Poly(hydroxybutyrate-*co*-hydroxyvalerate)/Titanium Dioxide Nanocomposites: A Degradation Study

Aleksandra Buzarovska,[1] Anita Grozdanov,[1] M. Avella,[2] G. Gentile,[2] M. Errico[2]

[1]*Faculty of Technology and Metallurgy, Rudjer Boskovic 16, Skopje, Republic of Macedonia*
[2]*Institute for Chemistry and Technology of Polymers, Via Campi Flegrei 34, 80078, Pozzuoli (NA), Italy*

ABSTRACT: Nanocomposites, based on a poly(hydroxybutyrate-*co*-hydroxyvalerate) (PHBV) matrix and titanium dioxide (TiO_2) nanoparticles and fabricated with a solvent-casting technique, were characterized with differential scanning calorimetry, thermogravimetric analysis, scanning electron microscopy, and Fourier transform infrared spectroscopy. The content of TiO_2 nanoparticles varied between 0.5 and 10 wt %. Degradation studies, including hydrolytic degradation in a strong base medium ($1N$ NaOH) and degradation under ultraviolet light at 365 nm, were performed. It was confirmed that the inorganic filler had no great influence on thermal properties such as the melting and crystallization temperatures. Improved degra-dation temperatures were also confirmed with the increase in the filler content. Degradation observations confirmed significant increases in hydrolytic erosion with the filler content increasing in comparison with the degradation of a pure PHBV film. Also, the photocatalytic activity of the inorganic filler TiO_2 in all investigated composites [irradi-ated at $\lambda = 365$ nm and immersed in a liquid medium (H_2O)] was evaluated. The degraded samples were ana-lyzed with Fourier transform infrared spectroscopy, which confirmed their increased crystallinity. © 2009 Wiley Periodi-cals, Inc. J Appl Polym Sci 114: 3118–3124, 2009

Key words: biodegradable; composites; degradation

INTRODUCTION

Biodegradable polymers (BPs) have received consid-erable scientific attention because of their biodegrad-ability and the fact that some of them could have mechanical properties similar to those of conventional synthetic thermoplastics.[1,2] Many efforts have been made to modify some of their unfavorable properties, such as rigidity and stiffness, and to reduce their high prices.[3] Besides the blending approach to modifying undesirable properties, interest in the fabrication of various composites based on BPs and different kinds of fibers, organic fillers, and nanoparticles has rapidly increased with the ultimate goal of enhancing their performance.[4,5] The most popular approach is to introduce nanoparticles into a polymer matrix and to produce polymer/nanoparticle composites. Nanopar-ticles have been employed to produce new nanocom-posites, such as layered silicates, layered titanates, carbon nanotubes, magnetite nanoparticles, and fluo-rine mica, as well as many others.[6] The modifica-tion of a biodegradable matrix with inorganic fillers (especially nanoparticles) could significantly affect the morphology, crystallization behavior, mechanical properties, and biodegradation.[7,8]

Poly(hydroxybutyrate-*co*-hydroxyvalerate) (PHBV), a representative of biodegradable polyesters, pos-sesses some problems, such as a slow crystallization rate, a high degree of crystallinity (x_c), and difficult processing.[9] For example, the temperature and crys-tallization rate of PHBV increase as a result of the effective nucleating effect of the organoclay.[10]

The preparation of PHBV nanocomposites contain-ing ceramic nanoparticles such as titanium dioxide (TiO_2) could be a route to enhance some of the bio-degradable properties of the polyester resin.

TiO_2 is an inexpensive and chemically stable inor-ganic filler. When irradiated with ultraviolet (UV) light, TiO_2 has great potential as a photocatalyst.[11] For example, TiO_2 has been found to be a successful photocatalyst in many BPs.[12,13] The photocatalytic degradation in many cases depends on the size and dispersability of the nanoparticles. Miyauchi et al.[14] revealed that the higher dispersability and smaller size of TiO_2 particles are more effective in the photo-catalytic degradation of a biodegradable matrix. The presence of nanofillers can also control the biodegra-dation rate. Besides its ability to be used as a photo-catalyst, TiO_2 could have many practical applications in water purification (e.g., antibacterial deodori-zation).[15] The incorporation of nanofillers could con-siderably affect the thermal and mechanical proper-ties of BPs. Fukuda and Tsuji[16] studied the effects of

Correspondence to: A. Buzarovska (abuzar@tmf.ukim.edu.mk).

the volume fraction, size, and crystalline type of TiO_2 particles on the mechanical properties and enzymatic hydrolysis of poly(lactic acid)/TiO_2 composite films. They confirmed that the enzymatic hydrolysis of the poly(lactic acid) matrix was accelerated by the addition of anatase-type TiO_2 particles, and the mechanical properties were almost the same as those of the pure polymer matrix.

In this study, PHBV/TiO_2 nanocomposites were prepared by a solution-casting method. The aim of this article is to evaluate the thermal properties and hydrolytic and photocatalytic degradation of PHBV films containing TiO_2 nanoparticles.

EXPERIMENTAL

Materials

PHBV, a product of Biomer (Krailling, Germany) containing 13% hydroxyvalerate with a weight-average molecular weight of 420 kD, was used as received. The TiO_2 was Degussa P25 (Dequssa AG, Germany) (ca. 80% anatase and 20% rutile) with a particle size around 21 nm.

Preparation of the PHBV–TiO₂ composite films

PHBV–TiO_2 composite films with different weight percentages of TiO_2 (0.5, 1, 2, 5, and 10%) were fabricated with a solvent-casting technique. The solutions were prepared by the dissolution of a polymer matrix (15% w/v) in hot chloroform with stirring for 5 h. After that, appropriately weighed quantities of TiO_2 were added to each solution, which was ultrasonically treated for 1 h. Ultrasonic energy was used to uniformly disperse TiO_2 nanoparticles in the solution and to incorporate them into the composites. The sonicated dispersions were then poured into Petri dishes, and the solvent was allowed to evaporate. The films were dried in a vacuum oven for 24 h.

Morphological analysis

The morphological analysis was performed with a Cambridge Stereoscan model 440 (Leica, Cambridge, UK) scanning electron microscope. Before observation, the specimens were metalized with a gold/palladium coating.

Differential scanning calorimetry (DSC)

The thermal properties and melting and crystallization behavior of PHBV in the investigated PHBV/TiO_2 composite films were analyzed with DSC (DSC7, PerkinElmer, Wellesley, MA).

The composite films were first heated from −20 to 170°C (run I), kept there for 1 min to erase their thermal history, and cooled at a cooling rate of 10°/min. The crystallized samples were reheated (run II)

up to 170°C at a heating rate of 10°/min. x_c of each sample was calculated as follows:

$$x_c = \Delta H_f / \delta H_f^o$$

where ΔH_f is the enthalpy of fusion and ΔH_f^o is the enthalpy of fusion of an ideal crystal, taken to be 109 J/g.[17]

Thermogravimetric analysis (TGA)

The thermal stability of the samples was analyzed with a PerkinElmer Pyris Diamond TGA/differential thermal analysis (DTA) thermal analyzer. The samples were heated under nitrogen from 30 to 600°C at a scanning rate of 10°/min. The degradation temperatures were determined as the temperatures corresponding to the maximum rate of weight loss.

Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra of PHBV–TiO_2 composite films were measured by the attenuated total reflection (ATR) method (64 scans were averaged at a resolution of 4 cm^{-1}) with a PerkinElmer Spectrum 100 FTIR instrument.

Hydrolytic degradation

Thin films (10 × 10 × 0.5 mm^3) were cut and kept in 0.1M NaOH for different times. After each period of degradation, the samples were removed, washed with distilled water, and vacuum-dried for 48 h. The weight loss (W_{loss}) was calculated with the following equation:

$$W_{loss}(\%) = \frac{W_0 - W_t}{W_0} \times 100$$

where W_0 is the initial weight of the polymer film and W_t is the weight at exposure time t in a solution of NaOH.

Photocatalytic degradation

UV treatment was conducted with a UV lamp (6 W) at $\lambda = 365$ nm. The distance between the UV lamp and the composite films was 2 cm. The weight loss was determined as for the hydrolytically degraded polymer films. The UV radiation was performed on composite films dipped into distilled water.

RESULTS AND DISCUSSION

Thermal properties

The first heating runs for pure PHBV and its composites (filled with different amounts of TiO_2 particles)
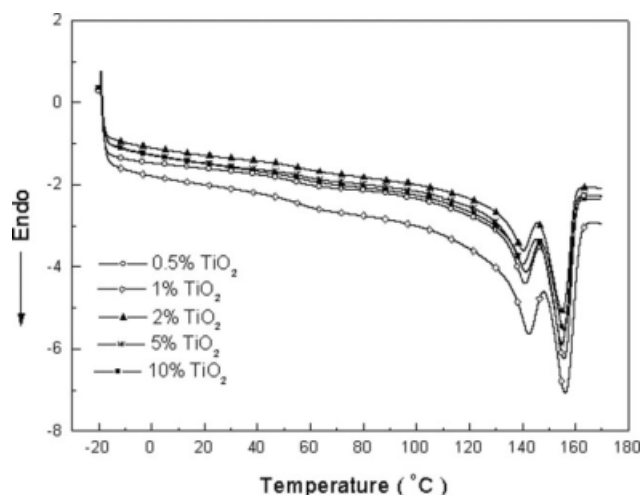
Figure 1 First heating runs for PHBV and its composites with TiO_2.

are presented in Figure 1. A double melting peak was observed for all the heated samples. According to the literature, the lower melting peak (T_{m1}) can be attributed to the melting of the primary formed crystallites, whereas the upper one (T_{m2}) can usually be related to species that recrystallized during the heating scan.[18,19] As presented in Table I, it can be assumed that the positions of the T_{m1} and T_{m2} peaks were almost independent of the TiO_2 content but slightly shifted to higher temperatures in comparison with the characteristic melting temperatures for PHBV. The estimated x_c values (Table I) were almost constant but were slightly lower than x_c of PHBV. These results showed no significant variations of the melting behavior of PHBV with the increase in the TiO_2 content.

Generally, the presence of nanoparticles could have a great influence on the crystallization behavior of the polymer matrix. Depending on their size and distribution, the nanofiller particles could have an ability to nucleate, thus affecting the nucleation density, spherulite size, and crystallization kinetics as well as brittleness of the polymer matrix.[20] Typical crystallization exotherms of PHBV/TiO_2 films are
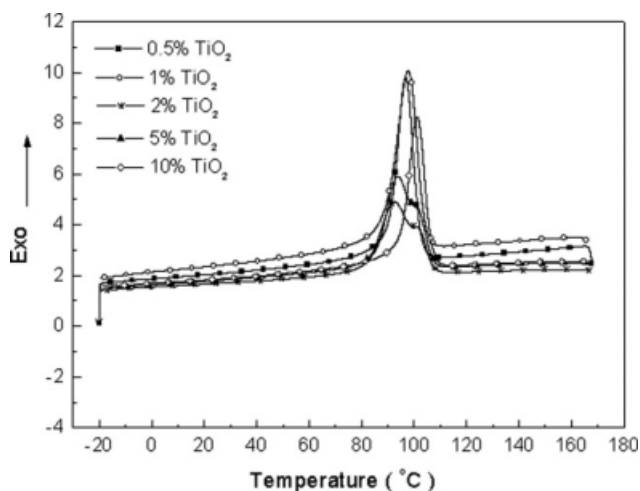
presented in Figure 2. The crystallization peaks of composite films containing 2 or 5 wt % TiO_2 are characterized with pronounced shoulders located at upper temperatures. This should be an indication that the crystallization was a result of two different mechanisms. It could be noted that the crystallization temperatures (T_c's) slightly increased (between 1 and 5°) with the increase in the TiO_2 content. These slight changes in the T_c values do not provide strong evidence that TiO_2 particles could have a significant nucleation effect on the polymer matrix crystallization. With the increase in the TiO_2 content in the investigated composites, a slight continuous increase in x_c could be observed, but it was still lower than x_c of PHBV. Thermograms of the second melting (run II) were characterized by double melting peaks that shifted to higher temperatures in comparison with the melting data derived from the first heating run (I). The degrees of crystallinity in all the composites had higher values, which were determined to be around 46 J/g. These results suggest that the addition of TiO_2 particles made no important contribution to the increase in the crystallinity of PHBV.

TGA, performed between 30 and 600°C, showed a one-stage degradation process. The characteristic TGA curves, presented in Figure 3(a), show that the degradation temperatures slightly increased with the increase in the TiO_2 content. In the DTA curves [Fig. 3(b)], single peaks, which slightly shifted to higher temperatures as the TiO_2 content increased, could be observed. The values of the degradation temperatures and DTA peaks are presented in Table II. From these results, it is obvious that the thermal stability of the composites improved with the increase in the content of this inorganic filler. Similar behavior could be found in many filled composites. Nanoparticles could improve the thermal stability of the systems, thus acting as thermal blockers against heat diffusion.[21]

FTIR characterization was performed to analyze the influence of the nanoparticles on the crystalline-sensitive absorption bands of PHBV. FTIR–ATR measurements in the region between 2000 and
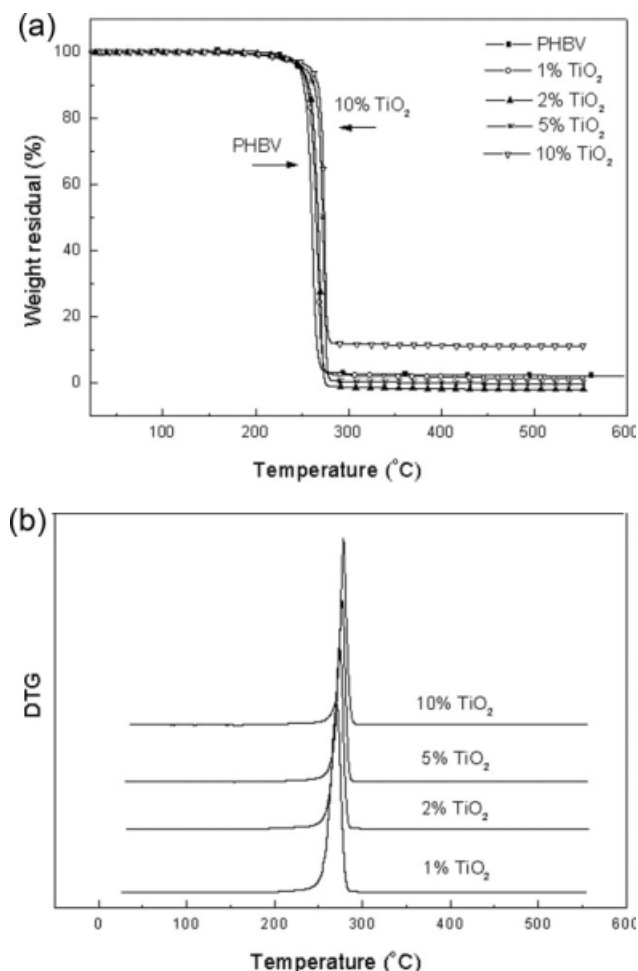
TABLE I
Melting Temperatures and Parameters for PHBV and Its Composites with TiO_2

Sample	TiO_2 (wt %)	Run I			Cooling		Run II		
		T_{m1} (°C)	T_{m2} (°C)	x_c	T_c (°C)	x_c	T_{m1} (°C)	T_{m2} (°C)	x_c
PHBV		138	152	48	96	46	145	155	48
PHBV/TiO_2	0.5	141	156	45	97	39	147	157	46
PHBV/TiO_2	1	142	156	45	98	42	148	157	46
PHBV/TiO_2	2	140	155	45	92, 101	42	147	157	46
PHBV/TiO_2	5	140	155	44	94, 102	42	147	157	47
PHBV/TiO_2	10	142	156	45	102	45	148	157	47

Figure 2 Crystallization exotherms for the PHBV/TiO₂ composite films.

TABLE II
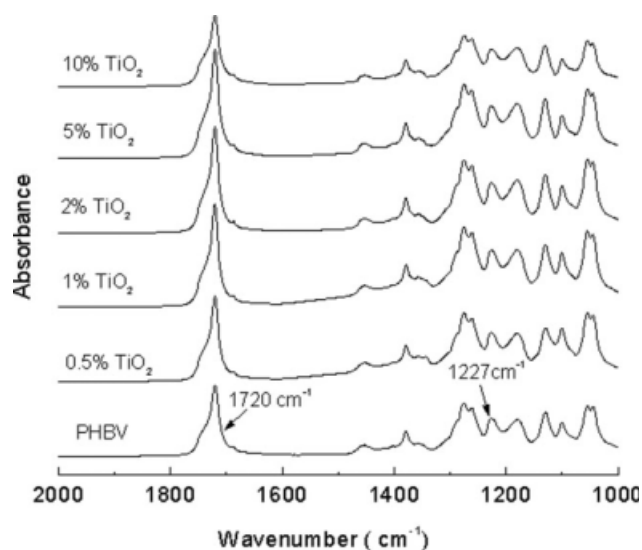**TGA and Derivative Thermogravimetry (DTG) Data for PHBV and Its Composites with TiO₂**

Sample	TiO₂ (wt %)	Decomposition temperature (°C)	DTG$_{(peak)}$ (°C)
PHBV		236	267
PHBV/TiO₂	1	253	270
PHBV/TiO₂	2	257	272
PHBV/TiO₂	5	262	276
PHBV/TiO₂	10	265	276

1000 cm^{-1} of all investigated films are presented in Figure 4. Certain changes in the intensities of some characteristic bands could be observed. That is, in-tensity changes in the crystalline C=O stretching band located at 1720 cm^{-1} and in the crystalline C—O—C stretching band at 1227 cm^{-1}, as well as the amorphous C—O—C band at 1180 cm^{-1}, could be observed.[22] The depression or increase in the crystal-linity of a certain system could not be judged only by the variation of the intensity of a certain band. Kansiz et al.,[23] for example, defined the crystallinity index (CI) as a ratio of the intensities of the bands positioned at 1228 and 1720 cm^{-1}. The CIs, calcu-lated according to this ratio, are presented in Table III. The estimated CIs were around 0.18 and almost constant but were slightly lower than the CI of pure PHBV. These results are in accordance with the DSC data, especially those derived from the first heating scans.

Degradation studies

Hydrolytic degradation

Hydrolysis in the degradation of polymers may be important in the initiation of polyester degradation. In this work, the hydrolytic degradation of the investigated composites and the pure PHBV

Figure 3 (a) Thermogravimetric curves for PHBV and its composites and (b) DTA curves for the PHBV/TiO₂ composites.

Figure 4 FTIR–ATR spectra for the PHBV/TiO₂ composites between 2000 and 1000 cm^{-1}.

TABLE III
CIs Derived from the $I_{1227cm^{-1}}/I_{1720cm^{-1}}$ Intensity Ratio with FTIR Absorption Data

| Sample	TiO$_2$ (wt %)	CI (wt %)	CI after 5 h of exposure (hydrolytic degradation)	CI after 23 h of exposure (UV radiation)
PHBV		0.22	—	—
PHBV/TiO$_2$	0.5	0.18	—	—
PHBV/TiO$_2$	1	0.18	—	—
PHBV/TiO$_2$	2	0.18	0.20	0.21
PHBV/TiO$_2$	5	0.17	0.18	0.23
PHBV/TiO$_2$	10	0.19	—	—

polymer matrix was carried out in a stronger base medium (1N NaOH) at 37°C to increase the rate of degradation. A systematic decrease in the normalized weight loss versus the time of exposure was detected in all investigated samples (Fig. 5). The rate of hydrolytic degradation increased with the increase in the TiO$_2$ content. This could be confirmed by the slopes of the initial dependence of the weight loss on the time of exposure. After each period of exposure, the composites showed a significantly higher weight loss than the pure polymer matrix (PHBV). The weight loss increased with the increase in the TiO$_2$ content. According to literature data, erosion rates are influenced not only by x_c but also by the structure of thin lamellar crystals. As the CIs in the investigated composites were found to be pretty independent of the TiO$_2$ content, this behavior, related to the increased hydrolytic degradation of the PHBV/TiO$_2$ composites, might be affected by the different morphologies of the systems.

Scanning electron microscopy (SEM) micrographs of the studied PHBV composites are presented in Figure 6. The morphologies of the nanocomposite films were not homogeneous as the morphology of the neat polymer surface was. Grooves, cracks, and pores were observed. Also, the formation of characteristic hemispherical cavities was found in the composite films.

Photocatalytic degradation

UV radiation could be a very important tool in the initiation of polymer degradation, thus controlling the biodegradability and biocompatibility of polyesters.[24]
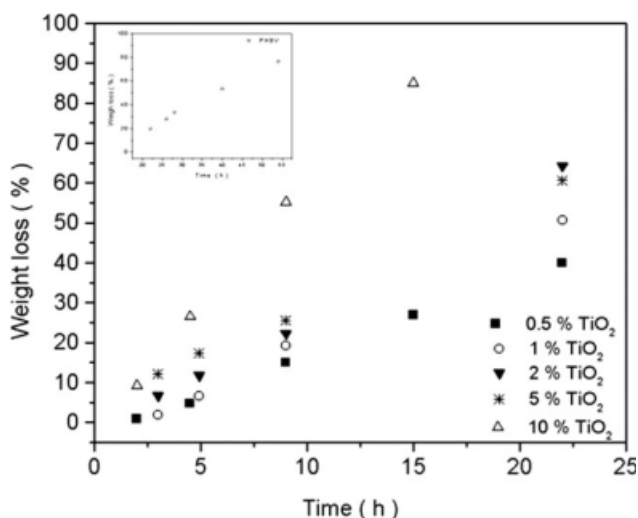
Figure 5 Weight loss values of the PHBV/TiO$_2$ composite films during hydrolytic degradation in 1N NaOH.
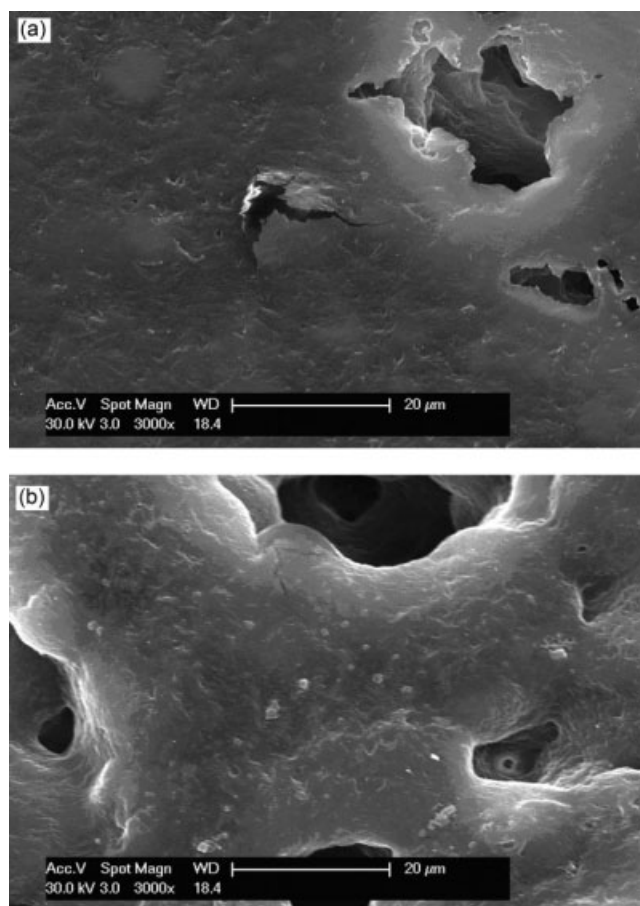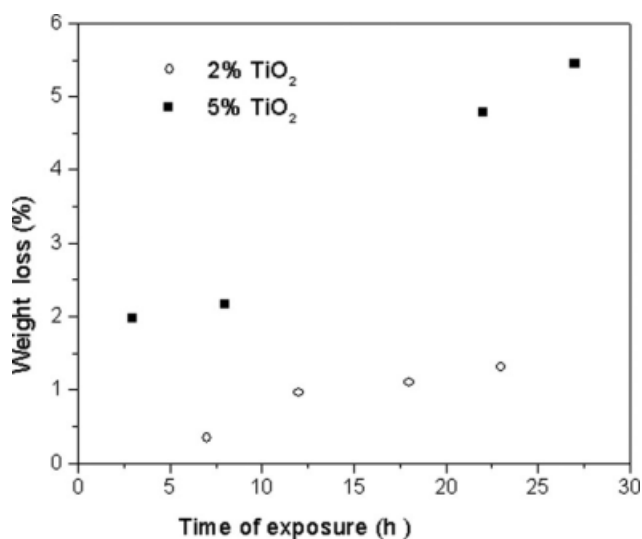

Figure 6 SEM micrographs of the PHBV composites containing (a) 1 and (b) 2 wt % TiO$_2$.

The weight loss of PHBV/TiO$_2$ composites was observed as a function of the radiation time (Fig. 7). Small changes in the weight loss, which was dependent on the TiO$_2$ content, were observed during 23 h of exposure, and this was also confirmed by the hydrolytic degradation of these systems. All the other investigated composites showed similar behavior that depended on the TiO$_2$ content. Further experiments with prolonged UV exposure are in progress to clarify the mechanisms of degradation under UV light.
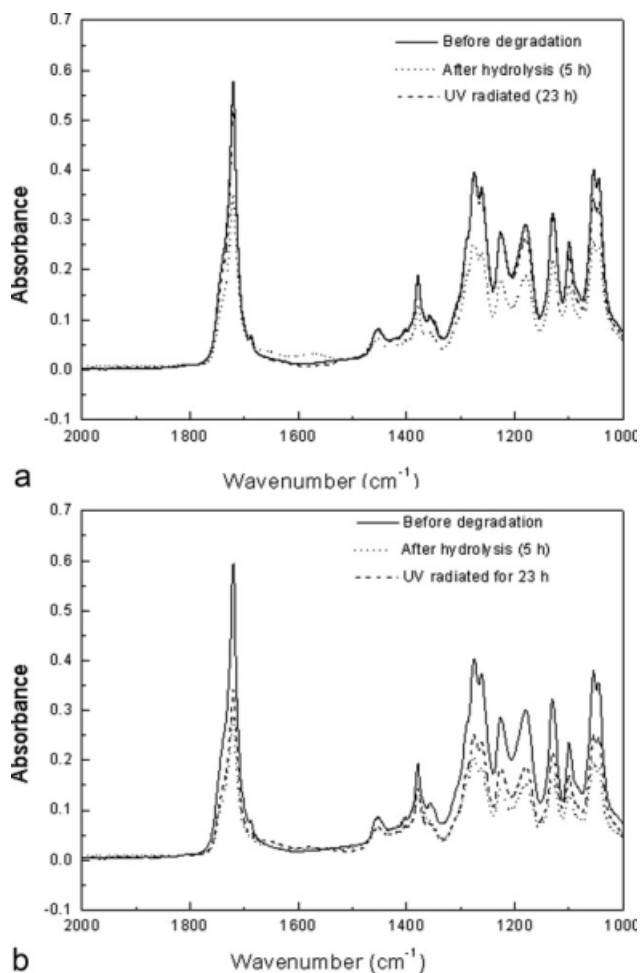
FTIR characterization of the hydrolytically and photocatalytically degraded films

Composite films degraded hydrolytically and by UV radiation were characterized with FTIR spectroscopy. FTIR–ATR spectra of PHBV/TiO$_2$ with 2 or 5 wt % TiO$_2$ (hydrolytically treated and UV-radiated) are presented in Figure 8(a,b). Some crystalline-sensitive bands increased in their intensity, whereas others decreased to a different extent in response to the greater crystallinity of the systems. The calculated CIs (e.g., the CIs for the composites containing 2 or 5 wt % TiO$_2$) are presented in Table III. Regardless of whether the polymer films were hydrolytically degraded or UV-irradiated, the CIs increased. This result supports the hypothesis that the degradation process preferentially occurs in amorphous domains, thus increasing the total crystallinity of the system.[9]

It is well known that the degradation rate of bacterial polyesters is strongly dependent on the x_c value and morphology. However, the x_c values and CIs (FTIR data) could not be invoked to explain the

Figure 8 FTIR spectra of degraded (hydrolytically treated and UV-radiation-treated) composite films containing (a) 2 or (b) 5 wt % TiO$_2$.

observed increase in the hydrolytic rate as well as degradation with exposure to UV radiation.

CONCLUSIONS

PHBV/TiO$_2$ nanocomposites were fabricated and characterized with DSC, TGA, and FTIR spectroscopy. It was shown that the presence of the TiO$_2$ nanofiller had no great influence on the crystallization and melting behavior of the pure PHBV polymer matrix. Significant acceleration of the degradation rates in a strong base medium was detected with the increase in the TiO$_2$ content. It was also confirmed that the TiO$_2$ particles enhanced the thermal stability and photocatalytic degradation of PHBV.

Figure 7 Weight loss/radiation time dependence for the PHBV composites containing 2 or 5 wt % TiO$_2$.

References

1. Bogoeva-Gaceva, G.; Avella, M.; Malinconico, M.; Buzarovska, A.; Grozdanov, A.; Gentile, G.; Errico, M. Polym Compos 2007, 28, 98.

2. Kaplan, D. L. Biopolymers from Renewable Resources; Springer: New York, 1998.
3. Yu, L.; Den, K.; Lin, L. Prog Polym Sci 2006, 31, 576.
4. Avella, M.; LaRota, M.; Martuscelli, E.; Raimo, M.; Sadocco, P.; Elegir, E.; Riva, R. J Mater Sci 2000, 35, 829.
5. Pluta, M.; Paul, M. A.; Alexandre, M.; Dubois, P. J Polym Sci Part B: Polym Phys 2006, 44, 299.
6. Yang, K. K.; Wang, X. L.; Wang, Y. Z. J Ind Eng Chem 2007, 13, 485.
7. Wu, T. M.; Chen, E. C. J Polym Sci Part B: Polym Phys 2006, 44, 598.
8. Wang, S. F.; Song, C. J.; Chen, G. X.; Guo, T. Y.; Liu, J.; Zhang, B. H.; Takeuchi, S. Polym Degrad Stab 2005, 87, 69.
9. Ha, C. S.; Cho, W. J. Prog Polym Sci 2002, 27, 759.
10. Choi, W. M.; Kim, T. W.; Park, O.-O.; Chang, Y. K.; Lee, J. W. J Appl Polym Sci 2003, 90, 525.
11. Cho, S.; Choi, W. J Photochem Photobiol A 2001, 143, 221.
12. Mizutani, M.; Skakibara, H.; Takeno, A.; Miwa, M.; Yokoi, T. Polym Prepr Jpn 2006, 55, 2305.
13. Yew, S.-P.; Tang, H.-Y.; Sudesh, K. Polym Degrad Stab 2006, 91, 1800.
14. Miyauchi, M.; Li, Y.; Shimizi, H. Environ Sci Technol 2008, 42, 4551.
15. Augugliaro, V.; Baiocchi, C.; Prevot, A. B.; Garcia-Lopez, E.; Loddo, V.; Malato, S. Chemosphere 2002, 4, 1223.
16. Fukuda, N.; Tsuji, H. J Appl Polym Sci 2005, 96, 190.
17. Scandola, M.; Focarete, M. L.; Adamus, G.; Sikorska, W.; Baranovska, I.; Swierczek, S.; Gnatowski, M.; Kowalczuk, M.; Jedlinski, Z. Macromolecules 1999, 30, 2568.
18. Bell, J. P.; Murayama, T. J. J Polym Sci 1969, 7, 1059
19. Organ, S. J.; Barham, P. J. J Mater Sci 1991, 26, 1368.
20. Qian, J.; Zhu, L.; Zhang, J.; Whitehouse, R. J Polym Sci Part B: Polym Phys 2007, 45, 1564.
21. Bruzand, S.; Bourmaud, A. Polym Test 2007, 26, 652.
22. Cheng, C.; Dong, L.; Yu, P. Eur Polym J 2006, 42, 2838.
23. Kansiz, M.; Billman-Jacobe, H.; McNaughton, D. Appl Environ Microbiol 2000, 66, 3415.
24. Shangguan, Y.-Y.; Wang, Y.-W.; Wu, Q.; Chen, G.-Q. Biomaterials 2006, 27, 2349.