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Study on the Synthesis and Biodegradation of Aliphatic Polyester

Chang Ying ZHU[1]*, Xiao Di KOU[1], Zhi Qiang ZHANG[1], Ying Cai YOU[1], Diao Hu Xin[2]

[1]Department of chemistry, Nankai University,
[2]Department of Micro-organism, Nankai University, Tianjin 300071

Abstract: An aliphatic polyester, poly(hexalene adipate) (PHA) and an aliphatic copolyester, poly (hexalene adipate succinate) (PHAS) were synthesized by direct condensation of corresponding binary acid and binary alcohol in the presence of a catalyst, p-toluene sulfonic acid. The biodegradation of these polyesters were studied in the laboratory by enzyme attack and outdoor soil burial. The results show that these polyesters have good biodegradability and the copolyester PHAS, even displayed a better biodegradability than the polyester PHA. In the presence of *Penicillium chrysogenum* the weight loss reached 18.3% for the PHAS (film thickness 1.0 mm) and 9.1% for the PHA (film thickness 1.0 mm) after 28 days. Outdoor soil burial tests indicate that these polyesters also have good biodegradability in natural conditions. The weight loss reached 14.2% for PHAS (film thickness 0.1 mm) and 6.7% for PHA (film thickness 0.1mm) after burying in soil for 36 days.

Keywords: Poly (hexalene adipate), poly (hexalene adipate succinate), biodegradation.

With the increasing use of one-off plastic products, the environmental pollution resulted from the plastic waste has become more and more serious. So many scientists have focused their attention on developing biodegradable polymers to substitute the traditional unbiodegradable polymers in the manufacture of disposable products. Thus the plastic waste can be treated by landfill or composting technique. It has been found that aliphatic polyesters possess better biodegradability compared with other synthetic polymers. Their biodegradability very much depends on the structure and molecular weight of the polyester[1,2]. Many investigations have been conducted to use aliphatic polyester to prepare ester-starch composite[3,4]. Some reports also have been found to use aliphatic polyester alone to make plastic materials[5,6]. Some scientists have predicted that the aliphatic polyesters and the blend of starch with them are the most promising biodegradable materials in the future[7].

In this paper, an aliphatic polyester, poly (hexalene adipate) (PHA) and an aliphatic copolyester, poly (hexalene adipate succinate) (PHAS) were synthesized by direct condensation of corresponding binary acid and binary alcohol. The biodegradation in the laboratory and in outdoor soil burial was studied.

Experimental

PHA was synthesized from equivalent moles of 1,6-hexandiol and adipic acid in the

presence of 0.4 mol% *p*-toluene sulfonic acid under nitrogen atmosphere. Xylene was used as a solvent and water removing agent. PHAS was synthesized from 1,6-hexandiol, adipic acid and succinic acid. The mole ratio of them was 1:0.5:0.5. Other conditions were the same as in the case of PHA. The molecular weight (Mn) of the polyesters were determined by the titration of standard KOH ethanol solution and calculated as follows:

$$Mn=W/(C\times V)$$

where W refers to the weight of polyester. C and V refer to the mole concentration and volume of the used KOH solution. The reaction extent (P) was calculated according to the following equation :

$$P=1-1/Xn$$

where Xn refers to the degree of polymerization. The biodegradation tests in the laboratory were carried out with polyester films of 1 mm thickness by *ca*. 0.5 g in weight. Each film was exposed to an aerated liquid medium at 37°C. The medium was either composed of 100 ml H_2O, NaCl, beef extract, peptone, and *Staphylococcus aureus* or 100 ml boiled potato-water solution, NaCl and *Penicillium chrysogenum*. The pH of the media was adjusted to the value of 7. The biodegradation of outdoor tests was carried out by burying the films into natural soil under 20 cm depth.

Results and Discussion

Table 1 shows the relationship of molecular weight (Mn) and reaction extent (P) with reaction time for the polycondensation of 1,6-hexandiol with adipic acid and **Table 2** shows the same relationship for the copolycondensation of 1,6-hexandiol with adipic acid and succinic acid in the presence of *p*-toluene sulfonic acid. Examination of **Table 1** and **Table 2** indicates that these two polycondensation reactions have similar reaction rate. P reached 0.994 after 30 h for both reactions. Although the p of copolycondensation approached to 0.995 when the reaction time further increased to 35 h, while the P of the polycondensation remained unchanged with the increase of the time, both of them reached reaction equilibriums at 35 h and 30 h respectively. Then Mn and P remained unchanged with the increase of reaction time. This means that the by product H_2O was not be able to be further removed by xylene.

Table 1 Dependence of molecular weight(Mn) and reaction extent(P) on reaction time of PHA

Time(h)	2	5	10	15	20	25	30	35
Mn	1128	6121	9320	12390	15830	19160	20020	20030
Xn	9.80	53.6	81.8	109	139	168	176	176
P	0.898	0.981	0.988	0.991	0.993	0.994	0.994	0.994

Table 2 Dependence of molecular weight(Mn) and reaction extent(P) on reaction time of PHAS

Time(h)	2	5	10	15	20	25	30	35	40
Mn	828	6275	8895	11890	14150	17090	19130	20160	20360
Xn	7.60	57.4	81.4	109	129	156	175	184	186
P	0.868	0.983	0.988	0.991	0.992	0.994	0.994	0.995	0.995

Figure 1 is the biodegradation results of PHA (Mn 20,125) in the presence of *Staphylococcus aurous* and *Penicillium chrysogenum*urve. *Staphylococcus aurous* and *Penicillium chrysogenum*urve can produce esterases during their growth. Esterases are effective catalysts of the degradation of the aliphatic polyesters. As can be seen, *Penicillium chrysogenum* demonstrated a better catalysis effect on the degradation of the polyester. The weight loss reached 9.1% after 28 days, whereas in the case of *staphylococcus aurous*, the weight loss was only 2.2% after 35 days.

Figure 1 Weight loss of PHA (1.0mm thickness) in the presence of *Penicillium chrysogenum and Staphylococcus aurous*

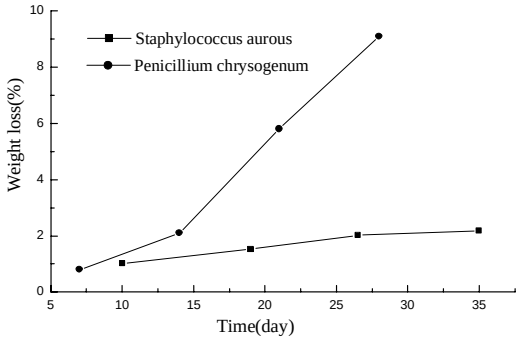


Figure 2 shows the difference of the biodegradability between PHA and PHAS. In the presence of *Penicillium chrysogenum*, PHAS displayed a weight loss of 18.3% after 28 days, while PHA only achieved a weight loss of 9.1% in the same time period. This suggests that the copolyester has a good microbial accessibility. This is because the corporation of a third monomer unit changed the regularity of the molecule of polyester and thus decreased the degree of crystallization, so it is more easily attacked by the microbe.

Figure 2 Weight loss of PHA (1.0mm thickness) and PHAS (1.0mm thickness) in the presence of *Penicillium chrysogenum*

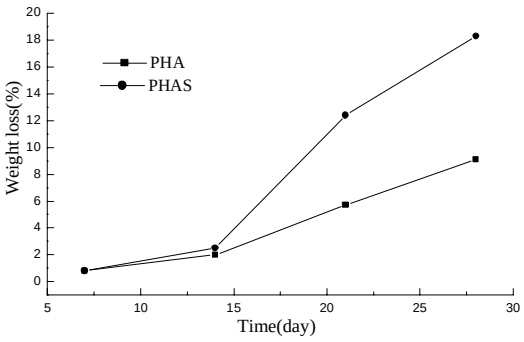
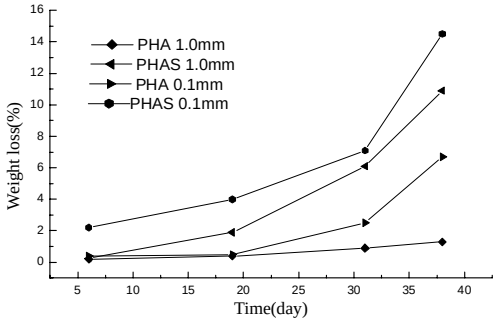


Figure 3 shows the results of the biodegradation in outdoor soil burial. The temperature of the weather was 15-20^{o}C during the experiments. From **Figure 3** one

can see that in the natural soil condition, both the polyester and the copolyester showed good biodegradability. Again the copolyester PHAS displayed a better biodegradability than the polyester PHA. The biodegradation rate also depends on the thickness of the film. When the films were 0.1 mm in thickness, the weight loss of PHA and PHAS reached 6.7% and 14.2% after 38 days, while when the thickness of the films was 1 mm, the weight loss was 1.3% and 11% respectively. These results further suggest that the addition of a third monomer in the synthesis of polyester can improve its biodegradability to a great extent.

Figure 3 Weight loss of PHA and PHAS in soil burial



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