate: 1.1 mol %/polyester) were added. The mixture was heated to 75°C for ~ 2.5 h in an oil bath. Subsequently, BD (0.9 mL) was added at 75°C for another 2.5 h. The mixture was heated to 80°C with the solvent completely distilled under



Scheme 2 Synthesis of a segmented polyurethane from poly(FA-*co*-DEG), BD, and TDI.

reduced pressure (~ 25 mmHg) for 1 h. The reaction was allowed to continue for another 1 h. The resultant polyurethane was purified in a similar manner described above.

Preparation of crosslinked samples

Each of the polymer samples was dissolved in chloroform in a concentration of 5 g dL^{-1} and cast into a Petri dish which had primarily been surface-treated with Sigmacoat® (Aldrich) to prevent adhesion of the cast film. After solidification by air-drying, the film obtained was thoroughly dried in vacuum at 60 and 80°C for 4.0 h each. Then the film was heat-treated in an oven for 5, 15, and 30 min at high temperatures (120–180°C) in air.

Acid value, hydroxyl value, and number average molecular weight

The hydroxyl values (Q_v) and acid values (X) were determined according to ASTM D 1957-63 and ASTM D 1980-67, respectively. They were utilized to determine the number average molecular weight (M_n) by the following equation,

$$M_n = \frac{56.1 \times n \times 1000}{Q_v + X} \quad (1)$$

Here, 56.1 is the molecular weight of KOH (g mol^{-1}), and n is the functionalities of hydroxy groups and carboxyl groups.

Intrinsic viscosity

The intrinsic viscosity [η] was measured by one-point method with 0.75% w/v polymer solutions in chloroform at 35°C in a constant-temperature bath using an Ubbelohde Viscometer. It was calculated by using the Solomonciuta equation,[13]

$$[\eta] = \sqrt{2(\eta_{s_p} - \ln \eta_{rel})}/C \quad (2)$$

Here, η_{sp} and η_{rel} are specific and relative viscosities, respectively.

^{1}H NMR spectrum

The 600 MHz ^{1}H NMR spectra were measured on a Bruker ARX spectrometer with samples dissolved in deuterated chloroform ($CDCl_3$) containing 0.03 or 1.0 vol % tetramethylsilane as the internal reference.

Gel permeation chromatography (GPC)

The number- [M_n (gpc)] and weight-average [M_w (gpc)] molecular weights were determined by GPC with a Shimadzu analyzer system comprising LC-10ADvp pump, a RID-10A refractive index detector, and a C-R7A Chromatopac data processor. A Tosoh gel GMHHR-M column was used with chloroform as eluent at a flow rate of 0.25 mL min^{-1}. A sample was injected at a concentration of 5.0 mg mL^{-1}. The molecular weights were calibrated as relative values to polystyrene standards.

FT-IR spectrum

Fourier transform infrared (FTIR) spectroscopy was conducted at room temperature using a NEXUS-670 Fourier transform infrared spectrometer (Thermo Nicolet, USA). The samples were prepared by a solution-casting technique (5% polyesters solution in chloroform) over a KBr crystal and dried under vacuum. Crosslinked polyester films (5-mm thick) were cut using a microtome and placed on a KBr crystal.

Conversion (C) of carbon–carbon double bonds

FT-IR spectra of the samples were recorded before and after heat-treatment at high temperature. The conversion (C) of carbon–carbon double bonds was determined from the ratio of absorbance intensities of aliphatic C=C (peak at 1650 cm^{-1}) against the C=O stretching band at 1730 cm^{-1} as the internal reference peak before and after heat-treatment of the specimen. C was calculated as follows,[7]

$$C(\%) = \left(1 - \frac{\frac{\text{Peak area at 1650 cm}^{-1}}{\text{Peak area at 1730 cm}^{-1}}(\text{after curing})}{\frac{\text{Peak area at 1650 cm}^{-1}}{\text{Peak area at 1730 cm}^{-1}}(\text{before curing})}\right) \times 100 \quad (3)$$

Sol–gel analysis

Sol–gel analysis was conducted by extracting the crosslinked sample with chloroform for 6 h using a Soxhlet extractor. The percent insoluble fraction (Q_s) was determined by the following equation,[6]

$$Q_s(\%) = \frac{W_t}{W_0} \times 100 \quad (4)$$

Here, W_0 and W_t represent the initial and final weights, respectively. Each measurement was performed on three separate samples.

Enzymatic degradation

A polyester or polyurethane sample was treated with porcine pancreas lipase (0.1 g L^{-1}) in standard

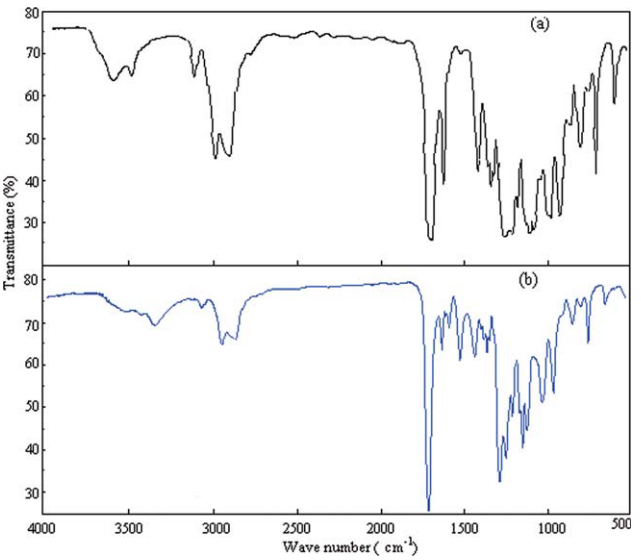


Figure 1 FT-IR spectra of (a) poly(FA-*co*-DEG) and (b) its segmented polyurethane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

phosphate buffer solution (pH = 7.4, 37°C). The weight remaining of the sample was calculated using the following equation,

$$\text{Weight remaining}(\%) = \frac{W_t}{W_0} \times 100 \qquad (5)$$

Here, W_0 and W_t represent the weights of the sample before and after the enzymatic degradation, respectively.

Peeling strengthen (T-peel test)

A polyurethane sample was first coated on a treated fabric, covered another fabric, and laminated under a certain pressure for 1–4 min at 100–170°C. The resultant laminate was cut to a size of 150 × 30 mm^2 and subjected to T-peel test at room temperature with an Instron 1011 tester (Instron, Canton, MA) at a peel rate of 0.1 m min^{-1}. The values obtained for five replicates were averaged (standard deviation was less than 5%).

RESULTS AND DISCUSSION

Crosslinking behavior of hydroxyl-terminated unsaturated aliphatic polyester and its segmented polyurethane

Figure 1 shows the FT-IR spectra of poly(FA-*co*-DEG) and the segmented polyurethane prepared from it. The broad bands around 3100 and 1650 cm^{-1} are attributed to the stretching vibration of the H—(C=C) group and the C=C bonds, respectively. The absorption bands around 1735 and 1140 cm^{-1} are attributed to the C=O stretching and asymmetrical C(=O)—O—C stretching, respectively. These bands can be found both in the spectra of poly(FA-*co*-DEG) and its segmented polyurethane. In spectrum of the polyurethane (b), broad absorption bands are shown around 3300 and 1600 cm^{-1} which are characteristic of the *N*—H and the —NH—CO—O— groups. No band is shown around 2270 cm^{-1} which is characteristic of the —NCO group. These data support that all the —NCO groups have completely reacted to give the target products successfully.

Although the unsaturated aliphatic polyesters can be crosslinked through their C=C bonds, the present polyester was not self-crosslinkable at ambient condition. Figure 2 depicts the temperature-dependent changes in Q_s of poly(FA-*co*-DEG) during the heat-treatment for different times. It is shown that the Q_s increases with increasing the heating temperature and time and that the present unsaturated aliphatic polyester poly(FA-*co*-DEG) has excellent self-crosslinking character at high temperature.

To investigate the effect of the heat-treatment on C=C bonds in unsaturated aliphatic polyesters, poly(FA-*co*-DEG) was heat-treated at 140°C. Figure 3 shows the FT-IR spectra of poly(FA-*co*-DEG) before and after heat-treatment at 140°C. A strong absorption band around 1735 cm^{-1} is assigned to the C=O stretching of ester units, while the band around 1650 cm^{-1} (depicted by an arrow) is assigned to C=C stretching of the FA units. The latter band is weaker in the heat-treated samples. Here, the former C=O stretching band is used as the internal reference, and the relative absorption intensity of C=C stretching band is determined for estimating the C=C bond content. The resultant C=C bond contents of the samples before (a) and after heat-treatments for 15 min (b) and 30 min (c) were 35.8, 18.5, and 7.3%, respectively, at 140°C, supporting the reduction of C=C bond content by the heat-treatment. According

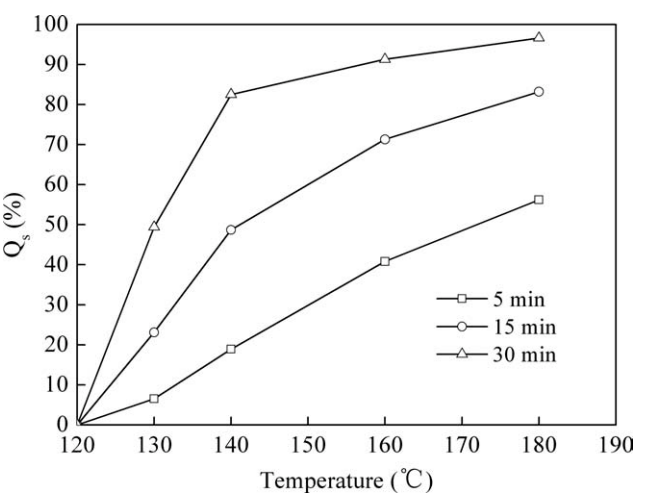


Figure 2 Effect of heat-treatment temperature and time on Q_s of poly(FA-*co*-DEG).

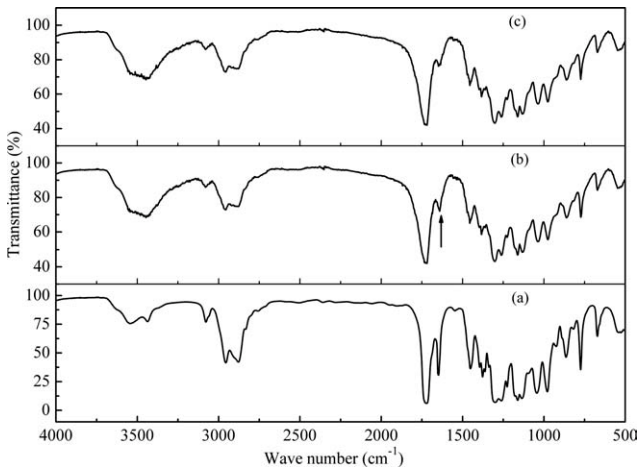


Figure 3 FT-IR spectra of poly(FA-*co*-DEG) before and after heat-treatment: (a) before heat-treatment; (b) heat-treatment 15 min at 140°C; (c) heat-treatment 30 min at 140°C.

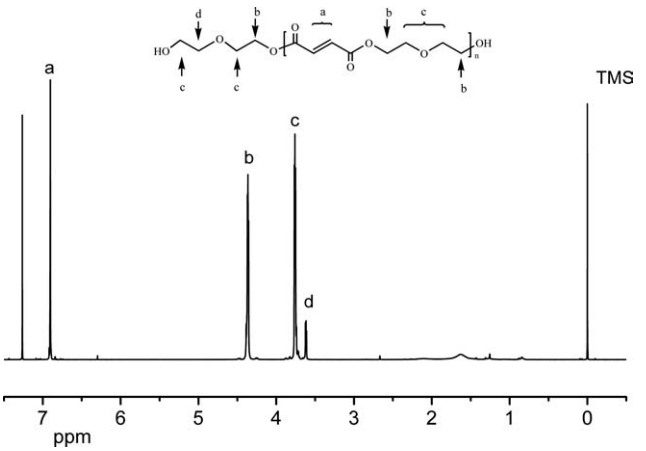


Figure 4 ^{1}H NMR spectrum of soluble part of the crosslinked poly(FA-*co*-DEG) sample which was heat treated 30 min at 140°C.

to Formula 3, the real conversion of C=C bonds are calculated as 48.3 and 79.6% after the heat-treatments for 15 and 30 min respectively, at 140°C. It is therefore indicated that the C=C bonds in poly(FA-*co*-DEG) have been opened partially. It was however found that the heat-treated polyester partly swell in chloroform which is a good solvent before heat-treatment.

Figure 4 shows the ^{1}H NMR spectrum of the soluble part isolated from the poly(FA-*co*-DEG) which was heat-treated for 30 min at 140°C. As compared with that of the original polymer, litter difference is observed in each signal to indicate that the soluble part has retained the original structure without being much involved in the crosslinking reaction. Table I compares the molecular weights of the original poly(FA-*co*-DEG) and the soluble part from the crosslinked part from the sample heat-treated for 30 min at 140°C. It is clearly shown that the number-(M_n) and weight-average (M_w) molecular weights of the soluble part have become much higher than those of the original. This fact supports that the partial interchain reaction of poly(FA-*co*-DEG) has occurred to form the chain-extended, soluble oligomers (trimer or tetramer in average) in between the crosslinked polymers.

Biodegradability of hydroxyl-terminated unsaturated aliphatic polyester and its segmented polyurethane

To examine the biodegradability of poly(FA-*co*-DEG), its enzymatic hydrolysis was conducted with a porcine pancreas lipase. Table II presents the properties of polyesters used to enzymatic degradation. Figure 5 shows the time-courses of weight remaining for as-prepared and heat-treated poly(FA-*co*-DEG). The heat-treatment was done at 140°C for 30 min, and by which the Q_s became 84%. This sample is denoted as poly(FA-*co*-DEG)*. A reference sample poly(SA-*co*-DEG) which was a saturated aliphatic polyester prepared from SA and DEG was also examined in as-prepared state for comparison. Both the original unsaturated aliphatic polyester poly(FA-*co*-DEG) and the saturated aliphatic polyester poly(SA-*co*-DEG) show similar time-courses, suggesting that the degradability is independent from whether the polyesters comprise C=C bonds or not. The heat-treated sample poly(FA-*co*-DEG)* showed very slow degradation because of the crosslinking.

The effect of Q_s on biodegradation of unsaturated aliphatic polyester poly(FA-*co*-DEG) was investigated. As shown in Figure 6, the higher the Q_s, the

TABLE I
Comparison of Original Poly(FA-*co*-DEG) and the Soluble Part of the Cross-linked Poly(FA-*co*-DEG) from GPC and ^{1}H NMR

Poly(FA-co-DEG)	M_n (gpc)[a] (g mol^{-1})	M_w (gpc)[a] (g mol^{-1})	PDI[a]	a/d[b]	M_n (^{1}H) [c] (g mol^{-1})
Original	2270	4750	2.09	3.9	1556
Soluble[d]	9170	13,500	1.47	5.4	–

[a] Determined by GPC measurement.
[b] The integral ratio of the ^{1}H NMR signals of a (—C<u>H</u>=C<u>H</u>—), and d (terminal C<u>H</u>$_2$CH$_2$OH).
[c] Determined by ^{1}H NMR spectra.
[d] From the sample heat-treated for 30 min at 140°C.

TABLE II
Properties of Polyesters Used to Enzymatic Degradation

	X (mgKOH g^{-1})	Q_v (mgKOH g^{-1})	M_n (g mol^{-1})	[η] (mL g^{-1})
Poly(FA-co-DEG)	1.7	51.6	2105	13.2
Poly(SA-co-DEG)	2.5	53.4	2007	12.8

higher the crosslinking degree, and the slower the enzymatic degradation of poly(FA-*co*-DEG). It is therefore indicated that the biodegradability of unsaturated aliphatic polyesters can be controlled by its crosslinking.

To compare the biodegradability of the segmented polyurethane with that of poly(FA-*co*-DEG), the enzymatic degradation of the polyurethane was also investigated. Figure 7 compares the results of the enzymatic degradation of poly(FA-*co*-DEG) and the polyurethane consisting of poly(FA-*co*-DEG), BD, and TDI. Polyurethane* represents the crosslinked polyurethane. Its Q_s was 83.2%. From Figure 7, the degradability of the segmented polyurethane is slower than that of poly(FA-*co*-DEG). Since the polyurethane is chain-extended, its molecular weight is much higher than that of the original poly(FA-*co*-DEG). With the increase in molecular weight, intra- and intermolecular entanglements are also increased to inhibit the enzymatic degradation of polyurethane. Furthermore, the urethane bonds, which may not be cleaved by the lipase, retard the degradation rate. Accordingly, the degradability of the crosslinked polyurethane is slower than that of the uncross-linked polyurethane.

Peeling strength of polyurethane

A segment polyurethane was prepared by using poly(FA-*co*-DEG) as the soft segment and poly(TDI-BD) as the hard segment. To investigate the effect of crosslinking degree on the peeling strength of the resulting polyurethane, the effects of laminating pressure, temperature, and time on peeling strength were measured.

Effect of laminating pressure on peeling strength of the polyurethane is presented in Figure 8. It can be found that the peeling strength increases with the laminating pressure increased, and then decreased above 2 kg cm^{-2} in laminating pressure. Maybe the polyurethane can easily penetrate into the fabrics by applying a too high pressure, and the polyurethane content between the fabrics becomes too short to attain a better lamination state.

At a constant laminating pressure of 2 kg cm^{-2}, the effects of laminating temperature and time on peeling strength were investigated. Figures 9 and 10 show the effects of laminating time and temperature on peeling strength, respectively. Peeling strength increases obviously with the laminating temperature increased or time elongated. This may be because the polyurethane can undergo crosslinking through its C=C bonds at high temperature as discussed earlier, improving the adhesion. Below 150°C in the laminating temperature or 160 s in the laminating time, the C=C bonds in the backbone of the polyurethane are only partially crosslinked to give the limited peeling strength. The decrease in peeling strength when above 150°C in the laminating temperature or 160 s in the laminating time is probably because too much polyurethane is

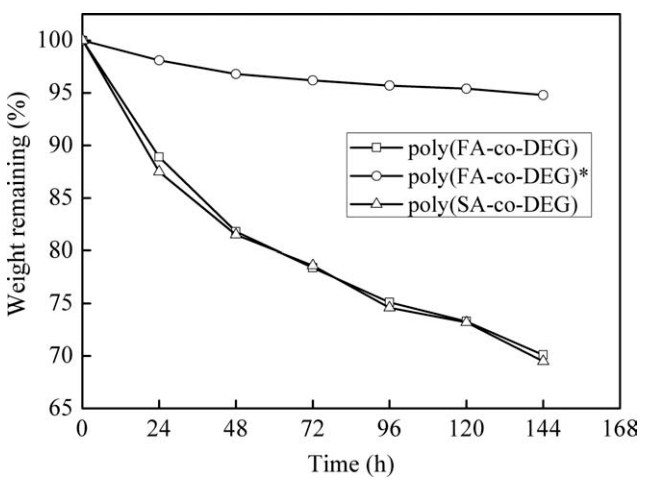


Figure 5 Enzymatic degradations of poly(FA-*co*-DEG), poly(SA-*co*-DEG), and the heat-treated sample denoted as poly(FA-*co*-DEG)*

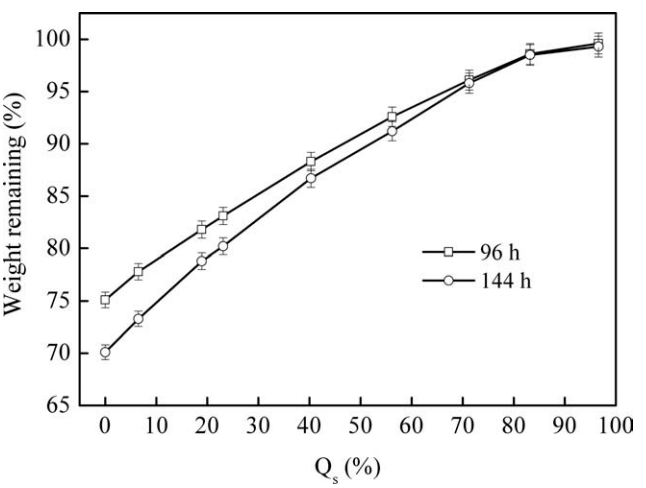


Figure 6 Effect of Q_s on enzymatic degradation.

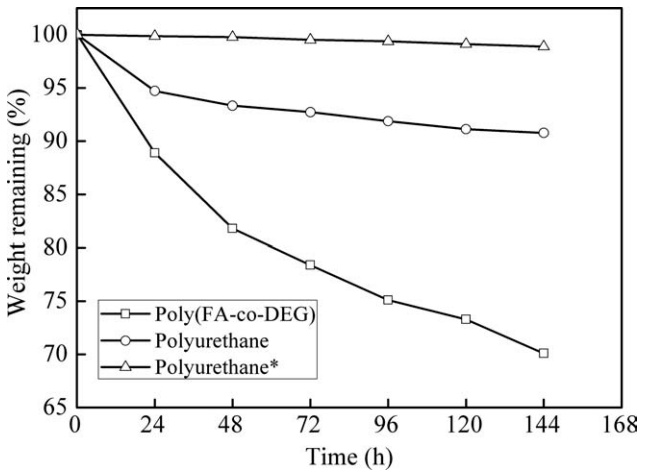


Figure 7 Enzymatic degradations of original poly(FA-*co*-DEG) and its segmented polyurethane, and crosslinked polyurethane denoted as Polyurethane*.

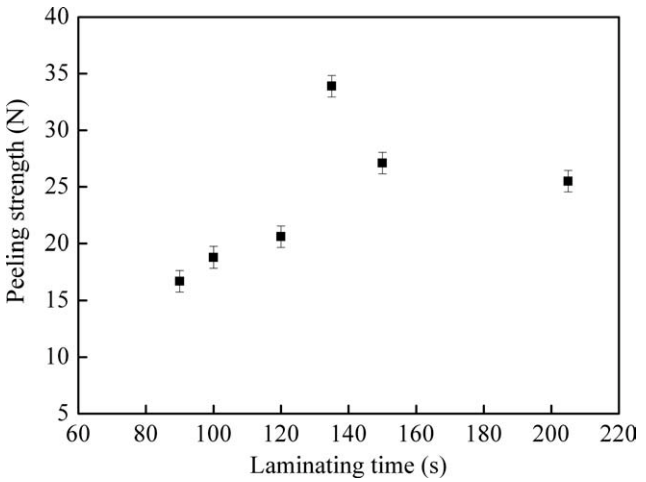


Figure 9 Effect of laminating time on peeling strength at constant laminating pressure (2 kg cm^{-2}) and temperature (150°C).

penetrated into fabrics to make the laminate layer thinner. The higher the temperature, the lower the viscosity of the polyurethane, this makes it easier to penetrate into the fabrics. Also the content of the polyurethane penetrated into the fabrics increases with time elongated.

CONCLUSIONS

A hydroxyl-terminated unsaturated aliphatic polyester, poly(FA-*co*-DEG), was prepared by melt polycondensation of FA and DEG. Its enzymatic degradation and crosslinking behavior were investigated to clarify the effect of the crosslinking degree on enzymatic degradation. The unsaturated aliphatic polyester showed biodegradation similar to that of the corresponding saturated aliphatic polyester, even thought it consisted of C=C bonds. However, the biodegradation of unsaturated aliphatic polyester became slower after the crosslinking. There was a tendency that the higher the crosslinking degree, the slower the biodegradation.

A segmented polyurethane was prepared from poly(FA-*co*-DEG), BD, and TDI. Its enzymatic degradation was slower than the original poly(FA-*co*-DEG), because the segmented polyurethane had higher molecular weight to attain increased intra- and intermolecular entanglements and its urethane bonds were not cleaved by the lipase.

The peeling strength of the polyurethane revealed good adhesion of the polymer to fabrics. The adhesion property was affected by laminating pressure, time, and temperature, because the C=C bonds were allowed to crosslink to increase the cohesive interaction of the polyurethane.

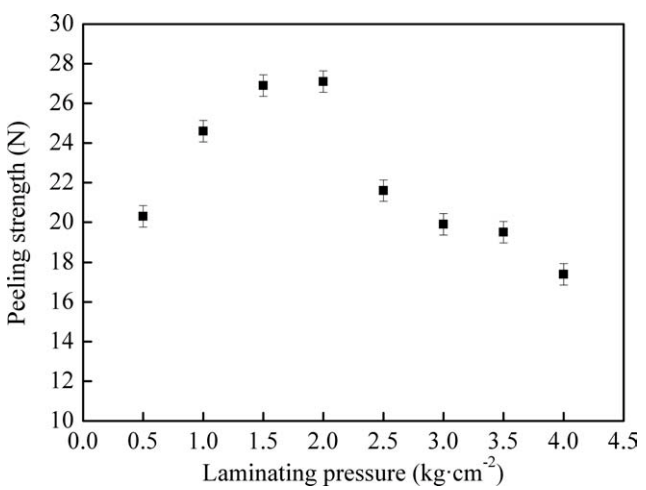


Figure 8 Effect of laminating pressure on peeling strength (laminating time was 150 s at 150°C).

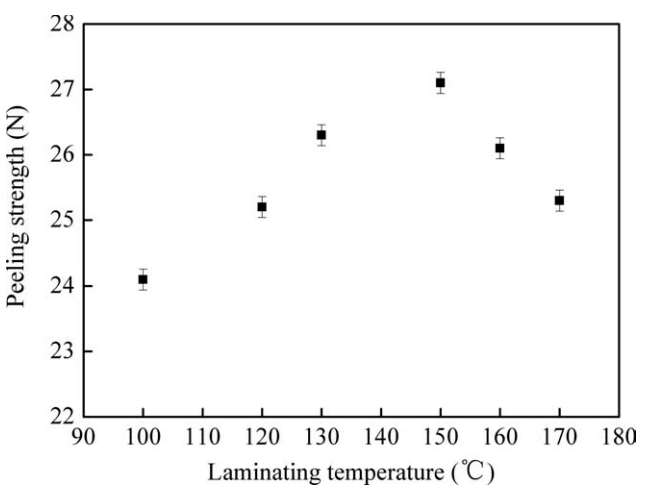


Figure 10 Effect of laminating temperatures on peeling strength at constant laminating pressure (2 kg cm^{-2}) and time (150 s).

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