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Polymer 40 (1999) 3703–3710

polymer

Compatibility and degradation of blends of poly(caprolactone)–poly(ethylene glycol) block copolymer and polypropylene

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Received 27 February 1998; received in revised form 24 April 1998; accepted 4 August 1998

Abstract

Blends of poly(caprolactone)–poly(ethylene glycol) block copolymer (PCE) with polypropylene (PP) were extruded followed by compression moulding. The compatibility and degradation behaviour of the blends were investigated. The results showed that the PCE phase tended to disperse as discrete particles in the PP matrix of the PP/PCE 75/25 blend. This discrete PCE phase was incompatible with the PP matrix. Maleic anhydride (MA) grafted PP was found to improve the compatibility between the PCE and PP phases effectively. Consequently, the MA-compatibilized PP/PCE 75/25 blend experienced significant losses in weight and tensile strength, compared with uncompatibilized PP/PCE 75/25 blend, after immersion in a buffer solution (pH = 6.0) at 45°C for extended periods of time. Water sorption and contact angle measurements also revealed that MA-compatibilized PP/PCE 75/25 blend is more hydrophilic than the uncompatibilized counterpart. The effect of the compatibilizing agent on the morphology and degradation behaviour of PP/PCE blends is discussed.

Keywords: Degradation; Polypropylene; Poly(caprolactone)–poly(ethylene glycol)

1. Introduction

Increasing environmental problems such as the disposal of plastic waste have renewed interest in the development of degradable polymers. Plastic waste is derived mainly from packaging materials such as rubbish bags, agricultural mulch films, food wrappers and containers. Synthetic polymers such as polyethylene and polystyrene are degraded in the presence of oxygen and ultraviolet rays [1,2]. However, the degradation process of polyethylene is extremely slow. Various approaches to render synthetic polymers degradable have been considered. Initial studies focused on the development of starch-based polymer blends to produce degradable plastics for many practical applications. This is because starch is abundant, inexpensive and a degradable natural raw material. However, starch is unsuitable for most uses as a plastic because of its poor physical and mechanical properties, and low dimensional stability [2,3]. Some efforts have been made to develop PCL/starch composites by blending the starch with polycaprolactone (PCL) [4]. PCL is a non-toxic aliphatic polyester with compatibility, permeability and capacity of blending with various polymers. The degradability of PCL in soil and seawater has been reported [5,6]. The degradation process of polymers, especially polyesters, take places through hydrolysis, thereby leading to molecular fragmentation or chain scission. Thus hydrolysis is the most important mechanism that controls the degradation of aliphatic polyesters. The hydrolysis of aliphatic polyesters begins with a water-uptake phase followed by hydrolytic splitting of the ester bonds. Benedict et al. reported that degradation proceeded in a selective manner, with amorphous regions being degraded prior to crystalline regions [7].

PCL is compatible with many polymers such as poly(vinyl chloride), chlorinated polyethylene, polycarbonate, poly(amide-6), poly(styrene-*co*-acrylonitrile) and ethylene terephthalate–caprolactone copolyester [8–13]. It should be noted that PCL also has some shortcomimgs. The degradation rate of PCL is slow because it has a high degree of crystallinity [14]. Moreover, the relatively high cost of PCL precludes high-volume production of this polymer for industrial applications. Several workers have attempted to improve the degradability of PCL through copolymerization. For example, copolymers based on PCL and poly(lactic acid) (PLA) have been synthesized, and the rate of hydrolysis of P(CL-*co*-LA) films is higher than that of PCL homopolymer [15].

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PII: S0032-3861(98)00623-5

Recently, Wang and Qiu [16] synthesized a poly(caprolactone)–poly(ethylene glycol) ABA-type block copolymer comprising PCL (A) and PEG (B) segments by copolycondensation of ϵ-CL with PEG mixtures in the presence of tetra-n-butyl titanate ($Ti(OBu)_4$) catalyst at high temperature. This copolymer is abbreviated as PCE in this paper. Similarly, Zhu et al. have also synthesized PCE copolymer by anionic ring-opening polymerization of ϵ-CL initiated by alkali metal alkoxide derivatives of PEG [17]. The degradation of PCE copolymer is reported to increase with decreasing crystallinity of the polymer, and can be controlled by adjusting the ratio of PCL to PEG components. Moreover, the degradation rate of PCE copolymer is relatively much higher than that of the PCL copolymer [16]. In this respect, it is advantageous to incorporate PCE into polyolefins in order to increase their decomposition rate. The physical properties of PCL/PEG block copolymer blended with polyolefins have been reported by Koleske [18]. But the morphological control and degradation behaviour of these blends were not reported. As blends of PCE and polyolefins are immiscible, compatibilization is needed to improve adhesion between the components. John et al. [19] reported that maleic anhydride (MA) can be grafted to PCL and the copolymer produced can be used as a compatibilizing agent for polymeric materials. More recently. Tjong and Bei prepared MA-compatibilized low-density polyethylene (LDPE)/PCE blends. The results showed that the maleated LDPE/PCE blends degrade substantially upon immersion in buffer solution, while the uncompatibilized LDPE/PCE blends are relatively unaffected [20].

In this study we have attempted to prepare degradable polypropylene (PP)/PCL film specimens by compression moulding and studied the effect of MA compatibilization on the morphology, degradation, static and dynamic mechanical behaviour of PP/PCE blends. For comparison, uncompatibilized and MA-compatibilized PP/PCL blends are also prepared and their various properties are investigated.

2. Experimental

2.1. Materials

PCL used in this work was purchased from Aldrich Chemical Company. The PCE block polymer was synthesized by copolymerization of ϵ-CL and PEG segments in the presence of $Ti(OBu)_4$, and was supplied by the Institute of Chemistry, Academia Sinica (China). The compositional ratio of PCL/PEG in PCE was fixed at 60/40 mol%. Its structural formula is

$$H–[–O–(CH_2)_5–CO–]_n–O–(CH_2CH_2O)_m–[CO–(CH_2)_5–O–]_n–H$$

PP is a commercial product of Himont Company (Profax 6331) with a melt flow index of 12 g/10 min. Maleic anhydride (MA) supplied by Fluka Chemie and dicumyl peroxide (DCP) produced by Aldrich Chemical Company were used for the maleation of PP. The average molecular weight of PCL and PCE was 65 000 and 66 000 g mol^{-1}, respectively.

2.2. Blend compounding

PCL and PCE were dried in an oven at 50°C for 48 h. PP/PCE blends were prepared in a Brabender twin-screw extruder at 200°C and at 40 rev min^{-1} in the following weight ratios: 100/0, 90/10, 75/25 and 60/40. The blends were pelletized upon exiting the extruder. These pellets were then compression-moulded into films with thicknesses of 0.2 and 2.4 mm.

Maleic-anhydride-grafted PP was prepared in the same extruder, the weight ratios of PP/MA/DCP being set at 96/6/0.3. Subsequently, we mixed 10% maleated PP and 90% PP in the Brabender extruder, again at 200°C and at 40 rev min^{-1}. The extudates were cut into pellets by the pelletizer. We designated these pellets as MAP in this paper. Finally, MAP/PCE blends with weight ratios of 100/0, 90/10, 75/25 and 60/40 were blended in the extruder, pelletized and compression-moulded into films of 0.2 and 2.4 mm thickness. For comparison, PP/PCL and MAP/PCL film specimens were also blended under similar processing conditions.

2.3. Thermal analysis

The thermal behaviour of the blends investigated was determined with a Seiko thermogravimetric and differential thermal analyser (TGA/DTA) (model SSC-5200). All scans were carried out from 30 to 600°C at a heating rate of 10°C min^{-1}. Dynamic mechanical analysis (d.m.a.) was conducted on rectangular specimens with dimensions of 40 mm × 12 mm × 2.4 mm with the aid of Du Pont dynamic mechanical analyser (model 983) at a fixed frequency of 1 Hz. Rectangular specimens were cut from the compression-moulded films. The temperature range studied was from $-$ 80 to 60°C with a heating rate of 2°C min^{-1}.

2.4. Static tensile tests

Tensile specimens with a gauge length of 37 mm were prepared from the compression-moulded films according to ASTM standard D882, and tested with an Instron tensile tester (model 4206). All tests were performed at a crosshead speed of 1 mm min^{-1}. Seven specimens of each composition were tested and the average values are reported.

2.5. Scanning electron microscopy (SEM)

The morphology of cryogenically fractured surfaces of the blends was examined in a scanning electron microscope (JEOL JSM 820). The surfaces were sputter-coated with a thin layer of gold before observation.

Table 1
Thermal properties of PP, MAP and some blends investigated

Specimen	T_m^1 (°C)	T_m^2 (°C)	T_m^3 (°C)	$T_{-5\%}$ (°C)
PP	—	—	168	387
MAP	—	—	173	355
PCL[a]	64	—	—	—
PCE[a]	66	—	—	—
PP/PCL 75/25	63	—	169	345
MAP/PCL 75/25	57	150	168	339
PP/PCE 75/25	63	—	165	322
MAP/PCE 75/25	61	147	167	323

[a] Data taken from [20].

2.6. Degradation measurements

Film specimens with dimensions of 150 mm × 150 mm × 0.2 mm were placed in a plastic container filled with buffer solution (pH = 6.0). The buffer solution was prepared from 0.2 M potassium benzene dicarbonic acid and a small amount of NaOH. The plastic container was then placed in a thermobath regulated at 45°C. The initial weight of the specimens was measured prior to immersion tests. The films were immersed in the buffer solution for various specified times, i.e., 1, 2, 3, 4, 5 and 6 months. They were removed periodically, washed with distilled water and dried in a desiccator filled with P_2O_5. Their weights were taken after drying to a constant weight. Furthermore, film specimens that had been immersed in the buffer solution for various times were also subjected to tensile tests.

2.7. Water sorption

For these measurements, the film specimens were immersed in the buffer solution (pH = 6.0) at 45°C for various specified times. The specimens were removed periodically, washed with distilled water, dried with filter paper and weighed (W_1). The film specimens were then dried over P_2O_5 to a constant weight (W_2). The amounts of water absorbed by the specimens were determined from the following equation:

$$\text{Water sorption (\%)} = \left[(W_1 - W_2)/W_2\right] \times 100 \qquad (1)$$

where W_1 is the weight of the specimen after water sorption, and W_2 is the weight of the dried specimen.

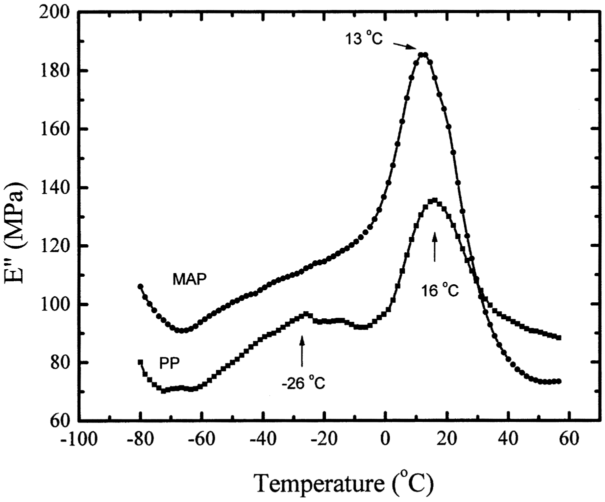


Fig. 1. Loss modulus spectra of PP and MAP.

2.8. Contact angle measurement

The contact angle of water on the specimens was determined with a FACE CA-D contact angle meter (Kyowa Kaimenkagaku Company) in air.

3. Results and discussion

3.1. Compatibility

3.1.1. Thermal behaviour

The melting temperatures (T_ms) of PP, MAP and some blends determined by the differential thermal analysis (d.t.a.) technique are listed in Table 1. For comparison, the melting temperatures of PCL and PCE determined previously by Tjong and Bei [20] are also tabulated. This table shows that the melting temperatures of PCL and PP phases in the PP/PCL 75/25 blend are 63 and 169°C, respectively. This implies that both phases are incompatible. Similarly, the PP and PCE phases in the PP/PCE 75/25 blend are also incompatible according to the large difference in melting temperature between these two phases. However, the melting point of the PP phase in the MAP/PCL 75/25 blend tends to shift to lower temperature, as a resulting of the grafting of PP with MA. Moreover, a new peak at 150°C is observed in the d.t.a. curve of the MAP/PCL 75/25 blend. In this respect, the compatibility between PP and PCL phases is improved by incorporating PP-grafted maleic anhydride in the blend. Similar thermal behaviour is observed for the MAP/PCE 75/25 blend. Table 1 also lists the 5% weight loss temperature ($T_{-5\%}$) determined by the thermogravimetric analysis (t.g.a.) technique for PP, MAP and some blends investigated. Apparently, $T_{-5\%}$ of PP is 387°C, but the addition of 25 wt% PCL or PCE to PP leads to a considerable reduction in $T_{-5\%}$. This implies that the thermal stability of the PP/PCL and PP/PCE blends is reduced owing to the incorporation of aliphatic polyester segments in these blends. Thus PP/PCE blends can degrade more easily than PP homopolymer.

Fig. 1 shows typical loss modulus versus temperature curves for PP homopolymer and MAP copolymer. It is apparent from the curve that PP homopolymer shows two relaxations; i.e., α-relaxation at 16°C and β-relaxation at -26°C. The β-relaxation is attributed to the glass transition of the amorphous phase [21,22]. The relaxation temperatures of PP determined by d.m.a. in this study are in good agreement with those of PP reported in the literature [23]. The α-relaxation temperature of MAP copolymer is slightly lower

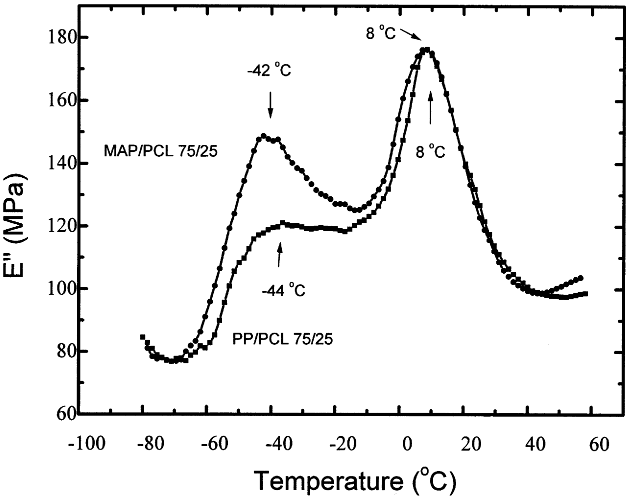


Fig. 2. Loss modulus spectra of PP/PCL 75/25 and MAP/PCL 75/25 blends.

than that of PP homopolymer. Fig. 2 shows the loss modulus spectra of PP/PCL 75/25 and MAP/PCL 75/25 blends. The glass transition temperatures (T_gs) of PCL and PCE are reported to be − 47 and − 46°C, respectively [20]. From Fig. 2, it can be seen that a broad transition occurs between the β-relaxation peak of the PP phase and the T_g of the PCL phase. This result suggests that the PP matrix and PCL phase are nearly immiscible. This broad peak tends to become sharper in the loss modulus spectrum of the MAP/PCL 75/25 blend, indicating that the compatibility between PP and PCL phases is improved considerably by grafting PP with maleic anhydride. A similar reducing trend is observed between the T_gs of PP and PCE in the compatibilized MAP/PCE 75/25 blend (Fig. 3).

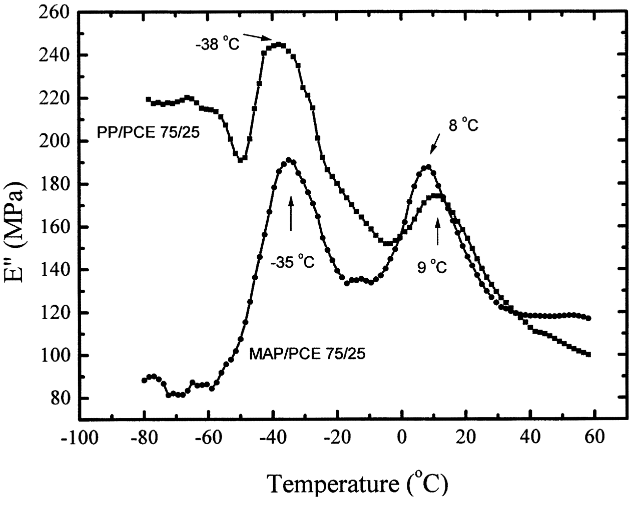


Fig. 3. Loss modulus spectra of PP/PCE 75/25 and MAP/PCE 75/25 blends.

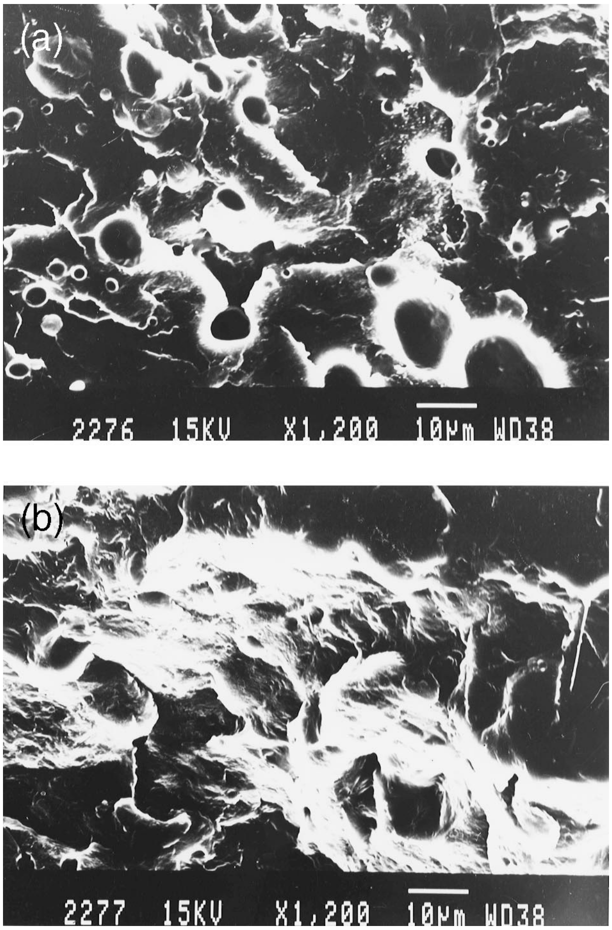


Fig. 4. SEM fractographs showing the morphology of (a) PP/PCL 75/25 and (b) MAP/PCL 75/25 blends.

From the dynamic mechanical analysis, it is apparent that PP and PCE as well as PCL phases are incompatible. For the MAP/PCE 75/25 blend, it is observed that the compatibility is improved considerably by blending PCE with maleated PP. As the PCE copolymer comprises PEG segments, it is believed that the functional groups of MAP would react with the terminal hydroxyl groups of PEG segments [24]. Since PEG forms complexes with carboxylic-acid-containing polymers, especially in solution, it appears that grafting of MA to PP tends to enhance the compatibility between the PP and PEG segments [22]. In other words, there exists an interaction between the functional groups of MAP and the hydroxyl terminal groups of the PCE phase in the MAP/PCE 75/25 blend.

3.1.2. Blend morphology

Fig. 4(a) and (b) are SEM micrographs showing the fracture morphology of PP/PCL 75/25 and MAP/PCL 75/25 blends. It can be seen from Fig. 4(a) that the PCL phase is dispersed as spherical particles with a diameter of about 2–10 μm in the PP matrix. Moreover, the boundary between the dispersed phase and the PP matrix is distinct. On the other hand, fine PCL particles are distributed uniformly within the PP matrix of the MAP/PCL 75/25 blend and the boundaries between these fine PCL particles and the PP matrix are obscure. The morphologies of the PP/PCE

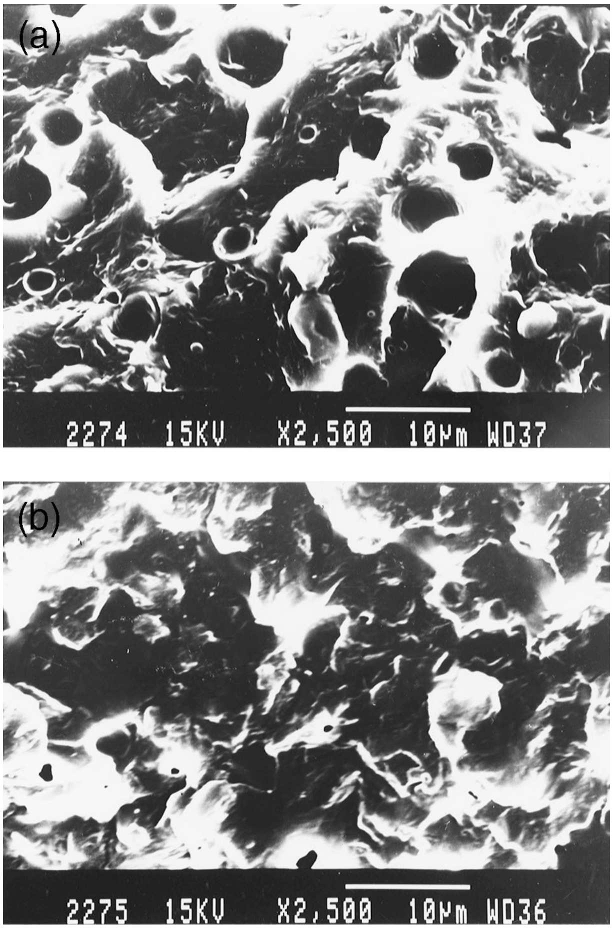


Fig. 5. SEM fractographs showing the morphology of (a) PP/PCE 75/25 and (b) MAP/PCE 75/25 blends.

75/25 and MAP/PCE 75/25 blends are similar to those of PP/PCL 75/25 and MAP/PCL 75/25, respectively (Fig. 5(a) and (b)). From SEM observations, it is evident that the functional groups of MAP interact with the PEG segments of the MAP/PCE 75/25 blend, thereby increasing the interfacial adhesion between PCE and PP, and consequently promoting a fine dispersion of PCE phase.

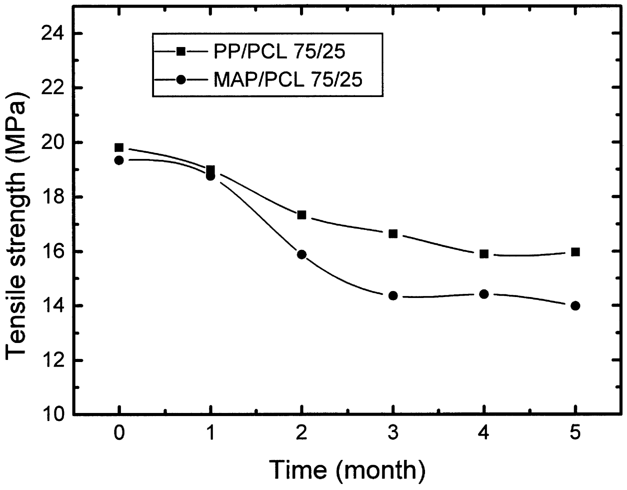


Fig. 6. Tensile strength versus time for PP/PCL 75/25 and MAP/PCL 75/25 blends.

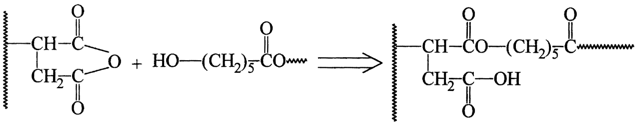
3.2. Degradation behaviour

3.2.1. Strength deterioration

The degradation of polymers is a very complicated process. The rate of degradation is generally affected by water absorption, chemical composition, crystallinity and chain scission [25,26]. The degradation of both uncompatibilized and MA-compatibilized PP/PCL and PP/PCE blends is evaluated by changes in the mechanical strength of the blends and in the weight loss of the polymers. Furthermore, a waxy appearance is observed in the blend containing 40 wt% PCE. In this case, degradation studies are mainly concentrated on the blend with 25 wt% PCE. Figs 6 and 7 show plots of the static tensile strength with time for the blends PP/PCL 75/25 and MAP/PCL 75/25, as well as PP/PCE 75/25 and MAP/PCE 75/25, respectively, after immersion in buffer solution for various periods of time. The MAP/PCE 75/25 blend exhibits a linear decrease in tensile strength with time. This can be attributed to degradation of the MAP/PCE 75/25 blend through hydrolysis during immersion in the buffer.

3.2.2. Weight loss

Fig. 8 shows the weight loss curves of PP/PCL 75/25 and MAP/PCL 25/75 blends exposed in the buffer solution at 45°C for various periods of time. This figure indicates that the PP/PCL 75/25 blend shows a very small increase in weight loss after immersion in buffer solution for 5 months. This is as expected because the degradation rate of PCL is relatively slow. However, the MAP/PCL 75/25 blend loses weight almost linearly during the first 2 months of exposure. After an initial rapid increase, the weight loss slows down gradually up to 4 months immersion, and increases again to 8.1% after 5 months. Apparently, there exists an interaction between the functional groups of MAP and PCL. It is suggested that the anhydride group, grafted on PP, can react with the terminal hydroxide of PCL during melt mixing, thereby giving an ester linkage. It has been reported that anhydride groups grafted on a polymer can react with the hydroxide group of polyester to form an ester linkage [27]. The possible reaction for the formation of ester linkages is suggested to be as follows



$$\begin{array}{l} -\text{CH}-\overset{\overset{\text{O}}{\|}}{\text{C}}\diagdown \\ \;\;| \qquad\quad\;\; \text{O} \\ \text{CH}_2-\underset{\underset{\text{O}}{\|}}{\text{C}}\diagup \end{array} + \text{HO}-(\text{CH}_2)_5-\overset{\overset{\text{O}}{\|}}{\text{C}}\text{O}\sim \Longrightarrow \begin{array}{l} -\text{CH}-\overset{\overset{\text{O}}{\|}}{\text{C}}\text{O}-(\text{CH}_2)_5-\overset{\overset{\text{O}}{\|}}{\text{C}}\sim \\ \;\;| \\ \text{CH}_2-\underset{\underset{\text{O}}{\|}}{\text{C}}-\text{OH} \end{array}$$

The ester linkages between the PCL and PP segments are more degradable because of their hydrophilic behaviour. Indeed, the water sorption measurements (discussed in the next section) clearly indicate that the MAP/PCL 75/25 blend absorbs more water than the PP/PCL 75/25 blend on

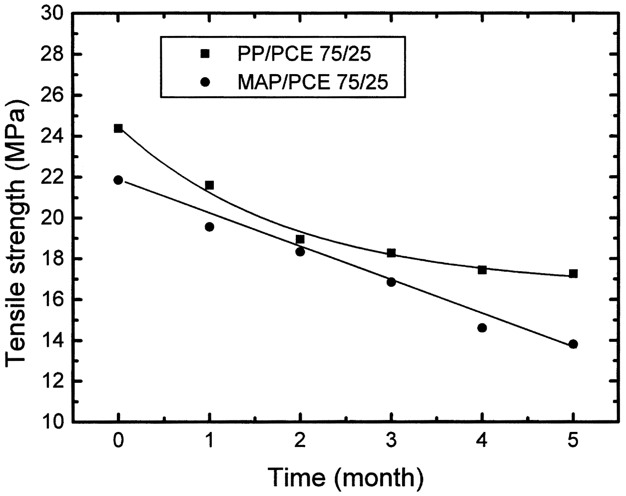


Fig. 7. Tensile strength versus time for PP/PCE 75/25 and MAP/PCE 75/25 blends.

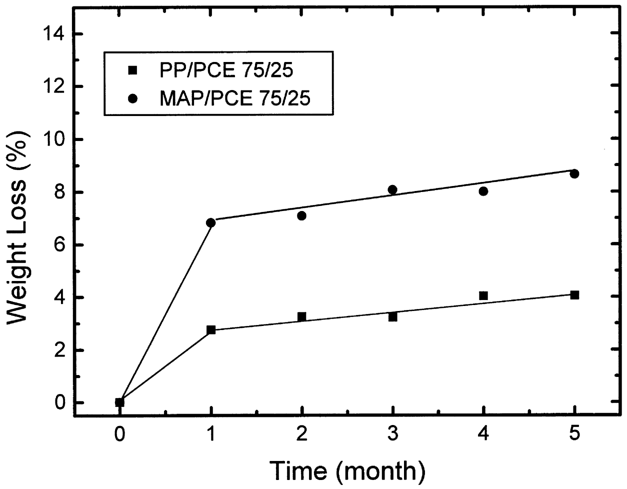


Fig. 9. Variation of weight loss with immersion time for PP/PCE 75/25 and MAP/PCE 75/25 blends.

exposure in buffer solution. The higher water absorption is favourable for the degradation of the MAP/PCL 75/25 blend.

The variation of weight loss with time for the PP/PCE 75/25 and MAP/PCE 75/25 blends is shown in Fig. 9. It can be seen that the weight loss increases rapidly for both the compatibilized and uncompatibilized PP/PCE blends during the first month of immersion in buffer solution. Afterwards, the weight loss of both blends increases only slowly for extended periods of immersion. It is noted that the MAP/PCE 75/25 blend exhibits a much higher weight loss than the PP/PCE 75/25 blend after exposure for extended times. Compared with Fig. 8, it is apparent that the PP/PCE 75/25 blend exhibits a higher weight loss than the PP/PCL 75/25 blend. This is due to the incorporation of PEG segments in the PCE phase of the PP/PCE 75/25 blend. Wang and Qiu reported that the degradability of the PCE block copolymer is considerably higher than that of PCL owing to the introduction of the PEG component. The degradability and water sorption of PCE copolymer can be controlled by changing the PEG content [16]. On the basis of weight loss measurements, it appears that PP-grafted maleic anhydride is very effective in increasing the degradation rate of PP/PCL and PP/PCE blends. This compatibilizer effectively improves the hydrophilicity of the blends by increasing the amount of water absorbed during immersion, as discussed in the next section. The degradability of MAP/PCE blends containing various PCE contents is summarized in Fig. 10. Generally, all these blends exhibit a similar degradation behaviour in buffer solution at 45°C, but the MAP/PCE 75/25 exhibits a slightly higher weight loss than the other two blends.

3.2.3. Microstructural change

It should be noted that the morphology of blends after immersion in a buffer solution can provide useful

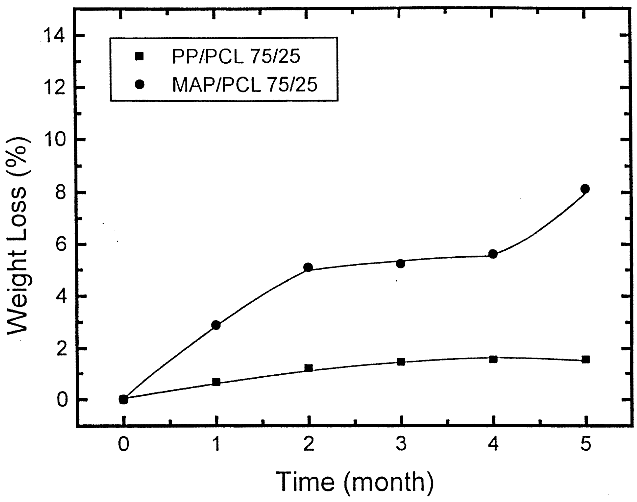


Fig. 8. Variation of weight loss with immersion time for PP/PCL 75/25 and MAP/PCL 75/25 blends.

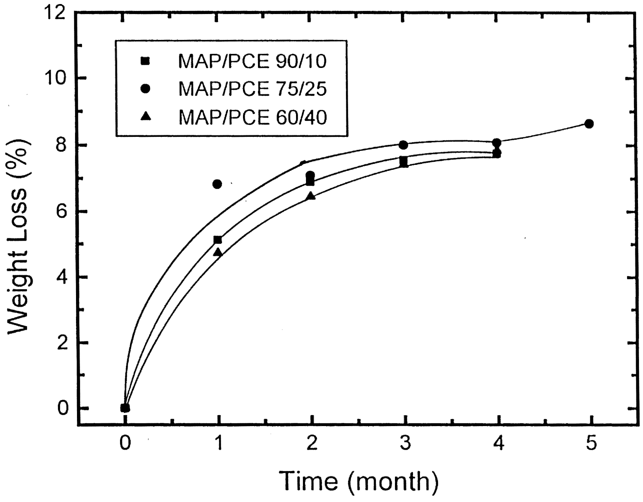


Fig. 10. Variation of weight loss with immersion time for MAP/PCE 90/10, MAP/PCE 75/25 and MAP/PCE 60/40 blends.

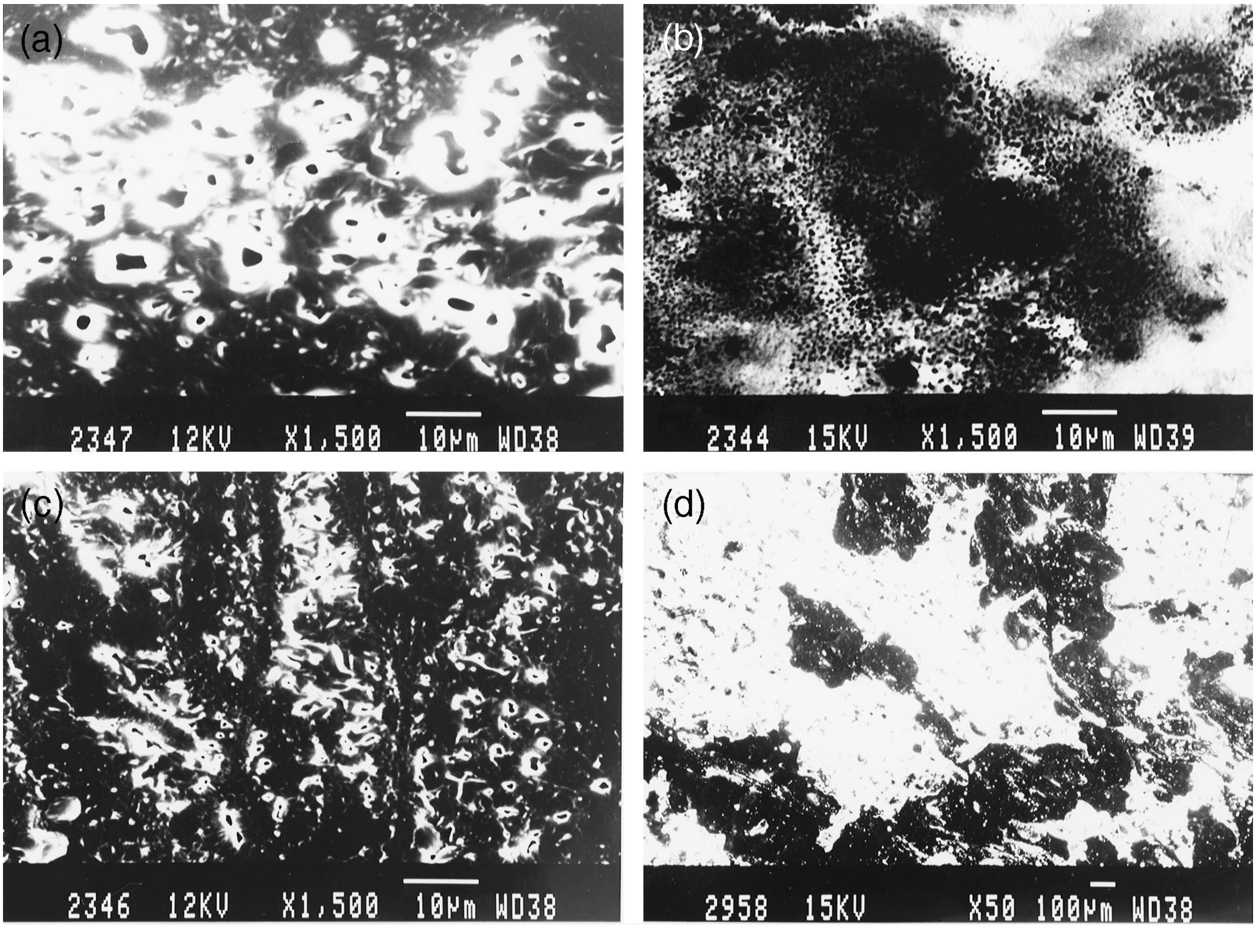


Fig. 11. SEM micrographs showing the surface appearance of (a) PP/PCL 75/25, (b) MAP/PCL 75/25, (c) PP/PCE 75/25 and (d) MAP/PCE 75/25 blends.

information concerning their degradation behaviour. Fig. 11(a) and (b) are SEM micrographs showing the surface morphology of the PP/PCL 75/25 and MAP/PCL 75/25 blends after immersion in buffer solution for 4 months. Small cavities can be readily seen in the PP/PCL 75/25 blend owing to decomposition of the dispersed PCL phase after prolonged immersion. On the other hand, numerous fine cavities are distributed within the matrix of the MAP/PCL 75/25 blend. It is suggested that the matrix of the MAP/PCL 75/25 blend can be decomposed ultimately as numerous dispersed particles are degraded. The surface appearance of the PP/PCE 75/25 and MAP/PCE 75/25 blends after immersion in buffer solution for 4 months is shown in Fig. 11(c) Fig. 11(d), respectively. Generally, more cavities are formed in the PP/PCE 75/25 than the PP/PCL 75/25 specimen after prolonged immersion. However, spallation of the surface layer occurs in the compatibilized MAP/PCE 75/25 blend because the fine cavities tend to link together to form larger voids. Thus it appears that MA-grafted PP is more hydrophilic than PP, thereby leading to a faster rate of molecular fragmentation.

3.2.4. Hydrophilicity

The amount of water absorbed by aliphatic polyesters during immersion plays a key role in enhancing their rate of degradation. Water content and contact angle of distilled water on the polymer surface are used to evaluate the hydrophilicity. Fig. 12(a) shows the water sorption as a function of immersion time for the PP/PCL 75/25 and MAP/PCL 75/25 blends in buffer solution. Apparently, the PP/PCL 75/25 blend shows little change in the percentage of water sorption during immersion for up to 5 months. However, the MAP/PCL 75/25 blends shows about a four to eight times increase in the uptake of water during immersion. It is interesting to see that the MAP/PCE 75/25 blend shows a linear increase in the percentage of water sorption (Fig. 12(b)). In this case, the diffusivity rate of water is increased, thereby enhancing the degradation rate of this blend as shown in Fig. 9. It has been reported that the hydrolysis of aliphatic polyesters starts with a water-uptake phase followed by hydrolysis of the ester bonds [28]. As mentioned above, numerous fine PCE particles are distributed within the PP matrix of the MAP/PCE 75/25 blend and there exists an interaction between the functional groups of MAP and PEG segments. Thus degradation of this blends starts with water uptake in the PCE phase, followed by the maleated PP matrix.

Finally, the results of water contact angle measurements for the specimens are listed in Table 2. It is noticed that the

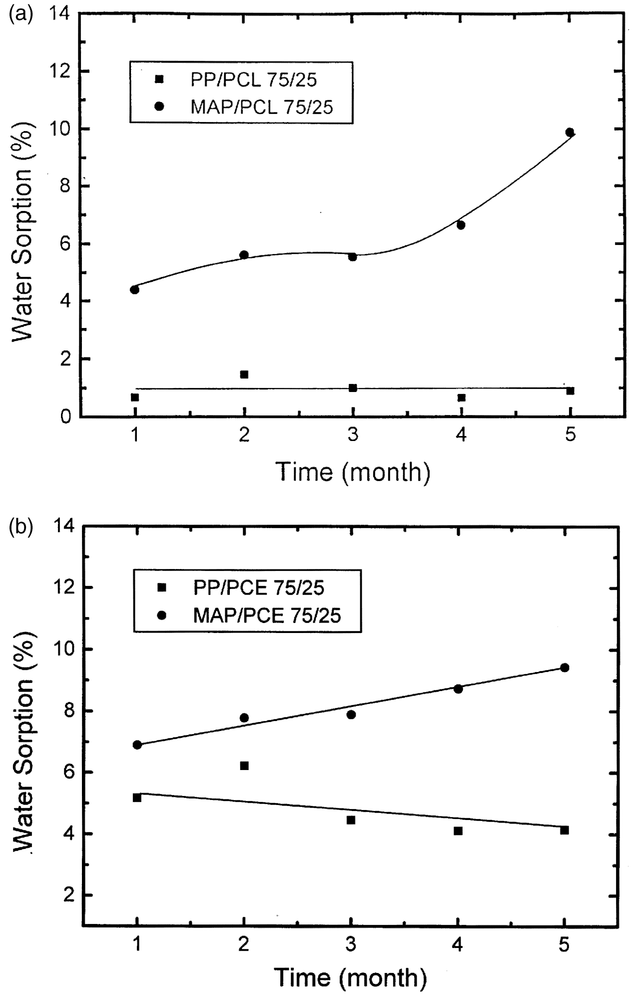


Fig. 12. Variation of water sorption with immersion time for (a) PP/PCL 75/27, MAP/PCL 75/25 and (b) PP/PCE 75/25, MAP/PCE 75/25 blends.

MAP copolymer has a smaller contact angle with water than the PP homopolymer. Moreover, the MAP/PCE 75/25 blend exhibits the smallest contact angle of 38.5°. It is noted that the MA-compatibilized PP/PCE and PP/PCL blends have smaller contact angles than their corresponding uncompatibilized counterparts. This implies that the MA-compatibilized blends are more hydrophilic than their uncompatibilized counterparts.

4. Conclusion

Blends of PCE and PP were prepared by extrusion followed by compression moulding. Immersion measurements showed that the PP/PCE 75/25 blend exhibits a relatively low weight loss after immersion in buffer solution for extended periods of time. SEM examination revealed that the PCE phase tended to disperse as discrete particles in the PP matrix of this blend. Furthermore, d.m.a. measurements indicated that the PCE and PP phases are incompatible. MAP was found to be very effective in improving the compatibility between PCE and PP phases. Water sorption and contact angle measurements indicated that the MA-compatibilized PP/PCE 75/25 blend is more hydrophilic than its uncompatibilized counterpart. In this respect, the MAP/PCE 75/25 blend exhibited significant losses in weight and tensile strength after immersion in buffer solution. SEM observation showed that fine cavities tend to link together to form larger voids, thereby resulting in spallation of the surface layer of the MAP/PCE 75/25 blend. Such preferential attack is responsible for the high degradation rate of the MAP/PCE 75/25 blend in buffer solution.

Table 2
Contact angles of film specimens with water

Specimen	Contact angle (°)
PP	93
MAP	89
PP/PCL 75/25	75
MAP/PCL 75/25	64
PP/PCE 75/25	64
MAP/PCE 75/25	39

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