Effects of the Energy Dissipation Rate and Surface Erosion on the Biodegradation of Poly(hydroxybutyrate-*co*-hydroxyvalerate) and Its Blends with Synthetic Polymers in an Aquatic Medium

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ABSTRACT: The anaerobic biodegradation of polymers by soil microorganisms was investigated in shaking flask cultures at different rotation speeds or energy dissipation rates. The polymers included poly(hydroxybutyrate-*co*-hydroxyvalerate) (PHBV), poly(ϵ-caprolactone) (PCL), polystyrene (PS), two binary PHBV/PCL blends (80/20 and 25/75 w/w), and a triple PHBV/PCL/PS blend (76/5/19 w/w/w). The specific degradation rate of PHBV found from the specimen's residual mass fraction with time was constant after a lag phase and was significantly affected by the agitation strength (<0.5 day^{-1} at 60 rpm or lower and >15 day^{-1} at 120 rpm or greater). Tiny polymer fragments were formed on the specimen surface and observed with scanning electron microscopy during degradation. The detachment of those fragments under high hydraulic shear stress caused surface erosion and renewal, resulting in the high degradation rate. The hydraulic shear stress (0.6 Pa) at an energy dissipation rate of 0.5 W/kg was a threshold level, above which the external force did not increase the degradation rate very much. PHBV degradation in the binary blends with compatible PCL was retarded, depending on the blend composition. Blending PHBV with noncompatible PS did not affect PHBV degradation, and the overall degradation rate of the triple blend was faster than the rate of PHBV alone because of the surface erosion of both PHBV and nondegradable PS fragments from the specimens. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1036–1045, 2002

Key words: poly(hydroxybutyrate-*co*-hydroxyvalerate) (PHBV); PHBV blends; polymer biodegradation; shear stress; degradation test

INTRODUCTION

With increased public concern about the disposal and management of plastic waste, which is accumulating in the environment at 25 million tons per year,[1] extensive efforts have been made to produce biodegradable plastics that can decompose in nature.[2] Tailoring polymers becomes important for various products with predetermined service lives, particularly the short-life-span packaging materials. Different strategies have been suggested and adapted for biodegradable materials, including (1) the use of cheap, synthetic, bulk polymers with a biodegradable com-

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ponent, such as a blend of polyethylene and starch;[3] (2) the introduction of biodegradable bonds or groups into synthetic macromolecules such as poly(ϵ-caprolactone) (PCL);[4] and (3) the use of natural polymers such as poly(hydroxyalkanoate)s (PHAs).[5] The development and promotion of biodegradable materials require precise measurements of their biodegradability in the laboratory and in the field. Field testing can reveal the real situation after the material specimens are exposed to terrestrial (soil, compost, and landfill) and/or aquatic (marine, river, lake, and sewage) environments.[6,7] Testing is usually time-consuming and expensive, and the results are usually not reproducible because of uncontrollable environmental conditions.[7] Laboratory tests under controlled conditions, therefore, are essential, especially as the first- and second-tier tests in a tiered system.[8] In agreement with traditional ways of measuring the biodegradability of medical materials, agitated flask cultures containing enzymes and/or microorganisms are widely adopted for polymer degradation in aquatic media.[9]

The biodegradability of a material is a measurement of its biodegradation rate, which is determined by material properties, environmental factors, and their interactions. A polymer with good biodegradability, such as PHA, may take weeks to decompose completely,[10] and a nondegradable polymer such as polyethylene could take a very long time (10 years) to lose less than 5% of its original mass.[11] Furthermore, one material can also have very different degradation rates, depending on the environmental conditions and the interactions between the specimens and the environmental factors.[12] Poly(hydroxybutyrate) (PHB) powder, for example, was metabolized by soil microorganisms more than 10 times faster than PHB films.[13] Accelerated degradation may be desirable for a quick laboratory screening and a kinetic study,[14] but the factors that affect the degradation rate should be clearly understood and quantitatively known as guidelines in the search for new materials or in the correlation of laboratory results to field tests.

Multiple phases and components are involved in polymer biodegradation in flask tests, including the solid phase (material specimens and microorganisms), the liquid phase (water, nutrients, enzymes, and metabolic products) and the gas phase (air, CO_2, and CH_4). The contact and mass transfer of the components among these phases should have a significant effect on the degradation rate of the solid specimens. Although homogeneous conditions are usually made or assumed in small laboratory facilities, little is known about the actual conditions, and even less is known about their effects on the degradation rate or the biodegradability of polymer specimens. This may cause uncertainties concerning material biodegradability in laboratory tests. One example is the agitation strength of the standard anaerobic biodegradation tests of polymers (ASTM D 5210-92 and ISO 11734). Agitation is optional in the ISO method but is required in the ASTM method to produce a homogeneous solution. Neither of them, however, specifies the agitation strength. This article reports a significant effect of the agitation strength in aquatic media on the degradation rate of one biodegradable polymer, poly(hydroxybutyrate-*co*-hydroxyvalerate) (PHBV), and its blends with a biodegradable synthetic polymer, PCL, and a nonbiodegradable polymer, polystyrene (PS). With the energy dissipation principle, the properties of turbulent eddies and the hydraulic shear stress were calculated for solutions shaken at different speeds. Combining the hydraulic analysis with the surface morphologies of the specimens under optical microscopy and scanning electronic microscopy (SEM), we propose that the shear stress above a threshold value removes tiny polymer fragments, resulting in very different degradation rates under different agitation strengths.

MATERIALS AND METHODS

PHBV (molecular weight = 400,000, 22% hydroxyvalerate), PS (molecular weight = 230,000), and PCL (molecular weight = 80,000) were purchased from Aldrich (Milwaukee, WI). Specimens of PHBV and its blends with PCL and PCL/PS were prepared by solvent casting. Polymers, according to their predetermined compositions, were dissolved in 8–10% (w/v) chloroform at 60°C overnight, and the solutions were left in clean glass dishes and dried slowly under room conditions for 1 week. The films were further aged for at least 2 weeks before analysis and testing. Polymer films were cut into discs 15 mm in diameter and about 0.1 mm thick (18–23 mg each). Flasks (125 mL), each containing three discs and a 50-mL test solution, were deoxygenated with a N_2 gas purge at 250 mL/min for 10 min [the dissolved oxygen (DO) concentration approached zero after 4 min], covered with a rubber stopper, incubated

at 30°C, and shaken at 0–180 rpm in a rotational incubator with a stroke of 31 mm. At different time points, one flask was sacrificed to measure pH, polymer mass, cell mass, and proteins. An average disc mass was calculated from the three disc specimens for error control.

The test solution was prepared as follows. Microbes were extracted from a local fertile garden soil to an aqueous medium according to a general procedure of soil microbiology.[15] The soil was soaked in tap water at 0.5 kg of soil/L for 1 h, and the suspension solution was filtered through No. 1 Whatman filter paper (Rotenburg, Germany) to remove the coarse particles (>11 μm). The filtrate (40 vol %) was mixed with a soil extract medium that contained (per liter) 1 g of glucose, 1 g of peptone, and 1 g of yeast extract. The mixture was incubated at 30°C for 24 h under anaerobic conditions after the oxygen was purged with nitrogen. The spent broth was used as a seed to prepare the test medium with a mineral solution containing (per liter) 3.8 g of K_2HPO_4, 2.65 g of KH_2PO_4, 0.48 g of $MgSO_4 \cdot 7H_2O$, 0.3 g NH_4Cl, and 1 mL of a trace element solution. The element solution contained (per liter) 200 mg of (NH_4)-$Fe(SO_4)_2 \cdot 6H_2O$, 5 mg of $ZnSO_4 \cdot 7H_2O$, 5 mg of $MnCl_2 \cdot 4H_2O$, 2 mg of $CuSO_4 \cdot 5H_2O$, 2 mg of $NaB_4O_2 \cdot 10H_2O$, and 2 mg of $NaMoO_4 \cdot 2H_2O$. The volume ratio of the broth to the mineral solution was controlled to give a constant initial cell concentration of 25 mg of dry cell mass per liter of test solution. Two types of controls were carried out in parallel. Nonbiological hydrolysis of PHBV was monitored in a sterile solution after the test solution was sterilized at 116°C for 15 min. The concentration change of seed cells in the absence of PHBV was also monitored in the same test solution.

Measurements

Weight loss is one of the most accurate and reliable means of evaluating the degradation extent of biodegradable polymers.[16] It was calculated from the initial specimen mass (W_0) and the instantaneous residual mass (W) with eq. (1):

$$\text{Weight Loss} = \frac{W_0 - W}{W_0} \times 100\% = \left(1 - \frac{W}{W_0}\right) \times 100\% \quad (1)$$

The mass of polymer specimens was determined with an analytical balance of 0.1-mg accuracy after the samples were gently washed to remove the attached biomass and were dried to a constant weight. The smallest recoverable polymer fragments after degradation were around 0.2 mg, about 1 wt % of the original polymer specimen. The fragments smaller than 0.2 mg were not recovered and were considered degraded. The final polymer utilization was described by cell growth or the turbidity increase in the test solution, which was measured with a spectrophotometer at 620 nm, and correlated with the dry cell mass concentration (1 Abs = 513.2 mg/L, r^2 = 0.992). The extracellular proteins attached to the specimen surface and dissolved in the test solution were measured with a Lowry protein assay kit (Sigma, St. Louis, MO), and there was a good linearity (r^2 = 0.966) between the absorbance at 600 nm and the protein concentration up to 400 mg/L. A zoom microscope (Nikon SMZ-U, Kanagawa, Japan) was used for routine monitoring of the polymer surface morphology. To reveal the details of surface erosion, we coated the polymer specimens with gold in a vacuum sputter and observed them with a scanning electron microscope (JEOL 6300, Peabody, MA).

RESULTS AND DISCUSSION

Time Course and Rate of PHBV Degradation

Figure 1 shows the typical time courses of PHBV weight loss associated with cell growth under anaerobic conditions. The soil microorganisms used the polymer as a carbon substrate and had a yield

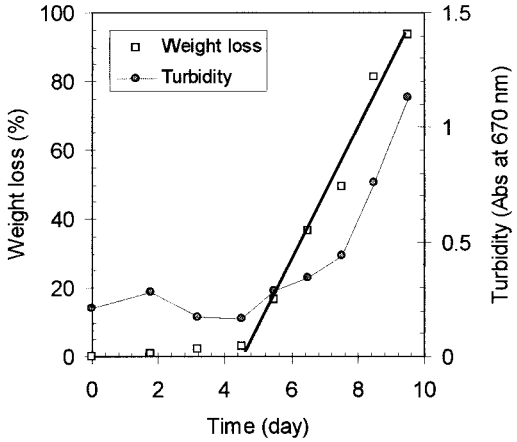

Figure 1 Biodegradation and utilization of PHBV by soil microbial organisms under anaerobic conditions at 30°C and 180 rpm.

of 0.17 g of cell mass/g of PHBV consumed. In the same solution but without PHBV, the turbidity of the seed cells declined to an undetectable level after 9 days. It is clear that PHBV was decomposed and used as the carbon source for cell growth and maintenance. The medium pH declined from 6.8 at the beginning to 6.3 when most PHBV (>80 wt %) had disappeared. The proteins attached to the polymer surface increased correspondingly from 0.2 to 1.8 mg/cm^2, and the total extracellular proteins in the test solution increased from 2 to 7 mg. In the control of an aseptic solution without microbial cells, no PHBV weight loss was observed in 3 months, a clear indication of no hydrolysis of PHBV in the test solution. The utilization of PHBV by the soil microorganisms was also compared with the glucose utilization under the same conditions. On glucose, the common carbon source for most microorganisms, the cells had a yield of 0.28 g of cell mass/g of sugar consumed, whereas the yield for PHBV was 0.17 g of cell/g of PHBV consumed. The medium pH declined from 6.9 to 4.7 because of the accumulation of fermentation acids such as acetic acid over a short period of time (6–7 h) of glucose consumption.

Figure 1 also shows that significant polymer weight loss occurred after a lag phase. Although the lag time was not consistent in different batches, polymer weight loss was linear with time, during which most of the polymer mass decomposed. Equation (2) gives a specific weight-loss rate based on the specimen's residual mass fraction (W/W_0):

$$-\frac{dW}{W_0 dt} = k \tag{2}$$

The value of the specific degradation rate k (19.8 day^{-1}) can be estimated from the slope of the linear section of the time course. Because the hydrophobic PHBV did not swell in an aqueous solution and had a constant density, the volume reduction rate is the same as the mass reduction :

$$-\frac{d(\rho V)}{(\rho V_0)dt} = -\frac{dV}{V_0 dt} = k \tag{3}$$

Effect of Agitation on the Degradation Rate

Figure 2 shows the values of k obtained under the same conditions, except for the rotation speed, which was controlled at one level from 0 to 180 rpm. Under static conditions, the polymer discs sat at the bottom of the flasks because their density was higher than that of water, and the solution was gently shaken manually every 24 h to make the solution uniform. In 60 days, no mass loss greater than the measurement error (1–5%) was observed, and loose attachment of microbial biomass was observed on the polymer surface. k was around zero. With a continuous gentle shaking at 60 rpm, the degradation rate was also quite low (k = 0.5 day^{-1}). Under a high agitation strength at 120 rpm or greater, the polymer degradation rate increased significantly, up to 15.4 day^{-1}. Figure 2 also shows that k approaches a plateau above 150-rpm agitation. Under aerobic conditions, the same effect of rotation speed on the PHBV degradation rate was also observed (data not shown here), and it was attributed to a high DO concentration under a high agitation strength, which led to high microbial activity in PHBV degradation. Under the anaerobic conditions, however, the promotive effect of agitation on PHBV degradation must be attributed to the effect of mixing and stirring on polymer degradation. Mixing could bring a uniform solution in the flasks and might promote mass transfer between the solid polymer phase and the bulk solution, as well as cell and enzyme contact with the solid substrate. The effect of mass transfer on polymer degradation, however, could become important only if the mass transfer was much slower than the polymer degradation. The utilization of PHBV in the test solution was quite slow compared with the utilization of common carbohydrate substrates such as glucose in regular fermentation. The maximum degradation rate found in this

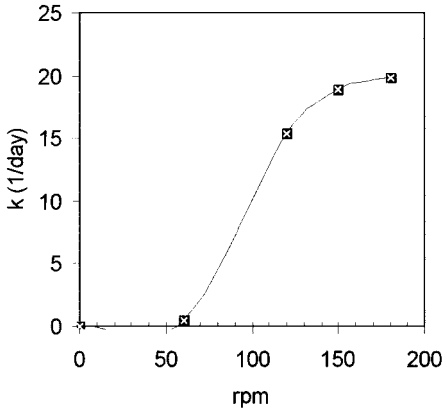

Figure 2 Effect of the rotation speed on the weight-loss rate of PHBV under anaerobic biodegradation.

study was around 19.8 g/g day, or 0.014 g/g min. The small amount of degradation products was easily and quickly mixed to uniformity in a small volume of solution (50 mL), even under gentle agitation conditions (60 rpm). Furthermore, there was a great increase in the degradation rate from 60 to 120 rpm, which implies a threshold point was reached in PHBV weight loss. Because the mass transfer usually has a linear or first-order dependence on the concentration gradient, the nonlinear effect of rotation speed on the degradation rate might imply a mechanical effect of agitation strength on material specimens rather than the concentration gradient or mass-transfer resistance.

Surface Morphology of PHBV Degradation

Figure 3 shows the morphology of PHBV films at different times under optical microscopy. The polymer surface on the 7th day during the fast linear weight loss (Fig. 1) had many small holes, and some surface area was worn out. The surface on the 3rd day before the weight loss went into the fast linear degradation, however, did not have these holes. The holes could be initiated by the action of the depolymerase or the cells after they had attached onto these sites, but it was not clear how this type of hole (0.03–0.1 mm in diameter) was developed. In a mixed solution, the extracellular depolymerase should have an equal chance of attaching onto the whole surface area. Figure 4 shows a more detailed morphology of PHBV films under SEM. With respect to the original, smooth surface, many tiny polymer fragments were formed after anaerobic degradation for 7 days. In the presence of a heterogeneous substrate (polymer films), the microbial cells or their extracellular depolymerase must attach onto the surface and then attack the exposed ester bonds (O═C—O) near the site.[17] The products of enzymatic hydrolysis might be monomeric acids that can be directly transferred into cells for utilization, but most likely the oligomers and tiny polymer fragments predominated because of the random distribution of exposed ester bonds from different chains of the macromolecules.[18] Fragmentation of the polymer surface might be further enhanced because of the presence of amorphous and crystalline zones on the surface.[19] The amorphous structure is easier to attack and degrade than the crystalline structure, resulting in fragments of the crystalline structure. The detachment of those tiny fragments from the surface, therefore, may have a significant effect on polymer degradation and the rate constant k. The vigorous agitation at 120 rpm or greater might

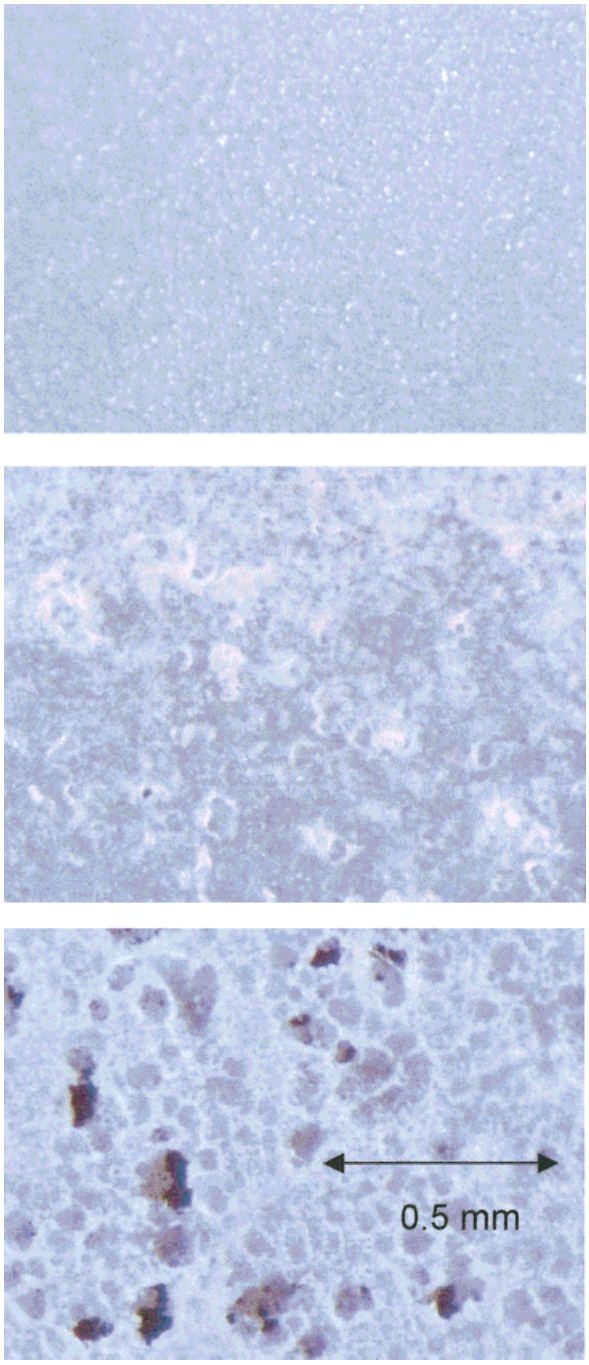

Figure 3 Surface morphology of PHBV specimens under anaerobic degradation: the original surface (top), the surface after 3 days (middle), and the surface after 7 days (bottom). The corresponding polymer mass loss is shown in Figure 1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

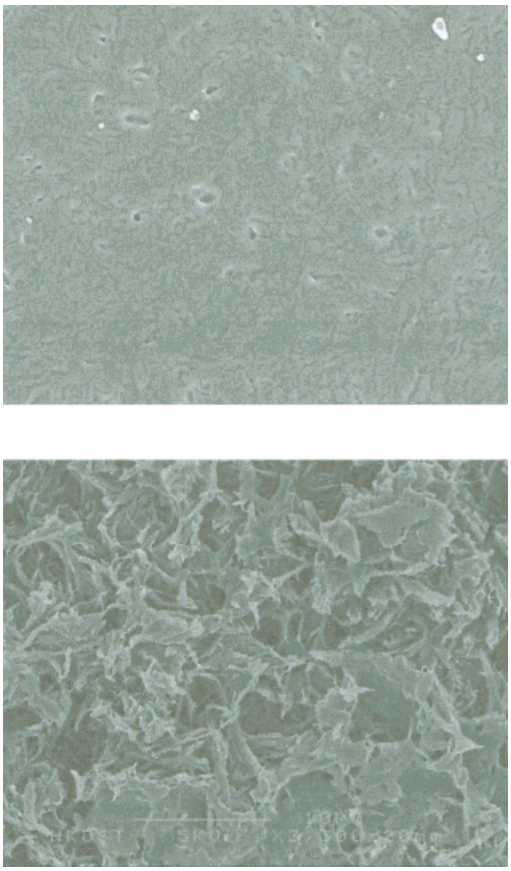

Figure 4 SEM surface morphology of PHBV films under anaerobic degradation at 0 (top) and 7 days (bottom). The bar represents 10 μm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

shear away these small fragments from the polymer surface. The removal of these tiny fragments from the polymer surface might have three promotive effects on polymer degradation: (1) renewed surface for further enzyme or cell attachment and attack, (2) removal of the protective biofilms on the polymer surface, and (3) increased mass loss of parent specimens. In the last case, the detached small fragments had a very large surface area and could be degraded much faster than the parent specimens. Their final utilization by cells was confirmed with continuous cell growth in the test solution. It can be reasonably concluded that biodegradation plus physical wear led to the formation of the macroholes on the polymer surface, as shown in Figure 3. A shear stress above a threshold value might be needed to shear away the tiny fragments that were connected to the polymer surface.

Shear Stress on Surface Erosion and Renewal

Liquid mixing is the result of the velocity gradient, or the shear rate (dv/dy), within the agitated medium. The shear rate brings about the momentum transport, heat and mass transfer, and also the shear stress in the liquid:

$$\tau = \mu\left(\frac{dv}{dy}\right) \tag{4}$$

The power input per liquid volume (ϵ_V), or energy dissipation rate, is widely used to measure the mixing effectiveness. When an Erlenmeyer flask is subjected to rotational shaking, the energy dissipation rate to the liquid can be estimated by the following experimental equation:[20,21]

$$\varepsilon_V = (1.09 \times 10^{-6})V^{-0.25}N^{2.81} \tag{5}$$

where ϵ_V is the energy dissipation rate per liquid volume (kw/m^3); V is the liquid volume (mL), and N is the rotation speed (rpm).

The rotational flow in flasks can be visualized as energy dissipation with large and unstable primary eddies down to a chain of smaller eddies and finally to viscous dissipation to heat. According to Kolmogoroff's isotropic theory of those smallest eddies, the microscale of the turbulent eddy, at which the eddy Reynolds number is equal to one, can be estimated with eq. (6):[22]

$$\eta = \left(\frac{\nu^3}{\varepsilon_m}\right)^{1/4} \tag{6}$$

where ν is the kinematic viscosity of the liquid (m^2/s) and ϵ_m is the energy dissipation rate per liquid mass (w/kg). Below this microscale, the turbulence is viscous-dissipation-dominated, and above this size, inertial forces are predominant.

The velocity of the eddy is determined as

$$u' = (\eta\varepsilon_m)^{1/3} \tag{7}$$

and its shear stress can be calculated from

$$\tau = \rho(u')^2 \tag{8}$$

Table I gives the energy dissipation rate, eddy scale, eddy velocity, and shear stress at different rotation speeds. Figure 5 further shows the relationship of the degradation rate k, the shear

Table I Energy Dissipation Rate, Turbulent Eddy Properties, and Shear Stress at Different Rotational Speeds in Flask Test

Rotation (rpm)	Energy Dissipation Rate (w/kg)	Eddy Scale (m 10^{-6})	Eddy Velocity (m 10^{-3}/s)	Shear Stress (Pa 10^{-3})
0	0.000	0	0	0
60	0.041	70	14	20
120	0.290	43	23	53
150	0.530	37	27	73
180	0.890	32	31	94

stress, and the energy dissipation rate (or power consumption).

At a low rotation speed, the predominant flow pattern in the flasks was close to a laminar flow, and the shear stress was mainly a viscous shear stress. The liquid flew over the polymer surface, developing a viscous boundary layer on the surface. This fluid flow had a weak strength and brought little polymer fragments away; therefore, the erosion and renewal of the polymer surface were slow. The polymer degradation was also quite slow. With an increase in power consumption, the degradation rate increased significantly and approached a plateau. This implies that tiny polymer fragments were significantly removed when the shear stress was above a level that might be related to the attachment strength of the fragments on the surface. Under a turbulent flow of high agitation intensity, the random fluid motions, or eddies, give rise to irregular velocity gradients and turbulent shear stress (Reynolds stress). The action of turbulent shear stress on polymer specimens is different from that of viscous shear stress. The interaction between the fluid eddies and the polymer fragments depends on their relative size. If the eddies are much larger than the fragments, little relative motion exists between the liquid and the discs because their densities are quite similar. Under this condition, the whole polymer disc is moving with the fluid current, and surface renewal would not be significant. If the eddies similar to the fragments in size, they cannot engulf the suspended discs but act on the polymer surface with predominant inertial forces. The inertial forces acting on the polymer surface might detach the tiny fragments quickly to promote further surface erosion and renew the surface area for the attachment of extracellular depolymerases. Under very high agitation strength, some eddies become so small that they mainly disappear as heat in the viscous liquid. It is likely that not all turbulent eddies are important in surface erosion and polymer degradation. The eddies that had an impact on the removal of the tiny polymer fragments might have the same size as the fragment (10–30 μm), as shown in Figure 4. This size was about the same as that of the eddies formed at a rotation speed of 150 rpm or greater (Table I).

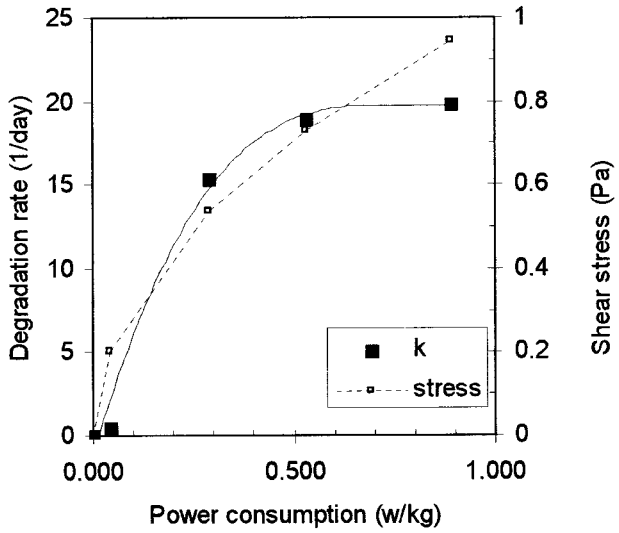

Figure 5 Effect of power consumption or energy dissipation rate on the eddy shear stress and PHBV degradation rate constant.

Degradation of the PHBV/PCL Binary Blends

Figure 6 gives the weight losses of PHBV, PHBV/PCL (80/20 and 25/75) blends, and PCL under anaerobic conditions at 30°C and 120 rpm. The linear weight loss with time was observed for all the materials, and their k values were determined from the slopes and are listed in Table II. PCL had a much slower degradation rate but a higher cell growth yield (0.3 g of cell/g of PCL) than PHBV (0.17 g/g). This was attributed to the

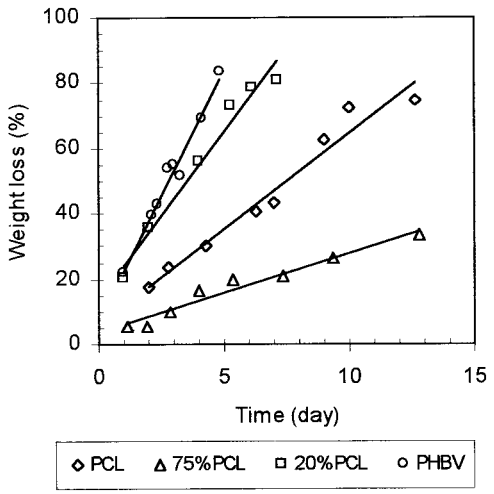

Figure 6 Biodegradation of PCL, PHBV, and PCL/PHBV blends under anaerobic conditions at 30°C and 120 rpm.

higher energy content of PCL (—$C_6H_{10}O_2$—) in comparison with that of PHBV (—$C_4H_6O_2$—). As expected, a small amount of slowly degradable PCL (20%) in a PHBV/PCL blend reduced the overall degradation rate. Although the binary blends of PHBV and PCL were immiscible,[23] they did exhibit a single glass-transition temperature and formed a compatible morphology that was homogeneous to the naked eye. Figure 7 shows the surface morphologies of the original specimens. Compared with the pure PHBV in Figure 3, the small amount of PCL (20%) was dispersed in the continuous PHBV domain phase, which hindered PHBV polymerase approaching the PHBV surface and the ester bonds. It was also observed that a large amount of PCL (75 wt %) gave the slowest degradation rate. The surface morphology of this blend is also given in Figure 7. It seems that PHBV (25%) was not dispersed in the PCL domain phase but mixed or even partially miscible with the amorphous phase of PCL. It was reported that little degradation was observed of a miscible solution of two biodegradable polymers, PHB and cellulose ester.[24] This may be attributed to the two types of depolymerases that cannot hydrolyze a solution of two types of ester bonds. However, an immiscible blend of PHB with poly(1,4-ethylene adipate) had a faster enzymatic degradation rate than simple PHB film.[25]

Degradation of the PHBV/PCL/PS Triple Blend

Figure 8 compares the weight losses of PHBV, 80/20 (w/w) PHBV/PCL, and 76/5/19 (w/w/w) PHBV/PCL/PS under anaerobic conditions at 30°C and 120 rpm. PHBV and PS were not only immiscible but also incompatible, with no interaction between two randomly distributed phases (data not shown here). A small amount of PCL (5 wt %) as a compatibilizer could improve the dispersion of PS in the PHBV domain phase, as shown in Figure 9. Small droplets of PS (<0.5 mm) were uniformly dispersed in the continuous phase of PHBV after chloroform was slowly vaporized. After a quite long lag time for adaptation, the degradation of this triple blend was picked up and showed linear degradation with time (from 5 to 60 wt % loss). The k value was estimated from the linear slope (18.6 day^{-1}) and is compared with the values for other materials in Table II. PS is a well-known nonbiodegradable synthetic polymer, but its presence (19 wt %) in the blend did not hinder the weight loss of the blend. First, unlike PCL, which was compatible and interactive to some extent with PHBV, PS did not affect the phase of PHBV very much because of its immiscibility and incompatibility with PHBV. Clear phase separation can be observed in Figure 9. The biodegradation of the PHBV domain phase, therefore, was not affected by the presence of the dispersed PS phase. Second, when PHBV around the PS droplets was degraded, the PS droplets were also removed from the blend specimens by the shear force of the agitation stress. This effect was similar to the removal of tiny PHBV fragments from the surface, as discussed previously: the detachment of those nonbiodegradable dispersed droplets from the specimens led to a faster weight loss than pure PHBV. The effect of surface ero-

Table II Specific Degradation Rates (Day^{-1}) of PHBV and Its Blends with PCL and PS Under Anaerobic Conditions at 30°C and 120-rpm Rotation Shaking

PHBV	PHBV/PCL (80/20)	PHBV/PCL (25/75)	PCL	PHBV/PS/PCL (76/19/5)
15.5	10.2	2.4	5.9	18.6

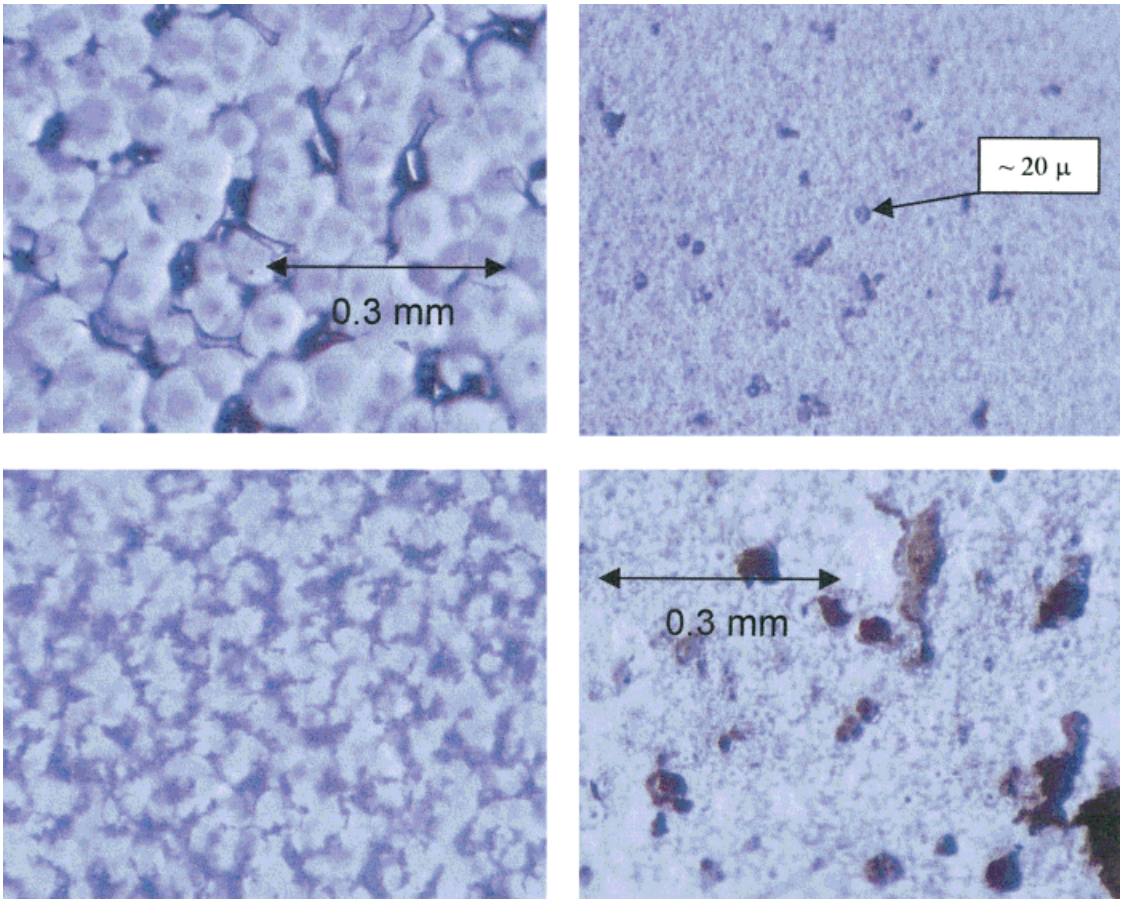

Figure 7 Surface morphologies of PCL film and two binary PHBV/PCL blends: pure PCL (left top), 25/75 PHBV/PCL (left bottom), 80/20 PHBV/PCL before degradation (right top), and 80/20 PHBV/PCL after degradation (right bottom). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

sion on polymer degradation was determined by two factors: (1) the intrinsic degradability of the polymers and (2) environmental factors such as agitation strength. Without the initial biodegradation of the polymer surface, shear stress had little effect on the degradation rate. A triple blend, 19/5/76 (w/w/w) PHBV/PCL/PS, with the biodegradable phase (PHBV/PCL) dispersed in the continuous nondegradable phase (PS), for example, decomposed very slowly, 100 times slower than the blend of the continuous PHBV domain. A smooth surface was observed because of the poor availability of biodegradable components, and the degradation rate was not related to the agitation strength.

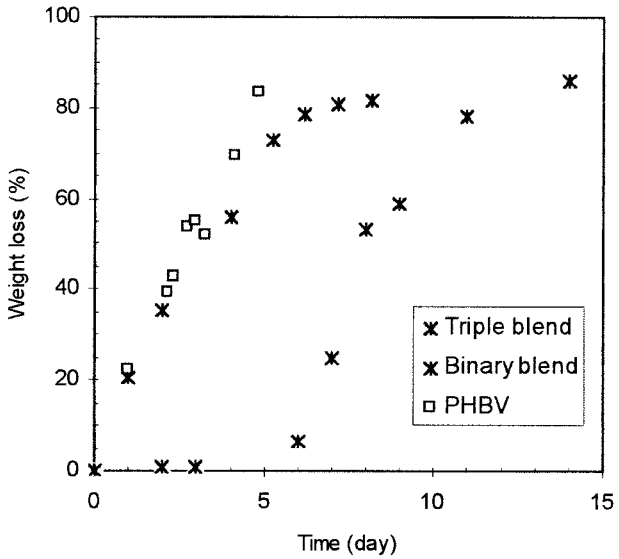

Figure 8 Biodegradation of PHBV, a binary 80/20 PHBV/PCL blend, and a triple 76/19/5 PHBV/PS/PCL blend under anaerobic conditions at 30°C and 120 rpm.

CONCLUSION

Agitation and hydraulic shear stress may significantly enhance the biodegradation of polymeric

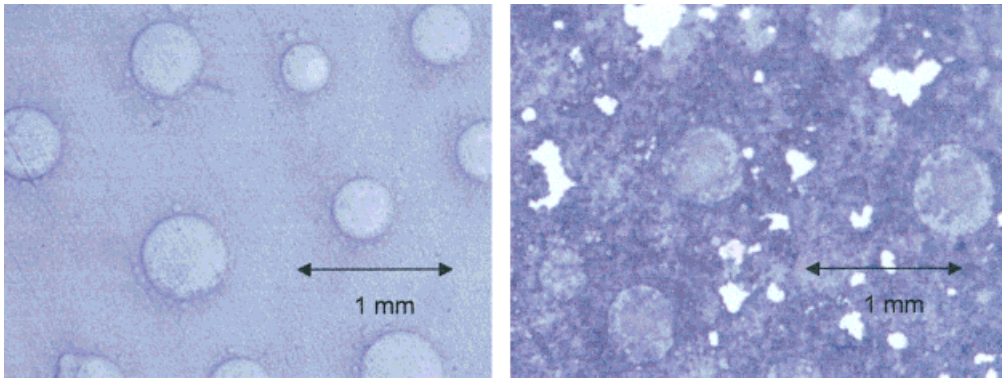

Figure 9 Morphologies of a triple 76/19/5 PHBV/PS/PCL blend before degradation (left) and after degradation (right) under anaerobic conditions at 30°C and 120 rpm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

materials in aquatic media. The fluid turbulence can promote mass transfer and give a homogeneous condition. More importantly, it may bring about turbulent shear stress, which can significantly affect the surface erosion of specimens and, therefore, the biodegradation rate because the turbulent eddies may have the right size and inertial force to tear the polymer fragments away from the degraded solid surface. This hydraulic effect can speed up biodegradability testing in the laboratory and can also be a major factor affecting material degradation in nature.

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