Morphology and Thermal Behavior of PP/EHDPET Blend Fibers by Alkaline Hydrolysis Treatment

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ABSTRACT: Polypropylene superfine fibers or cell porous fibers were prepared from the Bi-component blend fibers of polypropylene/easy hydrolytic degradation polyester (PP/EHDPET) by alkaline hydrolysis process. EHDPET is a kind of copolyester that can be rapidly hydro-degraded in the hot alkaline solution. This article discusses the kinetics of alkaline hydrolysis of EHDPET, and the effect of catalyst, bulk ratio, and the content of PP-grafted maleic anhydride on the alkaline hydrolysis process. Meanwhile, the morphological change of the outer surface of blend fibers during this process was also investigated by the technology of scanning electron microscope. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 3010–3014, 2000

Key words: polypropylene (PP); easy hydrolytic degradation polyester (EHDPET); blend fibers; alkaline hydrolysis

INTRODUCTION

The blend fibers with the sea-island (or matrix-fibril) morphological structure are usually obtained by the method of blend spinning of two immiscible polymers. Adjusting the parameters, such as composition, viscosity ratio, and elasticity ratio as well as process conditions during mixing, the two components can form the sea phase, or island phase, respectively.[1–3] If the sea phase (or island phase) is dissoluble, some correspondent dissolution processes will traverse the blend fibers into superfine fibers (or cell porous fibers) with high add-in value.

Polyesters (PET), and copolyester dyed by the cationic dye (CDP) can be degraded in alkaline solution.[4–7] Recent studies[8–9] synthesized a new type of copolyester, easy hydrolytic degradation polyester (EHDPET). EHDPET can rapidly dissolve in the hot alkaline solution with much higher hydrolysis rate than that of PET or CDP. Via the method of composite spinning or blending spinning, the expectant PET, polyamide (PA), or polypropylene (PP) superfine fibers or porous fibers will be made from the blends of EHDPET and general PET, PA, or PP during the alkaline hydrolysis process.

In the hydrolysis process, weight loss ratio of blend fibers is one of the main parameters, which can be a character of hydrolysis degree. In this article, we discuss the kinetics of alkaline hydrolysis of EHDPET, the thermal behavior and the morphological property of PP/EHDPET blend fibers during the hydrolysis process. Meanwhile, the relationships between the weight loss ratio and the catalyst, the bulk ratio, and the content of PP-grafted maleic anhydride (PP-*g*-MAH) on the alkaline hydrolysis process were also investigated.

EXPERIMENTAL

Materials

PP chips, a commercial product with melt flow index 35g/min (2.16 kg, 230°C), were obtained from Yanshan Petrochemical Corp. EHDPET chips were synthesized by Tianjin Petrochemical Corp. with intrinsic viscosity number η of 0.467, melt point T_m of 235.4°C, respectively. PET chips and CDP chips were obtained from Huayan Corp. Ltd. of Wuxi.

PP-*g*-MAH was obtained from the Beijing Institute of Chemical Engineering. Interface active agent SN, the trademark of $[R_{12-16}$ N $(CH3)_2$ $C_2H_5OH]NO_3$, was supported by Shanghai Finish Oil Factory.

Preparative Procedure

PET, CDP, EHDPET fibers as well as PP/EHD-PET blend fibers with different composition, were spun at 250–300°C through a single-hole tube-in-orifice type spinneret. The outer and inner diameters of the spinneret were 10 mm and 8 mm, respectively. The as-spun hollow fibers were stretched at room temperature, and the stretching ratio was 6.

Alkaline Hydrolysis Process

The stretched PP/EHDPET blend fibers were immersed in the $0.5M$ NaOH-H_2O solution for some time with stirring, which contains 0.5% (wt) SN (interface active agent). Weight loss ratio is calculated according to the following formula:

$$w\% = \frac{w_0 - w_1}{w_0} \times 100\% \qquad (1)$$

where w % = weight loss ratio; w_0 = the original weight of fibers, g; and w_1 = the weight of fibers treated by the alkaline process, g.

Scanning Electronic Microscopy (SEM)

The morphology of PP/EHDPET blend fibers was investigated by SEM (KYKY AMRAY1000 from Chinese Academy of Science) during the process of alkaline hydrolysis. The accelerated voltage was 5 kV and probe current was 5 mA. Specimens were coated with a thin golden layer before observation.
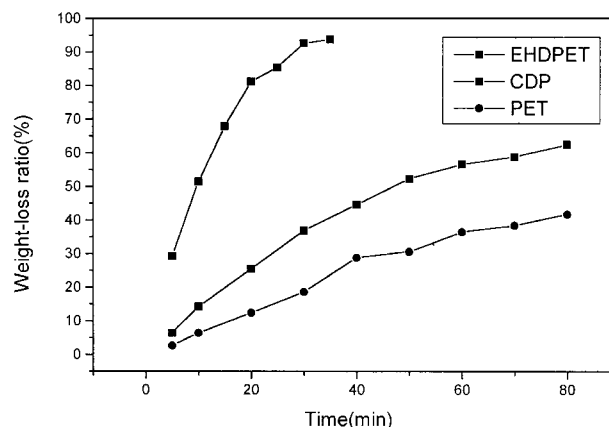

**Figure 1** Different fibers' relationship between weight loss ratio and time.

Differential Scanning Calorimeter (DSC)

DSC measurement was performed with a Perkin-Elmer model DSC-7500. During the thermal treatment and DSC scanning, the specimens were fully protected by dry nitrogen purge gas to prevent oxidation. Samples were rapidly heated from ambient temperature to 280°C at a heating rate of 100°C/min, holding for 3 min to destroy all crystalline nuclei. Then the samples were cooled to 100°C at a cooling rate 20°C/min, and naturally cooled from this temperature to 100°C; the crystallization curves were recorded at the same time. After this, the samples were heated to 280°C at a heating rate of 20°C/min, and the melting curves were recorded.

RESULTS AND DISCUSSIONS

Alkaline Hydrolysis Kinetics of EHDPET

The alkaline hydrolysis rates of PET, CDP, and EHDPET fibers are shown in Figure 1. Generally, the alkaline hydrolysis process of PET fibers are described as follows:

$$(2)$$
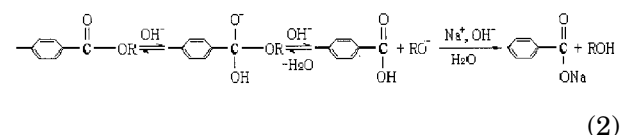
The process can be divided into two steps. The first step is the nucleophilic addition reaction. Carbon atoms in carbonyl groups are attacked by OH— groups. The second step is the elimination reaction. After releasing one H_2O molecule, the
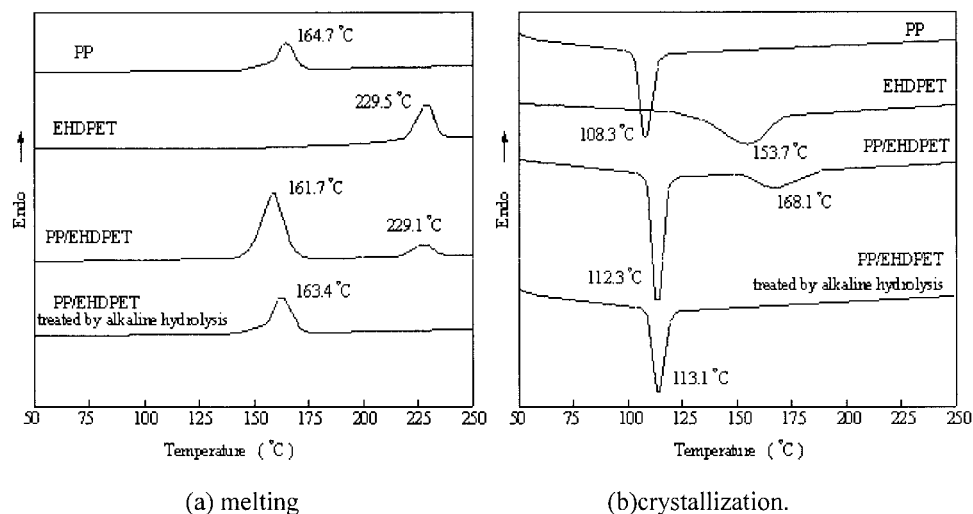
(a) melting   (b)crystallization.

Figure 2 DSC curves of PP/EHDPET blend fibers.

carbonyl bond breaks up to form —C_6H_4COO— and RO— groups, which finally react again with H_2O and NaOH to form —C_6H_4COO— and ROH. In other words, NaOH is only consumed in the counteraction with resultant carboxylic acid.

The hydrolysis rate of the CDP, which is one of sodium 5-sulfoisophthalate–modified PET fibers, is faster than that of PET, demonstrated by Figure 1. It can be explained by the strong electron suction of sulphonate groups in the molecular chains that accelerate the speed of nucleophilic reaction.
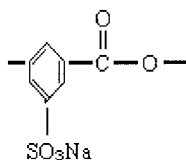
In EHDPET, sulfonate groups as well as other hydrosoluble polymers with low molecular weight were added in the polycondensation process. The active surface areas rapidly increase because of the correspondent function of sulfonate groups and the hydrosoluble polymers that were dissolved into water instantly. So the hydrolysis degree of the EHDPET was much more intense than that of PET or CDP at the same hydrolysis condition.

Thermal Behavior

Figure 2 shows the melting behavior and crystallization behavior of PP, EHDPET, and PP/EHD-

PET blends. In the melting curves of pure PP and EHDPET, pure PP has only a melt peak at 164.7°C, and pure EHDPET has a single melting peak at 229.5°C, as seen from Figure 2(a). The PP/EHDPET blend has two melting peaks corresponding to pure PP and EHDPET and the melting temperatures were 161.7 and 229.1°C, respectively. After treated by alkaline hydrolysis, the blend only left one melting peak of PP component. The cooling cures in Figure 2(b) have similarly changing trends compared with the melting curves. PP has a crystallization peak at 108.3°C, and EHDPET has a crystallization peak at
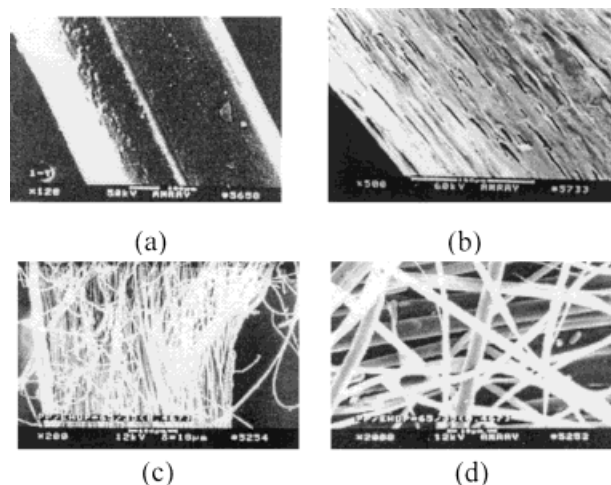

(a)   (b)

(c)   (d)

Figure 3 SEM micrographs of the outer surface of PP/EHDPET blend fibers during alkaline process: (a) untreated; (b) 40 min; (c) 3 h; (d) one part of Figure 1(c).
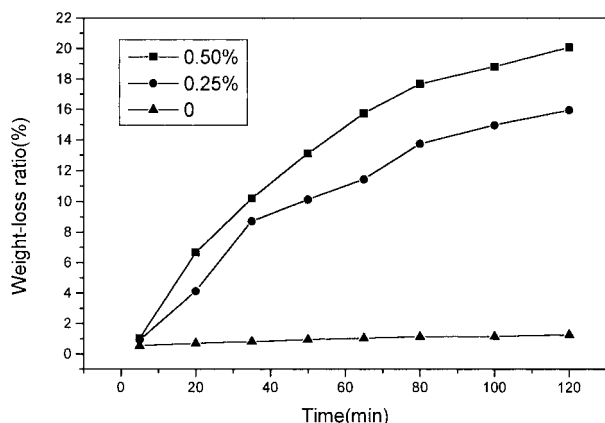
Figure 4 PP/EHDPET (70 : 30, wt %) relationship between catalyst concentration and weight loss ratio.

112.3°C. There was also only one PP crystallization peak left in the blend treated by the hydrolysis process.

Morphology Property of PP/EHDPET by Alkaline Process

There is no practical value to spin EHDPET alone, although it has a high hydrolysis rate. But via the method of composite or blend spinning, then treatment by the alkaline hydrolysis, the blend fibers of EHDPET/PET, PA, or PP can be changed into superfine fibers or porous fibers.

PP/EHDPET blend fibers have a typical sea-island (or so-called matrix-fibril) structure, in which PP is the main component.[9] PP will be as sea, EHDPET as islands or PP as island, EHDPET as sea by adjusting the bulk ratio and viscoelasticity of the blend system. The surface of blend fiber changed greatly during the process of the alkaline hydrolysis. Figure 3 is SEM micrographs of PP/EHDPET (the weight ratio is 65 : 35) treated by the alkaline hydrolysis or not. Observed from these micrographs, the outer surface of the untreated blend is quite smooth. However, many slits appeared in the surface after the alkaline hydrolysis. As the process continued, the hydrolysis degree of blend fibers was intensified. Three hours later, the EHDPET was entirely degraded, and the blend fiber was split into many superfine fibers.

Important Factors Affecting the Alkaline Hydrolysis of Blend Fibers

There were several factors affecting the alkaline hydrolysis of the PET fibers. Increasing the reac-

tion temperature, adding the alkaline concentration, and prolonging the reaction time increased the degraded rate.[4,10] Hereby we mainly discussed the effects due to the concentration of the catalyst, the bulk ratio, and the content percentage of PP-*g*-MAH on the PP/EHDPET blend fibers.

Concentration of Catalyst

The alkaline hydrolysis of EHDPET began from the surface of the above-mentioned fibers observed from the results of the SEM experiment. Hydrophobia PP component decreased the effective area contacted with OH^-, so the catalyst would greatly affect the hydrolytic degradation process of the PP/EHDPET blend fibers, as shown in Figure 4. It indicated that the degraded rate of blends was very slow without SN. With the increase of the concentration of SN, the hydrolysis rate of the blend was increased, and the weight loss was also increased.

There was a balance reaction in the alkaline solution with the existence of catalyst SN (R_4NX represents the molecular formula of the SN):

$$R_4NX + NaOH \leftrightarrow R_4NOH + NaX \qquad (3)$$

With long alkyl chains, R_4NX and R_4NOH would be promptly absorbed on the hydrophobic surface of fibers, and the OH^- groups also were transferred to the surface due to the reaction, then the OH^- groups reacted with the ambient carbonyl groups, which led to the braking of the ester bonds. But when the SN concentration was increased to a certain value, there were no clear effects of the further increase because the absorbency of OH^- had reached the balance state. This phenomenon is illustrated in Figure 4.

Bulk Ratio

The alkaline hydrolysis of EHDPET was a binary diffusion process, during which the reactants in the solution expended into the amorphous regions of the fiber surface; meanwhile the hydrolysis products diffused into the solution from the fiber surface. Among the blend of PP/EHDPET, with the increase of the EHDPET concentration, the hydrolysis rate of the blend increased, and the weight loss ratio also increased which is testified by the results of Figure 5.

To add compatibilizers in the immiscible blend system is one of the popular ways to improve the

mechanical properties and the spinning property of the blends. The polarities of PP and EHDPET are opposite, and their compatibility is relatively poor, so the blend of PP/EHDPET is hard to spin. In this experiment, the spinning property of PP/EHDPET blend was greatly improved by adding PP-*g*-MAH. But the content of PP-*g*-MAH would affect the hydrolysis rate. From Figure 6, it is observed that the hydrolysis rate prevalently decreased after the presence of PP-*g*-MAH in the blend. Also, the more content of PP-*g*-MAH, the lower the hydrolysis rate and the weight loss.

CONCLUSIONS

Compared with PET and CDP, EHDPET has the larger alkaline hydrolysis rate. The alkaline hydrolysis process affected the surfaces of PP/EHDPET blend fibers. Via the method of composite or blend spinning, then treated by the alkaline hydrolysis, the blend fibers of PP/EHDPET can be changed into superfine fibers or porous fibers. Increasing the concentration of catalyst, multi-
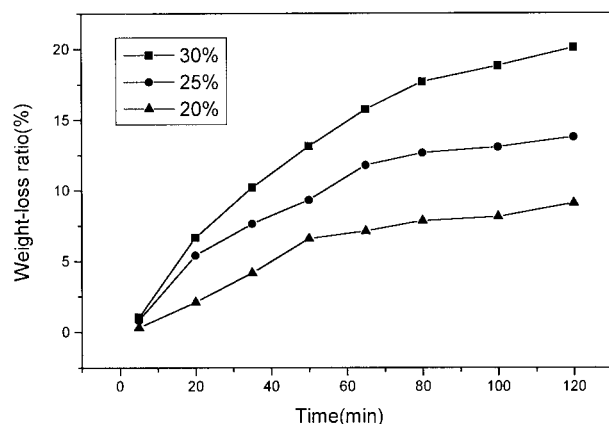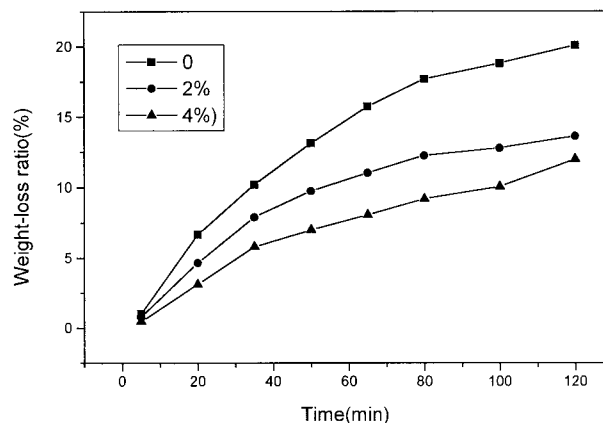

Figure 6 PP/EHDPET (70 : 30, wt %) relationship between content of the PP-*g*-MAH and weight loss ratio.

plying the content of EHDPET, and decreasing the content of the compatibilizer in the blend can all increase the rate of the alkaline hydrolysis.

Figure 5 PP/EHDPET relationship between bulk ratio and weight loss ratio

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