Effect of Hydrophilicity on the Biodegradability of Polyesteramides

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ABSTRACT: The effect of surface hydrophilicity was induced from the amide units in the polyesteramide. The surface energies and compositions of the polyesteramides were studied by employing contact angle and interfacial tension measurements and ESCA analysis. Biodegradability was evaluated form various methods including activated sludge test, enzyme hydrolysis, and soil burial test, which determine the amount of evolved CO_2, weight loss, and TOC values, respectively. It was found that the introduction of amide groups to the aliphatic polyester improved the biodegradability, although the increase of biodegradation rate was not directly proportional to the amide content. The biodegradability of aliphatic polyesters increased with the addition of amide functionality. Therefore, it can be concluded that the addition of appropriate contents of hydrophile enhanced the biodegradability of aliphatic polyesters as well as their physical properties. Also, the experimental results revealed the relation between hydrophilicity and biodegradability of polyesteramides. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2708–2714, 2003

Key words: biodegradable; copolymerization; hydrophilic polymers

INTRODUCTION

Recently there has been growing interest in developing biodegradable polymers as a solution to the problems of plastics waste. In general, polyesters with a low degree of crystallinity, low molecular weight, and low T_g are susceptible to biodegradation. However, these features have adverse effects on the performances of polymers.[1–3]

Most of the micro-organisms and enzymes are active in humid conditions, and therefore, the surface moisture is an important factor in biodegradation.[4] Hydrophilicity promotes the enzymatic degradation due to the abundance of water molecules on the surface. It was reported that proper balance of hydrophobic and hydrophilic characteristics favors the biodegradation.[5–9] Therefore, it would be desirable to establish the relationship between hydrophilicity and biodegradability of the aliphatic polyesters.

The purpose of this study was to elucidate the effect of polymer hydrophilicity in improving biodegradability to suggest the resulting data for the development of new polymer products with improved property and serviceability. For these purposes, polymer hydrophilicity was varied by copolymerizing the amide groups with the biodegradable aliphatic poly-ester. The introduction of amide groups was expected to improve the hydrophilicity of aliphatic polyesters by improving the biodegradability and to increase serviceability at the same time. The first step of the study was to estimate the surface hydrophilicity by measuring surface energy and ESCA. The second step was to evaluate the biodegradability employing activated sludge test, enzyme hydrolysis, and soil burial test. From these tests, the amount of CO_2 evolved, the amount of TOC soluble, and weight losses were measured. Also, surface changes and fungi growths were observed through the optical and scanning electron microscopy.

EXPERIMENTAL

Sample preparation

The amide group was introduced by adding 1,4-butanediamine when adipic acid or sebacic acid was polymerized with 1,4-butanediol. The G.P grades of adipic acid, sebacic acid, 1,4-butane diol, and 1,4-butane diamine (Junsei Chemical) were used without purification.

To regulate the higher reactivity of diamine to acid than that of diol, amide salts were first synthesized with adipic acid or sebacic acid and 1,4-butanediamine in isopropyl alcohol solution at 0°C under nitrogen atmosphere for 2 h. Assuming 100% trimers, mol ratios of butane diamine/butane diol were 100/0, 95/5, 90/10, 85/15, 80/20, and 70/30. After adding 0.5

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TABLE I
Characterization of PBAD and PBSE Series

Identification	Feed composition Diol/Diamine	Real composition Amide contents (%)[a]
PBAD	100/0	0
PBAD5	95/5	5.77
PBAD10	90/10	13.07
PBAD15	85/15	17.74
PBAD20	80/20	26.55
PBAD30	70/30	37.4
PBSE	100/0	0
PBSE5	95/5	7.66
PBSE10	90/10	16.04
PBSE15	85/15	26.16
PBSE20	80/20	34.13
PBSE30	70/30	45.30

[a] Calculated from ^{1}H-NMR spectrometry in trifluoroacetic acid.

wt % titanium butoxide (Aldrich) as a catalyst and premixing at 30°C for 30 min esterification was carried out at 190°C under nitrogen atmosphere for 2 h. Polycondensation was performed at 240°C under high vacuum for 5–8 h.

The obtained copolymer composition was confirmed using 400 MHz ^{1}H-NMR(Bruker) after the sample were dissolved in deuterated trifluoroacetic acid. Table I shows the real composition, feed composition of PBAD, and PBSE series. The real compositions calculated from ^{1}H-NMR area ratio, have higher amide content than feed compositions because of the higher reactivity of the diamine.

The polymer was compression molded to the film of 0.5–0.6-mm thickness between Teflon sheets.

Enzyme

The enzyme used for biodegradation study was "lipolase 100L" (NOVO Co.), which is a lipase obtained from *Aspergillus oryzea*.

EXPERIMENTAL METHODS

Measurement of interfacial tension

FACE surface tensionometer (model CBVP-A3) was used to measure the surface tension of polymer films in water and methylene iodide. The measurements were made at 20 ± 2°C and 65 ± 10%, and more than 10 measurements for one sample was done and averaged.

Measurement of contact angle

The film was washed for 5 min in ultrasonic washer in a detergent solution and rinsed with distilled water and dried at room temperature in a vacuum oven until a constant weight was achieved. The contact angles

were measured using a FACE contact anglemeter (model CA-DT · A) at 20 ± 2°C and 65 ± 10% R.H. by the sessile drop method. The contact angles of liquid drops in contact with each film were measured at 10 different places and the values were averaged.

ESCA (electron spectroscopy for chemical analysis)

Using the ESCA analyzer, ARIESARSC 10MCD 150 (VSW, England), the chemical compositions (C, O, and N) of the sample surface was analyzed. As an X-ray source, Anode Mg (1253.6 eV) and A l(1486.6 eV) were used, Ar ion was sputtered on the sample surface for about 30 s at the pressure of 10–10 Torr.

Measurement of moisture absorption

The samples were cut into the size of 4 × 4 cm and were dried in a vacuum oven at 20°C for 48 h, and the dry weight was measured. The wet weight was measured after exposing the sample at 20 ± 2°C, 75 ± 2% R.H. for 48 h. The amount of moisture absorbed on the sample was determined by the weight gain.

Evaluation of biodegradability

Carbon dioxide evolution test

Relative biodegradability was calculated from the ratio of the actual amount of carbon dioxide evolved to the theoretical amount of carbon dioxide to be evolved, according to ASTM D 5209-92.[10]

Enzymatic degradation

Polymer specimen (25 mg) and 2 mL of phosphate buffer (KH$_2$PO$_4$/NaHPO$_4$, pH 7.00) were placed into a test tube and 10,000 LU (lipase unit) of lipase was added. After degradation to run in the mixture in an incubator at 37°C for a while, the mixture was filtered through a membrane of 0.2°C thick and TOC (total organic carbon) dissolved in the filtrate was measured.[11]

Soil burial test

Natural soil was filled in a box 13 cm in depth. Each sample was cut into the same size and buried in the soil in 3 cm depth and was allowed to degrade for 46 days. During the degradation period, water was supplied at a regular interval.[12]

Degree of biodegradability through weight loss

After the soil burial test, biodegradability was measured through weight loss: weight loss (%) = [(A−Rs)/A} × 100; whee A is the sample weight

before degradation, and *Rs* is the sample weight after degradation.

Observation of surface appearance change

Changes in the appearance of sample surfaces were observed before and after biodegradation using an optical microscope (OLYMPUS, EHS204752) magnified by 100× and scanning electron microscopes (ESM, JEOL, JSM-840A) magnified by 1000×.

RESULTS AND DISCUSSION

Surface hydrophilicity

Figure 1 shows the total surface energy and its polar force component of the polymer film estimated from the surface tension and the contact angle measurements. Although the total surface energy and the polar
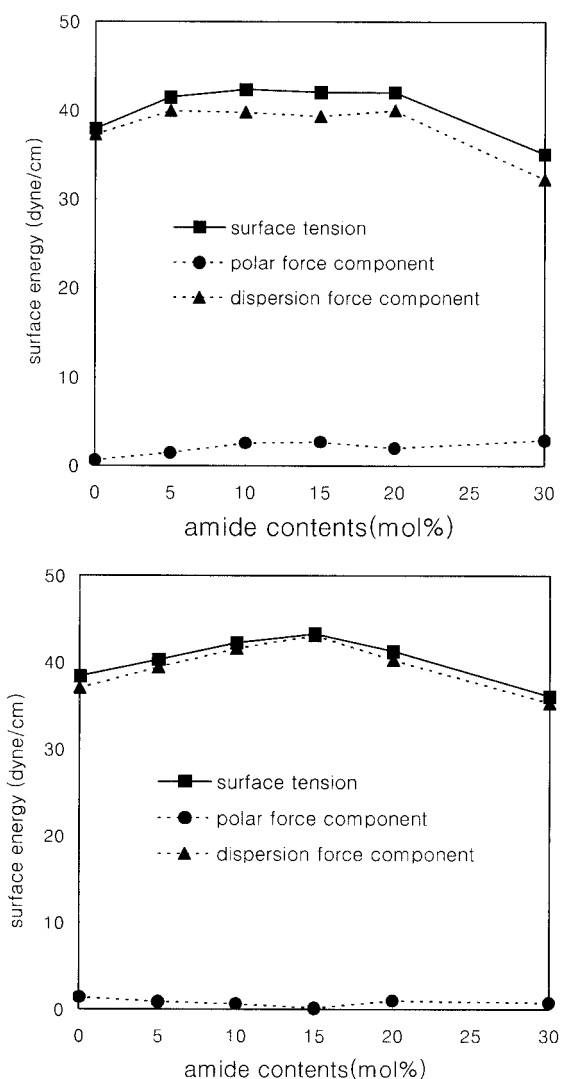

Figure 1 Surface energies of PBAD and PBSE containing various degrees of amide groups.

TABLE II
C, N, O Contents in PBAD Series by ESCA

	PBAD	PBAD5	PBAD10	PBAD15	PBAD20	PBAD30
C	64.32	66.39	72.45	69.64	69.90	77.47
N	0	0	3.25	3.09	1.49	2.29
O	23.44	26.99	21.58	24.45	25.34	16.89

farce component increased with the introduction of amide groups as expected, the increase was not directly proportional to the amide content. It can be seen that the surface energy reached at the highest value for PBAD20, but further increase of amide content resulted in an adverse effect. In the PBSE series, the surface energy maximum arrived at 10% of amide content.

ESCA analysis

Because it was shown that surface energy did not increase in proportion to the amide group content, the chemical composition on the film surface was analyzed through ESCA. Table 2 shows the relative chemical composition of the PBAD surfaces. Nitrogen was detected from the samples containing amide groups, but the nitrogen contents were not directly proportional to the amide contents.

From these results, it was shown that the surface energy and the nitrogen content increased with the introduction of the amide groups up to a certain level of content and then decreased. However, there was a close relationship between the surface energy and the nitrogen content.

It was also revealed that the amide contents from ESCA analysis were quite smaller than the real amide contents in Table I. These phenomena suggested that the surface structure of the polymer may not be the same as the internal structure and the surface structure could possibly change according to the outside circumstances. There is a tendency for polar groups not to appear on the surface to minimize the free energy of polymers. Internal entropy gets larger as polar groups arrange inwards to result in a stable state due to decreased overall free energy. Thus, surface becomes less polar compared with the composition of the bulk polymer in many cases.[13] Especially, because the film used in this study was cast in contact with the polytetrafluoroethylene plate, it is quite possible that the polar groups would rearrange internally.[14]

Moreover, when more than two components are mixed or copolymerized, different components tend to separate, and this phenomenon is called "phase separation."[14] From the aspect of surface energy, the tendency to lower surface energy is stronger for the block copolymers because the contribution of the hydrophobic component to surface energy is larger in

TABLE III
Moisture Regain of PBAD Series

	PBAD	PBAD5	PBAD10	PBAD15	PBAD20	PBAD30
Moisture absorbancy (%)	0.108	0.415	0.508	1.332	0.962	1.206

block copolymers than in random copolymers.[15] It is therefore thought that the possibility of phase separation would enhance as the number of amide group increases and thus the surface energy decreases accordingly.

Change in moisture regain

Moisture regains of the specimens were measured, because moisture accessibility indirectly reflect the presence of hydrophilic groups and degree of crystallinity. As shown in Table III, moisture regains were low in all the specimens with the values under 2% and PBAD15 showed the highest moisture regain, representing a close relationship with the results of surface energy and surface element. It can be thought that the high moisture regain of PBAD30 may have been due to a high content of hydrophilic groups inside the polymer even though they are expected to have higher crystallinity.

Biodegradability

Biodegradability from the activated sludge test

Figure 2 shows the biodegradability estimated from the relative amount of CO_2 evolved during the activated sludge test. Among the PBAD series, biodegradability was the highest for PBAD20 and the biodegradability of PBAD30 was lower than that of PBAD homopolymer. Compared with the surface energy, the sample with higher surface energy showed faster degradability, suggesting a close relationship between surface energy and biodegradability. In the case of PBSE series, a high biodegradability was shown for the sample with the amide contents of 5 and 10%, suggesting also the tendency of a high degradability in samples with high surface energy.

  PBSE showed a slower degradation rate, probably due to the fact that PBSE involves less ester bonding that undergoes partial hydrolysis, and the carbon chain length of sebacic acid in PBSE is longer than that of adipic acid in PBAD, resulting in more hydrophobicity. This phenomenon also can be seen in Nagata's study on the degradability of aliphatic polyesters, which consist of 2–12 carbons in the main chain. He reported that the degradability of the aliphatic polyesters decreased with the increase of carbon chain length due to the reduced hydrophilicity.[7]

Change in appearance after decaying in the activated sludge

Figure 3 shows microscopic photographs of the PBAD film surfaces after degradation for 50 days in the activated sludge. We can see that cracks formed to result in an irregular surface, and fungi grew on the surface and the color turned brown. Degradation occurred most severely in PBAD20, and the film thickness also decreased significantly with many parts torn off. The degradation rate was slower in PBSE compared with PBAD so that the film change was not significant, with
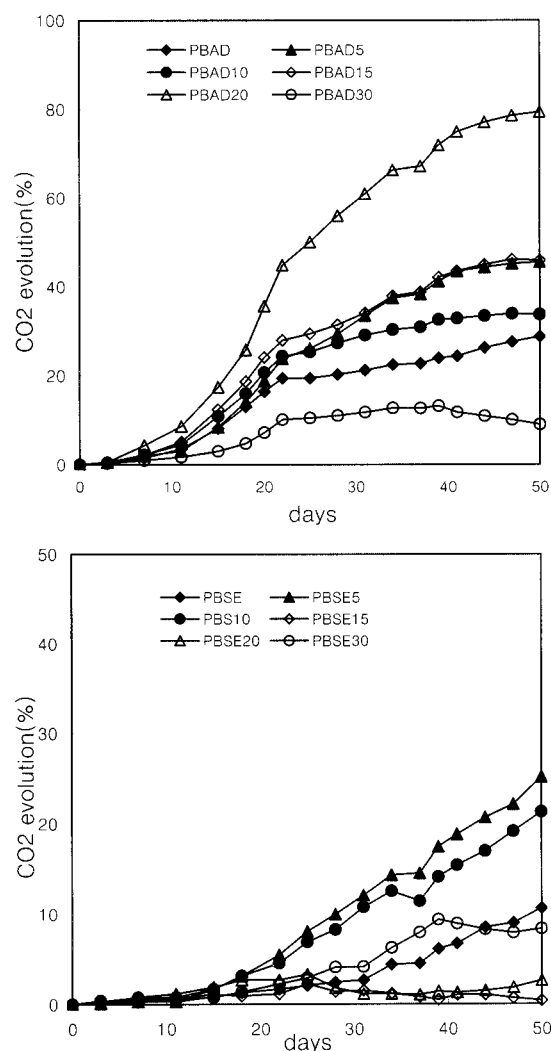

Figure 2 Biodegradabilities of PBAD and PBSE series determined from the amount of carbon dioxide evolved by the activated sludge test (at 37°C, p H 7).
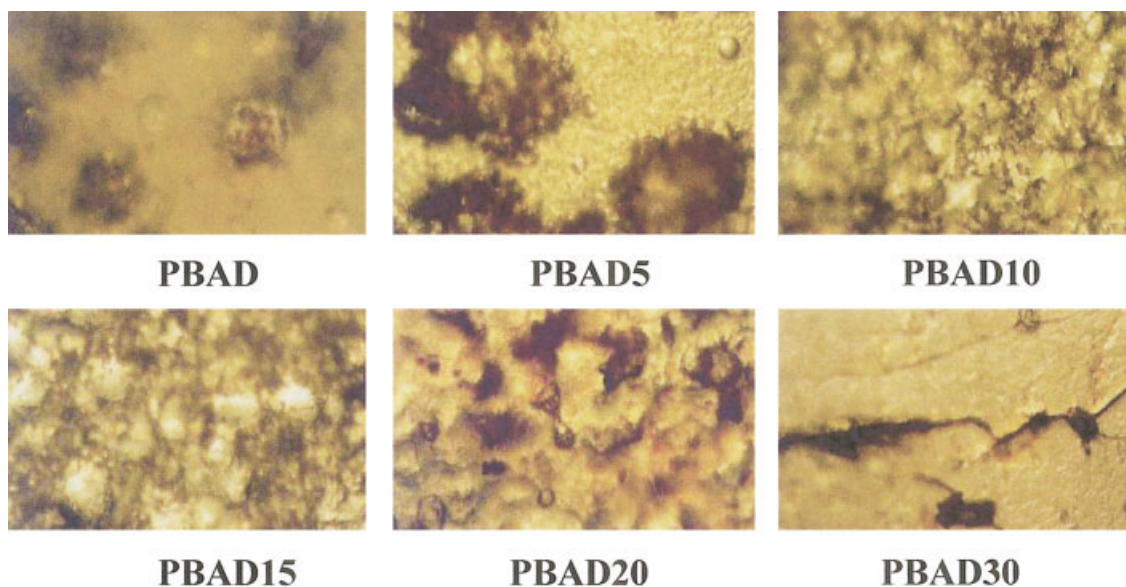
Figure 3   Micrographs of decomposed PBAD series films in activated sludge test (×100).

almost no part torn off after degradation. In the PBSE series, PBSE5 and PBSE10 changed in appearance most remarkably.

Figure 4 represents SEM photographs (×1000) of the surfaces of the PBAD and PBSE series after degradation in the activated sludge, where more detailed structures can be seen. The PBAD20 and PBSE5 samples with high degradation rates showed the severe damage with many holes formed on the surface, whereas the PBAD and PBSE samples showed little damage with a few microorganisms attached.

One interesting point is the phenomenon of film cracking in both the PBAD and PBSE containing 30% amide groups. Although almost no fungi were formed, deep cracks were formed or the films were broken into pieces, suggesting that the process of degradation in these samples was different compared with other samples. It is thought that when the samples contained about 30% amide groups, the crystalline region became denser due to the increased H-bonding, and phase separation could have occurred between crystalline and amorphous regions. This could have resulted in the degradation region and crystalline region being separated, forming spaces for cracks to occur easily. Thus, the degradability decreased beyond certain amount of amide groups due to the phase separation, because moisture could not penetrate into the dense crystalline phase.
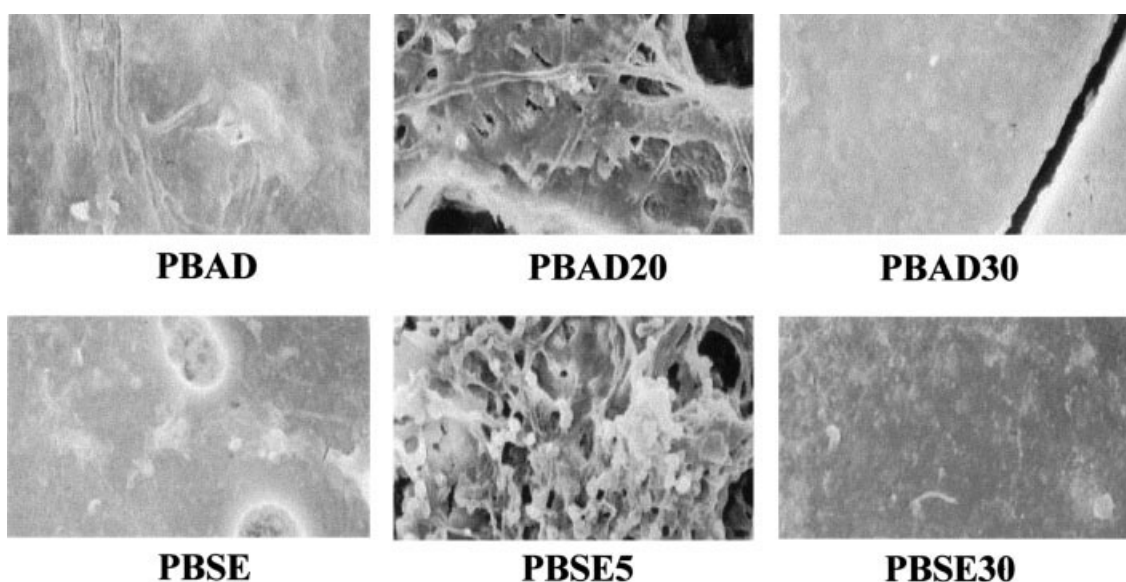

Figure 4   Scanning electron microphotographs of decomposed PBAD and PBSE series in activated sludge test (×1000).

Biodegradability from the enzyme hydrolysis

Figure 5 represents the amounts of TOC obtained after degradation with lipase for 46 h. The total amounts of organic carbon produced from the degradation of the PBAD series were usually larger than 1500 ppm, but those of the PBSE series were significantly smaller, suggesting slower rates of degradation. It was shown that TOC was the highest in PBAD20 among the PBAD series and in PBSE5 among the PBSE series, indicating a similar tendency with the result from the amount of CO_2 evolved but faster degradation.

Biodegradability from soil burial test

Figure 6 shows the weight loss rate of the specimens buried in natural soil for 50 days. Compared with the weight loss of up to 60% in the activated sludge for 50 days, the weight loss was all under 6% in soil, indicating the fact that degradation due to soil is significantly lower but showing the similar tendency. Thus, it was confirmed from three different evaluation methods that biodegradability was improved when aliphatic polyester contained amide groups but not directly proportional to the amide group content, and was generally high in the samples with large surface energy, i.e., high hydrophilicity.

Micro-organisms including the bacteria, microbes, and fungi are known to secrete enzymes to degrade polymers. In the biodegradation process, micro-organisms use enzymes near the polymer surface and enzymes usually cause degradation on the polymer surface because it is not easy for them to penetrate into the internal part of polymer.[27] Thus, the chemical composition of the surface is expected to be a very important factor in biodegradation. Furthermore, the increased surface hydrophilicity is thought to be a favorable factor, which can facilitate expansion of the
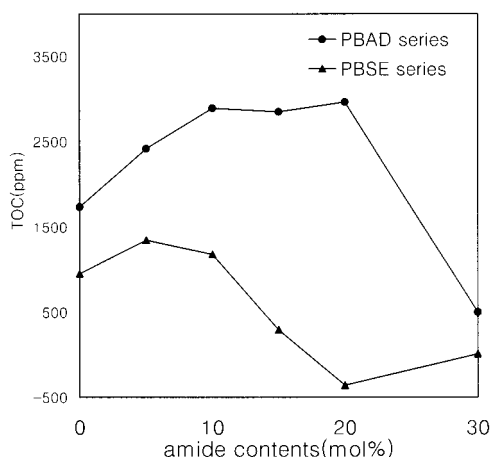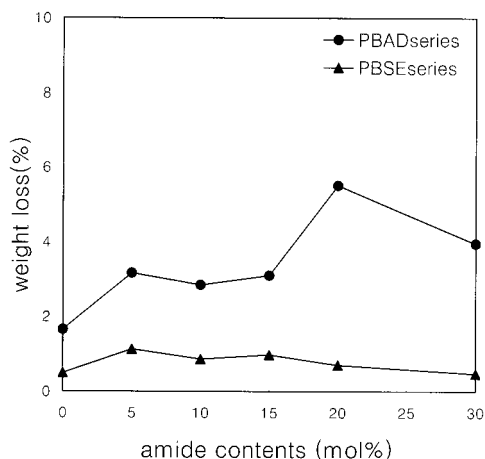
Figure 6 Weight loss of PBAD, PBSE series by the soil burial (burial time: 50 days).

film by moisture and promote hydrolysis process. Therefore, it is believed that the physiochemical characteristics of the surface where micro-organisms and moisture access determines the biodegradability.

CONCLUSIONS

Among the various factors affecting biodegradability, we focused on the effect of surface hydrophilicity of the polymer on the biodegradability in this study. For this purpose, polymer hydrophilicity was varied by copolymerizing the biodegradable aliphatic polyesters with amide groups. The introduction of amide group was expected to improve biodegradability through easier accessability of water molecules as well as to enhance durability by making hydrogen bonding possible. Surface energy and the amount of nitrogen on the surface increased with the addition of the amide group, but decreased beyond a certain level. The increase was seen with the addition of the amide group up to 20% in the PBAD series, and with the addition of the amide group up to 10% in the PBSE series. Biodegradability increased with the introduction of amide groups between 10–20%, probably due to the decreased regularity of random molecular structure, but beyond this level of amide content biodegradability began to decrease with changed molecular structure. Those samples with high biodegradability also showed severe damage and fungi formation on the surface. The samples containing highest levels of the amide group such as PBAD30, PBSE20, and PBSE30 showed very low biodegradability but showed deep cracks on the films. Our results suggest that biodegradability has a close relationship with surface hydrophilicity, and the presence of moisture is a favorable condition in biodegradability. Because biodegradation of polymers progresses mainly with hydrolysis by the enzyme action and thus surface hydrophilicity,

Figure 5 TOC (total organic carbon) of water-soluble components produced by enzymatic hydrolysis for 46 h (at 37°C, pH 7).

which affects moisture accessibility, it will become an important factor in biodegradation.

References

1. Park, Y. H. J Korean Fiber Soc 1991, 28, 9.
2. Kim, I. B.; Lee, M. C.; Seo, I. S.; Shin, P. K. Polymer (Korea) 1995, 19, 727.
3. Doi, Y.; Fukuda, K. Biodegradable Plastics and Polymers; Elsevier: New York, 1994.
4. Domb, A. J.; Kost, J.; Wiseman, D. M. Handbook of Biodegradable Polymers; 1998, p. 451.
5. Bitritto, M. M.; Bell, J. P.; Brenckle, J. M.; Huang, S. J. J Appl Polym Sci Appl Polym Symp 1979, 35, 405.
6. Sawhney, A. S.; Hubbell, J. A. J Biomed Mater Res xxxx, 24, 1397.
7. Nagata, M.; Kiyotsukyri, T. Eur Polym J 1994, 30, 1277.
8. Nagata, M. Marcromol Rapid Commun 1996, 17, 483.
9. Park, M. W. ; Kim, J. h.; Song, S. K. J Korean Fiber Soc 1996, 33, 790.
10. ASTM Standard Test Method D 5209-91. Standard test method for determining the asrobic biodegradation of plastic materials in the presence of municiple sewage sludge.
11. Maeda, Y.; Nakayama, A.; Kawasaki, N.; Hayashi, K.; Aiba, S.; Yamamoto, N. Polym J 1997, 29, 836.
12. AATCC Technical Method 30-1993. Antifungal Activity, Assessment on Textile Materials : Mildew and Rot Resistance of Textile Materials.
13. Yoshido, A. Science of Surface; Kyum Ji Sa, 1996.
14. Yosomiya, R.; Morimoto, K.; Nakajima, A.; Ikada, Y.; Suzuki, T. Adhesion and Bonding in Composite; Marcel Dekker Inc.: New York, 1990, p. 42.
15. Hamid, S. H.; Amin, M. B.; Maadhah, A. G. Handbook of Polymer Degradation; Dekker: New York, 1992, p. 224.