Atactic Poly(methyl methacrylate) Blended with Poly(3-D(−)hydroxybutyrate): Miscibility and Mechanical Properties

S. CIMMINO,[1] P. IODICE,[1] C. SILVESTRE,[1] F. E. KARASZ[2]

[1] Istituto di Ricerca e Tecnologia delle Materie Plastiche, CNR, Via Toiano, 6, 80072 Arco Felice (Naples), Italy

[2] Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003

ABSTRACT: Atactic poly(methylmethacrylate), aPMMA, was blended with poly(3-D(−)hydroxybutyrate), PHB, up to a maximum composition of 25% of polyester, at 190°C in a Brabender-like apparatus. The resulting blends quenched from the melt to room temperature were completely amorphous, and exhibited a single glass transition using DSC and DMTA, indicating miscibility of the components for this time–temperature history. Tensile experiments showed that at room temperature the 10/90 and 20/80 PHB/aPMMA blends exhibited higher values of strain at break, and slight decreases of the modulus and stress at break compared to neat aPMMA. The tensile energy at break was almost twice that of neat aPMMA. Tensile tests were also performed at 80°C, at which point the 25/75 and 20/80 PHB/aPMMA blends are above T_g, while the 10/90 and neat aPMMA are below T_g. The stress–strain curves obtained were functions of the physical state of the amorphous phase, and also depended on the difference between the test temperatures and T_g. In particular, comparing the neat aPMMA and the blends, decreases of the modulus and stress at break and a respectable increase in the strain at break were observed in the latter. Finally, the results were commented considering the thermal degradation of PHB in the melt during the blend preparation. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 746–753, 2000

Key words: poly(3-D(−)hydroxybutyrate); atactic poly(methylmethacrylate); blends; thermal properties; dynamic mechanical thermal properties; tensile properties

INTRODUCTION

There has been some effort devoted to finding applications for poly(3-D(−)hydroxybutyrate) (PHB). The PHB is a naturally occurring aliphatic polyester produced by bacterial fermentation, and has attracted interest for medical and agricultural applications because of its biodegradability and good biocompatibility. High production cost, low impact resistance, and very narrow processing window have, nevertheless, limited its use. To overcome these limitations, two processes have been attempted: copolymerization and blending. The copolyesters obtained are usually more expensive than PHB, have a complex composition distribution, and the properties are finally not as good as expected. Blending seems more promising. Several studies have been reported, including blends of PHB with poly(ethylene oxide) (PEO),[1] poly(vinyl acetate) (PVAc),[2] poly(epichlorohydrin),[3,4] cellulose esters,[5] atactic poly(methyl methacrylate) (aPMMA),[6–10] and poly(vinylidene chloride-*co*-acrylonitrile) (P(VDC-AN)).[11]
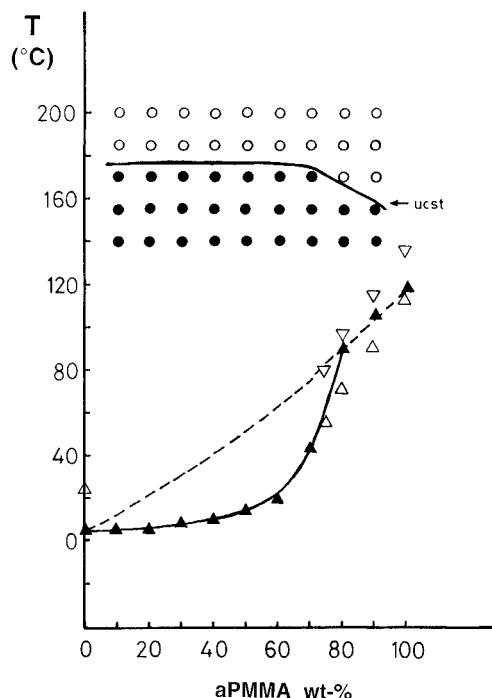

Figure 1 Phase diagram of PHB/aPMMA blends: (○) one-phase region; (●) two-phase region; (▲) experimental DSC T_g of miscible blends (from ref. 8); (- - -) T_g curve predicted by Fox equation (from ref. 8); (—) T_g curve obtained by Kovacs' theory (from ref. 8). (△) DSC T_g and (▽) tan δ of melt-mixed samples.

Particular attention has been paid to the PHB/aPMMA system. Thus, in ref. 7 it is reported that the two components form a single glassy amorphous phase in compositions up to 20 wt % of PHB at room temperature; at concentrations of PHB higher than 20 wt %, the blends consist of neat PHB coexisting with a constant composition PHB/aPMMA mixture. We have found[8] that there is a temperature–composition range where the two components are miscible in all compositions. The phase diagram proposed by us has an upper critical solution temperature curve (ucst) (Fig. 1). The miscibility of PHB-rich blends can be detected only with quasi-instantaneous quenching from the one-phase region to temperatures lower than T_g. The fastest cooling rate obtainable with differential scanning calorimeter (DSC) is not sufficient to maintain the homogeneous melt phase for the 90/10 and 70/30 PHB/aPMMA blends during cooling. For aPMMA-rich blends, i.e., 20/80 and 10/90 PHB/aPMMA blends, a lower cooling rate is sufficient to preserve the amorphous character. The Fox equation fits the T_g-composition data only for the blends with PHB contents up to

30%. The T_g's of the blends with higher PHB content have been described by the Kovacs theory.[12,13] It was also shown[9] that if miscible blends are crystallized from the cold, the presence of the crystalline phase does not permit the phase separation of the amorphous components. Recently, Avella et al.[10] have undertaken a reactive blending procedure via water suspension polymerization of the acrylic monomer precursor in the presence of PHB. The compositions obtained were limited to 80/20 and 70/30 PHB/aPMMA, i.e., PHB-rich blends. A slight increase of the critical energy release factor (G_c) was found for these blends, which was attributed to the presence of grafted chains formed during the polymerization.

The aim of the present article was to obtain miscible aPMMA-rich blends and to study their properties by directly mixing the homopolymers in the melt, at temperatures corresponding to the one-phase region (open circles, Fig. 1). In fact, according to the results of ref. 8, it seems possible to obtain miscible blends at room temperature by melting the components at $T >$ ucst, and then cooling to $T < T_g$ at a rate sufficient to maintain the homogenous state and avoid phase separation. The temperature gap between the ucst and the T_g values of the aPMMA-rich blends (right side of Fig. 1) is not as large as for the PHB-rich blends. If this aim can be achieved, the aPMMA-rich blends will have T_g values lower than neat aPMMA, and might be expected to be less brittle than aPMMA itself.

EXPERIMENTAL

Materials

The polymers used were poly(3-D(−)hydroxybutyrate), PHB, generously supplied by Zeneca B.P., with $M_w = 790 \times 10^3$, $M_n = 260 \times 10^3$, and atactic poly(methylmethacrylate), aPMMA, (BDH) with $M_w = 116 \times 10^3$.

Preparation of Blends

Binary blends were obtained by mixing the aPMMA and PHB components in a Brabender-like apparatus (Rheocord EC of HAAKE Inc., New Jersey, USA). Particular care was given to the mixing time and temperature to limit thermal degradation of the PHB.[14,15] The mixing was performed at 190°C, 32 rpm for 4 min, then the mixing chamber was rapidly cooled. The blended polymers reached 120°C in 1 min and then room temperature in other

4 min. The mixing ratios of PHB/aPMMA (wt/wt) blends were 25/75, 20/80, 10/90, and 0/100.

In this article the blends will be reported as PHB/aPMMA ratios (not aPMMA/PHB), even if the major component was aPMMA. This is to maintain consistency with the symbolism used in ref. 8.

The DMTA spectrum and DSC thermogram of neat PHB were obtained on samples obtained by solution casting from the chloroform, which, after precipitation, were kept in a vacuum oven at 70°C for 8 h.

Preparation of Compression-Molded Samples

The blended polymers, obtained from the mixer, were first cut in small pieces and then compression molded in a heated press at a temperature of 190°C for 2 min without applied pressure to allow complete melting. After this period, a pressure of 100 bar was applied for 2 min. Then the plates of the press, fitted with cooling coils, were rapidly cooled to room temperature using cold water. The cooling system took 1 min to cool from 190 to 150°C, 2 min from 190 to 120°C, 3 min from 190 to 90°C, 5 min from 190 to 60°C, 6 min 30 s from 190 to 50°C, and 11 min from 190 to 30°C (room temperature). Finally, the pressure was released and the mold removed from the plates. The mold had a parallelepiped shape (100 × 70 mm). Samples 2.0 mm thick were used for the DSC, DMTA, and WAXS experiments, and 1.0 mm for tensile tests.

Thermogravimetric Analysis

Thermogravimetric analysis was performed from 30 to 500°C at a heating rate of 10°C/min by using a Mettler TG-50. The experiment was performed in air to obtain information on the thermal stability of the polymers and blends in more extreme situation, even if the thermal decomposition of PHB is not greatly influenced by presence of air or nitrogen.[14] Moreover, to investigate the formation of volatile products during the total period used for the blend preparation, isothermal thermogravimetric analysis at 190°C was performed on the blends and homopolymers up to 60 min.

Thermal Analysis

The calorimetric properties of the compression-molded samples were investigated using a differential scanning calorimeter (Mettler DSC-30).

The sample (about 12 mg) was heated from −50 to 200°C at the rate of 10°C/min. The glass transition temperature (T_g) was determined at the maximum of the peak in the transition zone obtained by applying the first derivative procedure included in the Mettler software.

WAXS Measurements

Wide-angle X-ray scattering measurements (WAXS) were carried out on a Philips (PW 1050 model) powder diffractometer (CuNi-filtered radiation) equipped with a rotating sample holder. The WAXS experiments were performed to detect crystallinity in the blends.

Dynamic Mechanical Measurements

Dynamic-mechanical data (DMTA) were collected at 1 Hz and at a heating rate of 3°C/min from −50 to 170°C, under nitrogen, using a Dynamic Mechanical Thermal Analyser MK III, Polymer Laboratories, configured for automatic data acquisition. The experiments were performed in the bending mode.

Parallelepiped-shaped specimens (10 × 7 × 2 mm) were cut from the compression-molded samples.

Tensile Tests

Dumbbell-shaped specimens were cut from 1 mm-thick sheets and used for the tensile measurements. Stress–strain curves were obtained using an Instron machine (Model 1122) at 25 and 80°C, at a crosshead speed of 10 mm × min^{-1}, gauge length = 22 mm, and nominal strain rate = 0.45 min^{-1}. Modulus, stress, and strain at yield and at break were calculated from these curves averaged over 10 specimens. Before the stress–strain measurement at 80°C, the sample was allowed to equilibrate for 30 min.

RESULTS AND DISCUSSION

Figure 2 shows the thermogravimetric curves of PHB, aPMMA, and their three blends. The PHB curve presents no loss of weight up to 260°C, indicating that during the heating no volatile products are formed up to this temperature, although a remarkable decrease of M_w certainly occurs, as will be discussed below. After 260°C, a sharp weight loss centered at about 280°C is observed. The aPMMA curve shows no weight loss up to 310°C, followed by a one-step loss centered at about 350°C. The blends show a decomposition process in two steps. The first step is likely due to
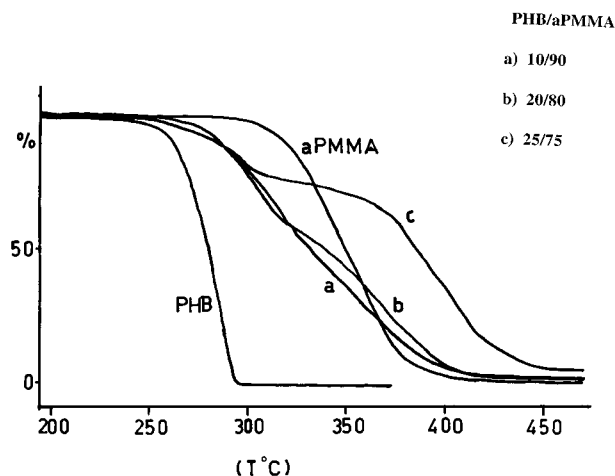
PHB/aPMMA

a) 10/90

b) 20/80

c) 25/75

Figure 2 Thermogravimetric curve of PHB, aPMMA, and PHB/aPMMA blends.

Table I   Glass Transition and Computed Molecular Weight of PHB as a Function of Thermo-oxidation at 190°C

Time (min)	$M_n \times 10^{-3}$	T_g (°C)
0	260	4
1	183	3.5
3	115	3
4	97	2.5
5	84	2
10	50	1
15	35.5	0.5
20	27.5	0
25	22.5	−0.5
30	19	−2
40	14.5	−3
50	12	−6
60	10	−9

the weight loss of PHB, and the second one to aPMMA. It is relevant to note that the second step of the weight loss for the 25/75 blends occurs at T higher than that of plain aPMMA. The reason for this trend is not clear at the moment, and will be investigated later. It is assumed that plain aPMMA and that present in the blends does not undergo any significant thermal degradation. In fact, the mixing process and the compression molding was performed at a T lower than the ceiling temperature, 220°C;[16] the decomposition is reported to occur at a temperature higher than the ceiling temperature; the T_g of aPMMA compression-molded sample kept at 190°C for 15 min resulted in an unchanged compared to an unprocessed sample; the isothermal thermogravimetric analysis performed at 190°C exhibited constancy of the weight up to 60 min, time much longer than that used for the sample preparation.

The polymer that undoubtedly undergoes thermal decomposition during the sample preparation is the PHB. The PHB degrades and consequently decreases its M_w as soon as is heated at $T > T_m$ for only a few seconds. In this work the components have been first mixed and then compression molded at the same temperature (190°C), and the total time is about 8 min. Moreover, this time must be added to the time required, after the mixing and the compression molding, cooling to 150°C, where it can be assumed that the degradation stops.[14,15]

So the total permanence time is about 10 min. To have an idea of the degree of thermal degradation undergone by the PHB in the blends, plain PHB has been thermo-oxidated in the DSC up to

60 min, and then scanned to measure the T_g. Table I reports the time of thermo-oxidation, the corresponding calculated M_n, and the T_g. The M_n has been calculated according to refs. 14 and 15. It is worth observing that 1 min at 190°C produces a fall of M_n from 260×10^3 to 183×10^3, but the T_g results almost unchanged (3.5°C). According to Table I, the blends, after the compression molding, should contain PHB with an M_n of $\cong 50 \times 10^3$. The isothermal thermogravimetric analysis exhibited no weight loss for plain PHB and blends after a period of 10 min, whereas a loss of 1.4% in weight was found after 60 min.

Figure 3 shows the normalized thermograms of PHB, aPMMA, and PHB/aPMMA blends. The PHB thermogram is presented at low magnification to show the entire melting peak and a part of
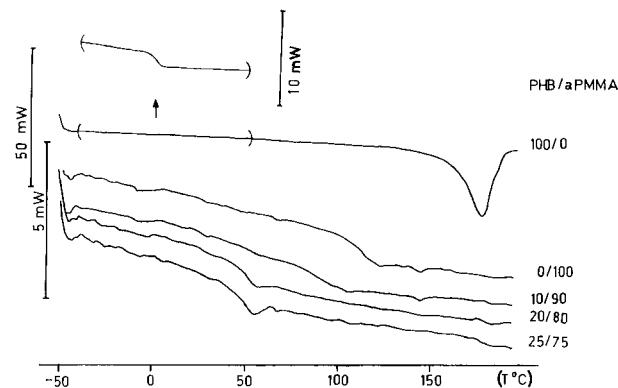

Figure 3 DSC thermograms of aPMMA, PHB, and PHB/aPMMA blends.

Table II   Glass Transition Temperature of PHB/aPMMA Blends

PHB/aPMMA (wt %)	T_g (°C) by DSC ± 1	T_g (°C) by DSC (a) ± 1	T_g (°C) by DMTA ± 2
0/100	115	119	135
10/90	90	107	113
20/80	70	90	94
25/75	55	—	78
100/0 (b)	4	5	25
100/0 (c)	1	—	—

[a] Data from ref. 8.
[b] Solution-casting sample.
[c] Sample thermo-oxidated at 190°C for 10 min (see Table I).

it at high magnification for the T_g. The T_g of aPMMA is found at 115 ± 1°C. The unprocessed PHB exhibits $T_g \cong 4 \pm 1$°C, whereas the sample thermooxidated at 190°C for 10 min exhibits $T_g \cong 1 \pm 1$°C (see Table I). The three blends exhibit a single T_g, whose value decreases with PHB content. The values of the T_g are reported in Figure 1 and Table II, and compared to those obtained for quenched samples discussed in ref. 8, which had experienced a less aggressive thermal history. The blend thermograms do not show any endothermic peak, indicating that the blends do not contain any crystallized PHB, and are completely amorphous. This was confirmed by WAXS experiments (see Fig. 4).

The spectra of the aPMMA and blends exhibit the characteristic broad peak of amorphous material, whereas the spectrum of the neat PHB shows the characteristic peaks of a semicrystalline material.
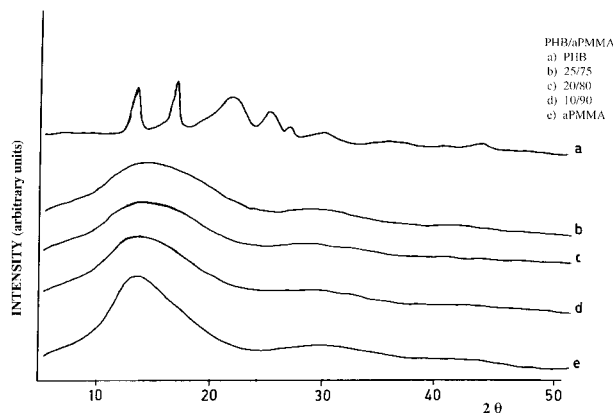
Figures 5 and 6 show the tan δ and the storage

modulus of aPMMA, PHB, and the blends as obtained by DMTA.

The tan δ (Fig. 5) of neat PHB shows a broad peak (α-transition) centered at about 100°C, and a sharp peak with a maximum at 25°C (β-transition). The α-transition is related to the rearrangement in the crystalline phase, while the β-transition corresponds to the glass transition of the amorphous PHB molecules. The PHB also displays a γ-transition, in the range of −80 to −100°C, attributed to the presence of moisture in the sample.[17] Atactic PMMA has several relaxation peaks.[18] The α relaxation (T_g) is reported in the range of 120 to 140°C. The β-relaxation is a small mechanical relaxation and assigned to the local motions of the —$COOCH_3$ side groups. This relaxation is detected as a broad peak at about 10°C. The aPMMA is reported to have several other secondary relaxations, assigned to absorbed water, for the rotation of α-methyl groups and rotation of ester methyl groups. These are at temperatures lower than those investigated here (be-
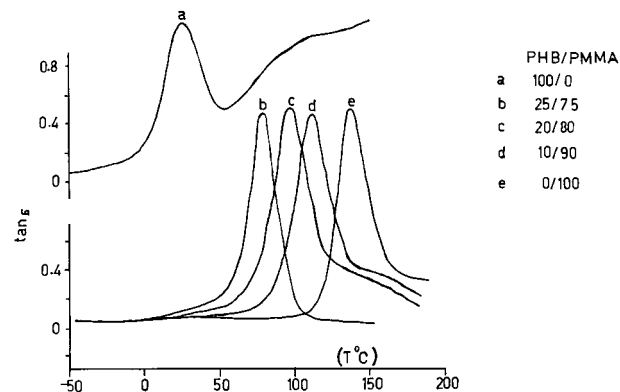

Figure 4   WAXS spectra of aPMMA, PHB, and PHB/aPMMA blends.
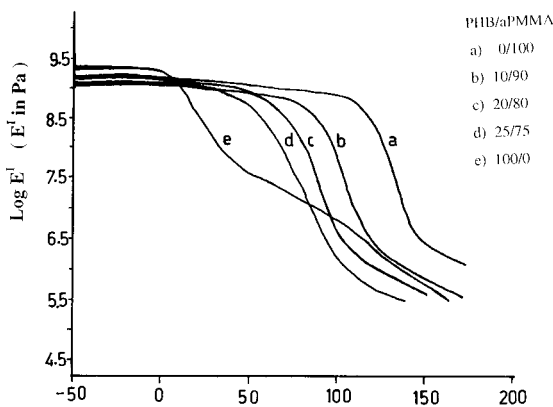

Figure 5   Tan δ of aPMMA, PHB, and PHB/aPMMA blends.

Figure 6 Storage modulus of aPMMA, PHB, and PHB/aPMMA blends.

low −50°C). The tan δ of the neat aPMMA (Fig. 5) clearly shows the α-transition peak at $T \cong 135°C$, whereas the β-transition is hardly observable at the resolution used. The tan δ spectra of the blends clearly show the presence of a single transition, whose location in the temperature plane decreases with PHB content. The values of tan δ are reported in Table II and plotted in Figure 1. It must be considered that the T_g obtained by tan δ are generally always higher than those obtained by DSC. Figure 6 shows the storage modulus, E'. At $T < T_g$, the PHB exhibits values of E' higher than neat aPMMA and the blends. At $T > T_g$, and up to about 50°C, the storage modulus decreases sharply because of the transition of the amorphous molecules from glassy to rubbery state. At $T > 50°C$ the decrease is less rapid because of the presence of the crystalline phase. The aPMMA shows a constant plateau of E' up to the T_g, then it decreases sharply for the transition from the glassy to rubbery state. For the blends the extension of the E' plateau decreases with the addition of PHB.

The results obtained by DSC and DMTA indicate the possibility of obtaining amorphous miscible blends of aPMMA and PHB at room temperature by mixing the components in the melt state. This was shown to be possible already in ref. 8, where the samples were prepared by solution casting, and cooling from one phase region to room temperature was performed in the DSC under nitrogen atmosphere. In the present investigation, much larger samples (several hundred grams) were prepared in a Brabender-like mixer. The presence of a single T_g for the blends indicated that the cooling rate used in this investigation was fast enough to preserve the miscibility of

the components formed at $T >$ ucst and avoid phase separation during the cooling in the two-phase region (see Fig. 1).

From Table I and Figure 1 it is observed that the 10/90 and 20/80 melt mixed blends show T_g values of 20–30 degrees lower than those reported in ref. 8. The differences between these blends and those of ref. 8 are the molecular mass of PHB and the blend preparation. In ref. 8, the PHB had an $M_w = 159 \times 10^3$, $M_w/M_n = 3.2$, and $T_g = 5 \pm 1°C$, and the blend preparation by solution casting could not produce any degradation. In this work, the starting material had a $M_w = 760 \times 10^3$ and $M_w/M_n = 3$, and at the end of blend preparation the blend very likely contained PHB with an $M_n = 50 \times 10^3$. So the differences of the T_g's could be attributed to different methods of blend preparation that produces degradation PHB with the formation of PHB molecules with low molecular mass.

Nominal stress–strain curves of aPMMA and PHB/aPMMA blends at 25 and at 80°C are shown in Figures 7 and 8, respectively; the tensile parameters are reported in Tables III and IV. Table III also includes the energy at break, defined as the energy required to break a test piece in a conventional tensile test. The area below the stress–strain curves can be reasonably used as a guidance on the impact strength of a material when the failure is brittle.[19] It was shown for brittle behavior that the energy from stress–strain curve has a remarkable correlation with those obtained by other methods such as izod and falling-weight impact tests.[20] The tensile curves obtained here were characteristic of brittle mate-
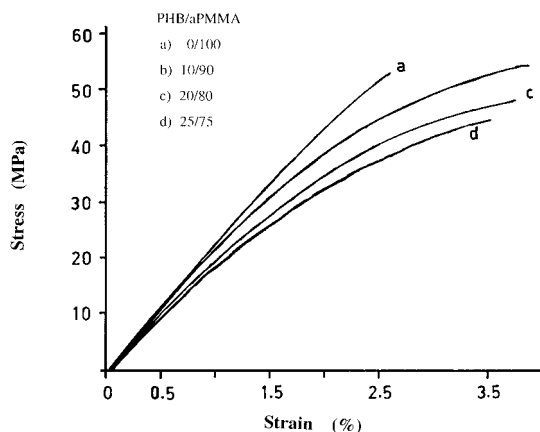

Figure 7 Stress–strain curves of aPMMA and PHB/aPMMA blends at 25°C: (a) aPMMA; (b) 10/90; (c) 20/80; (d) 25/75.
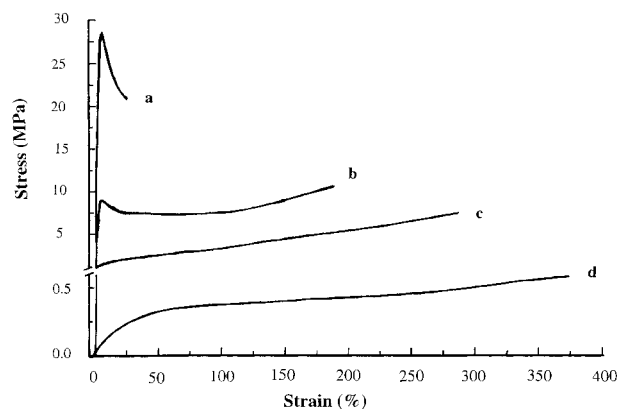
Figure 8 Stress–strain curves of aPMMA and PHB/aPMMA blends at 80°C: (a) aPMMA; (b) 10/90; (c) 20/80; (d) 25/75.

rials, with high values of E and σ_b, and low values of ε_b. At 25°C, both the aPMMA and the blends are in the glassy state. Even though brittle behavior was seen for all the samples, some important differences with the composition were observed. The modulus decreases slightly with the addition of PHB to aPMMA. The stresses at break of pure aPMMA and the 10/90 blend are similar, whereas a slight decrease is observed for the other two blends. The strains at break for the three blends are almost equal, and higher than the same parameter of aPMMA. The value of the energy to break increases with the addition of PHB to aPMMA. The 10/90 blend has the highest energy to break; it is almost twice that of aPMMA. For the other two blends a slight decrease is observed with increasing PHB content, but the values of the energy are higher than that of neat aPMMA. The decrease of energy to break of the blends with the PHB could be due to the inevitable thermal decomposition of the PHB in the blends. But in any case, all the three blends examined were less "brittle" than plain aPMMA.

Nominal stress–strain curves of the samples tested at 80°C are shown in Figure 8, and the tensile parameters are reported in Table III. The reason to perform tensile test at 80°C was because at this temperature the T_g of aPMMA and 10/90 blend are slightly above the temperature of the test (see Fig. 1), whereas the T_g of the 20/80 and 25/75 blends are below. So much more difference in tensile behavior was expected (compared to the curves at 25°C), which would also evidence the decrease of T_g of the blends with PHB.

The aPMMA exhibits a yield point, but soon after there is the break of the sample. The 10/90 blend also shows yielding, but the stress at yield is much lower than that of aPMMA. The other two blends do not show any yield, and the samples extend to high strain before the break. Finally, we note a strong decrease of the modulus with increase of the PHB content. The results of aPMMA are accounted for by considering that although the temperature of the experiment is lower than the T_g, it is close to the softening interval of the material ($T_g - 35$°C). Thus, at 80°C the modulus of aPMMA is lower than that at 25°C, and the sample can yield and extend up to about 35%. The 25/75 blend at 80°C is, instead, in the rubbery state: the T_g, as measured by DSC, is about 25°C lower than the temperature of the experiment. Therefore, this blend shows very low values of modulus and stress at break, and high elongation at break. To ascertain if the 25/75 blend can undergo phase separation at 80°C during the 30 min of equilibration before the stress–strain test, the following DSC experiment was performed. About 10 mg of the blend were held at 80°C for 45 min, then quenched at −50°C and scanned at a rate of 10°C/min. The DSC obtained is identical to that reported in Figure 3, so it can be concluded that the blend remained miscible during the 30 min for the temperature equilibration before the tensile test at 80°C. The 10/90 and 20/80 blends have a T_g just above and below the temperature of the experiments—the former at 90°C, the latter at 70°C. Therefore, the 20/80 blends exhibits lower

Table III   Tensile Parameters of PHB/aPMMA Blends at 25°C

PHB/aPMMA (wt %)	E (MPa)	σ_b (MPa)	ε_b (%)	Energy at Break (J/m^3) $\times 10^6$
0/100	2600 ± 150	53 ± 8	2.6 ± 0.5	71 ± 8
10/90	2300 ± 200	55 ± 5	3.8 ± 0.4	133 ± 15
20/80	2100 ± 180	49 ± 5	3.7 ± 0.4	112 ± 13
25/75	2000 ± 200	45 ± 7	3.5 ± 0.6	103 ± 10

Table IV   Tensile Parameters of PHB/aPMMA Blends at 80°C

PHB/aPMMA (weight %)	E (MPa)	σ_y (MPa)	ε_y (%)	σ_b (MPa)	ε_b (%)
0/100	980 ± 40	29 ± 4	6 ± 1	21 ± 2	35 ± 7
10/90	370 ± 20	8 ± 1	5.0 ± 0.3	9 ± 1	170 ± 15
20/80	115 ± 9	—	—	7.4 ± 0.5	280 ± 14
25/75	5 ± 1	—	—	0.4 ± 0.1	370 ± 20

modulus and stress at break than the 10/90 blend, but higher strain at break. The 20/80 and 25/75 blends exhibited high elongation at break, and no yielding point. The molecules of these blends are at temperature of the test in the rubbery state, due the great decrease of T_g with the addition of PHB, and so they easily relax the stress of the experiment reaching high values of ε_b and exhibiting no yield point.

CONCLUSION

In this article it has been shown that the aPMMA can be mixed with PHB at $T > T_m$ of PHB and form miscible blends stable at room temperature. The three blends investigated were amorphous, and were formed by a single homogenous phase. DSC and the DMTA analyses showed the presence of a single T_g whose value is function of the composition. The T_g decreased as the PHB content increases. The trend of the T_g values of the blends was similar to that obtained by samples prepared by solution casting. Due to their lower T_g's compared to aPMMA, at room temperature the blends exhibited energies at break higher than that of aPMMA. In particular, the blend containing 10% PHB showed a decrease of modulus of 11% compared to pure aPMMA, but the tensile energy increased by about 87%. This property makes the blend a possible alternative to aPMMA in those applications where higher fracture energy is required. To have an industrial interest, it was chosen in this investigation to prepare the blends by melt mixing. This procedure produces, of course, degradation of PHB. The PHB degradation should not be considered a phenomenon completely negative if the starting molecular mass is high and if the time of mixing and compression molding is limited. The formation of low molecular mass of PHB favors the miscibility of the two components, and the miscibility is a prerequisite for the attainment of the properties of these blends.

REFERENCES

1. Avella, M.; Martuscelli, E. Polymer 1988, 29, 1731.
2. Greco, P.; Martuscelli, E. Polymer 1989, 30, 1475.
3. Dubini Paglia, E.; Beltrame, P. L.; Canetti, M.; Seves, A.; Mercandalli, B.; Martuscelli, E. Polymer 1993, 34, 996.
4. Sadocco, P.; Canetti, M.; Seves, A.; Martuscelli, E. Polymer 1993, 34, 3369.
5. Scandola, M.; Ceccorulli, G.; Pizzoli, M. Macromolecules 1992, 25, 6441.
6. Canetti, M.; Sadocco, P.; Siciliano, A.; Seves, A. Polymer 1994, 35, 2884.
7. Lotti, N.; Pizzoli, M.; Ceccorulli, G.; Scandola, M. Polymer 1993, 34, 4935.
8. Siciliano, A.; Seves, A.; De Marco, T.; Cimmino, S.; Martuscelli, E.; Silvestre, C. Macromolecules 1995, 28, 8065.
9. Cimmino, S.; Iodice, P.; Sivestre, C. Thermochim Acta 1998, 321, 89.
10. Avella, M.; Errico, M. E.; Immirzi, B.; Malinconico, M.; Falcigno, L.; Paolillo, L. Macromol Chem Phys 1998, 199, 1901.
11. Lee, J.; Nakajima, K.; Ikehara, T.; Nishi, T. J Polym Sci Part B Polym Phys 1997, 35, 2645.
12. Kovacs, J. A. Adv Polym Sci 1963, 3, 394.
13. Braun, G.; Kovacs, A. J. In Physics of Noncrystalline Solids; Prins, J. A., Ed.; North-Holland: Amsterdam, 1965.
14. Grassie, N.; Murray, E. J.; Holmes, P. A. Polym Degrad Stabil 1984, 6, 95.
15. Kunioka, M.; Doi, Y. Macromolecules 1990, 23, 1933.
16. Sawada, H. In Encyclopedia of Polymer Science and Engineering; J. Wiley and Sons: New York, 1985, p. 719, vol. 4.
17. Scandola, M.; Pizzoli, M.; Ceccorulli, G.; Cesaro, A.; Paoletti, S.; Navarini, L. Int J Biol Macromol 1988, 10, 373.
18. McCrum, N. G.; Read, B. E.; Williams, G. In Anelastic and Dielectric Effects in Polymeric Solids; Wiley: London, 1967, p. 238.
19. Hulse, G. In Physics of Plastics; Ritchie, P. D., Ed.; The Plastic Institute: London, 1965. Chap. 3, page 120.
20. Evans, R. M.; Nara, H. R.; Bobalek, E. G. Soc Plastics Eng J 1960, 16, 76.