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0032-3861/98/$ - see front matter

Blends of amorphous and crystalline polylactides with poly(methyl methacrylate) and poly(methyl acrylate): a miscibility study

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Blends of amorphous and crystalline polylactides (PDLA and PLLA) with poly(methyl methacrylate) (PMMA) and poly(methyl acrylate) (PMA) have been prepared. Thermal behaviour and miscibility of these blends along the entire composition interval were studied by differential scanning calorimetry (d.s.c.). The results were compared with those obtained by dynamic mechanical analysis (DMTA). Only one T_g was found in PDLA/PMA and PDLA/PMMA blends, indicating a high degree of miscibility in both systems. Nevertheless, the PDLA/PMMA blend presented enlargements of the T_g width at high PMMA contents. In this case, additional evidence of complete miscibility was obtained by studying the evolution of the enthalpic recovery peaks which appear after different thermal annealing treatments. When the polylactide used was semicrystalline (PLLA), once the thermal history of the blends had been destroyed, crystallization of PLLA was disturbed in both blends PLLA/PMMA and PLLA/PMA, but in a rather different fashion: in the first case crystallization was almost prevented while in the second one it was favoured. This behaviour was explained in terms of the effect of the higher stiffness as indicated by the value of T_g for PMMA compared to that for PMA. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The increasing use of biodegradable polymers in medicine as controlled release devices, surgical implants or biodegradable sutures has promoted, over the past two decades, intensive research into new materials with potential applications in this field. The control of the degradation behaviour, based on the structure-morphology-property relationship has been the driving force of a great number of these studies.

Nowadays, polyesters derived from α-, β- and ω-hydroxyacids such as poly(lactide), poly(glycolide) or poly(ε-caprolactone) are the most important biodegradable polymers. The optimization of properties like rate of biodegradation, mechanical properties or hydrophylic/hydrophobic balance has been mainly achieved, so far, by copolymerization with other monomers[1–8] or oligomers of poly(ethylene glycol)[9–11], poly(dimethylsiloxane)[12] or even poly(isobutylene)[13], among others. Blending of polymers or copolymers might, however, offer a more cost-effective way to modify polymer properties and it can represent, in some cases, an alternative to copolymerization. Macroscopic properties such as impact and tensile strength, barrier properties and degradation behaviour can be modified by a favourable choice of the second component of the blend. Thus, the final properties will depend not only on the chemical composition of the blend but also on its physical characteristics, such as glass transition temperature, crystallinity and morphology which, in turn, are a direct consequence of the compatibility between the components in the blend. In this sense, fewer attempts have been made to use the blend concept with biodegradable polymers and most of them have been published recently[14–30]. For instance, Langer *et al.*[20] have used poly(L-lactide)/pluronic blends as protein-releasing matrices. Poly(L-lactide) (PLLA) has also been blended with poly(ε-caprolactone)[14]; in spite of their apparent immiscibility there is a mutual disturbance of the degradation behaviour. Amorphous poly(lactide) (PDLA) also seems to be immiscible with ethylene-vinyl acetate copolymer[23], but depending on the preparation method, different grades of homogeneity can be achieved which results in different degradation profiles. PDLA is, however, miscible with poly(vinyl acetate)[18]; in this case, the degradation behaviour depends on the physical aging of the blends. There is another interesting work which shows the important role played by the miscibility between the components: Pitt *et al.*[25] studied a blend of poly(vinyl alcohol) (PVA) and a copolymer of lactic and glycolic acids. This blend is miscible when the PVA contents are higher than 70% and immiscible at lower contents; the resulting change of morphology from an immiscible to a miscible blend dramatically increases the hydrolitic degradation of the polyester as a consequence of a redistribution of the absorbed water.

In order to obtain new bioerodible systems based on polylactide, we prepared several copolymers by radical copolymerization of PLLA macromonomers with hydrophobic monomers like methyl acrylate and methyl methacrylate, and hydrophilic monomers such as N,N'-dimethyl acrylamide and N-vinyl pyrrolidone[31]. In order to check the

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differences between copolymers and blends, and establish the advantages or disadvantages of each one, we also prepared blends of amorphous and crystalline polylactide with the homopolymers derived from each of the comonomers used in the synthesis of the different copolymers mentioned above. As part of a whole study that has included the swelling and hydrolitic behaviour of both copolymers and blends, we would like to present here the miscibility study carried out with the hydrophobic systems, that is, polylactide/poly(methyl methacrylate) and poly(lactide)/poly(methyl acrylate).

EXPERIMENTAL

Materials

High molecular weight amorphous and crystalline polylactides (PDLA and PLLA) were synthesized by ring opening polymerization of *rac*-DL-lactide and L-lactide, respectively, using tin octoate as catalyst[32]. Molecular weight and molecular weight distributions were determined by using a gel permeation chromatograph (Waters 150-C ALC/GPC) operating at 25 or 30°C in THF or chloroform and calibrated with polystyrene standards. The universal calibration method was applied to PLLA on the basis of the following Mark–Houwink equations, valid in chloroform[33,34] at 25°C:

$$[\eta] = 1.12 \times 10^{-4} M_n^{0.73} \text{ (PS) and}$$

$$[\eta] = 7.4 \times 10^{-5} M_n^{0.87} \text{ (PLLA)}$$

For PDLA, the following viscometric relationships, valid in THF[35] at 30°C, were used:

$$[\eta] = 1.25 \times 10^{-4} M_n^{0.717} \text{ (PS) and}$$

$$[\eta] = 5.49 \times 10^{-4} M_n^{0.639} \text{ (PDLA)}$$

The resulting molecular weights were $M_{n\,\mathrm{PDLA}} = 110\,000$ and $M_{n\,\mathrm{PLLA}} = 100\,000$, and the molecular weight distribution was 2.1.

Poly(methyl acrylate) (PMA) ($M_w = 38\,000$, based on PS standards) was purchased from Aldrich and poly(methyl methacrylate) (PMMA) ($M_p = 480\,000$) from Polymer Laboratories.

Blend preparation

Blends were prepared either by casting from dioxane solution or by the solution/precipitation method (dioxane/hexane). Before thermal analysis, samples were dried in vacuum at 70°C for 1 week.

Measurements

T_g measurements were carried out in a Perkin-Elmer DSC-2C. All the samples were twice scanned from 0 to 200°C at a heating rate of 20°C min^{-1}. The second run was taken after fast cooling of the sample (cooling rate 320°C min^{-1}). Unless indicated, the glass transition temperatures correspond to those measured in the second run.

Enthalpy relaxations were carried out under the following procedure: samples were heated at 20°C min^{-1} from 0 to 200°C; fast cooled from 200 to 0°C; heated at 20°C min^{-1} up to the selected annealing temperature and annealed for a selected time at that temperature; fast cooled to 0°C and finally scanned at 20°C min^{-1}.

DMTA measurements were carried out in a dynamic mechanical thermal analyzer from Polymer Laboratories, at a frequency of 1 Hz and 4°C min^{-1} heating rate. Samples for DMTA measurements were prepared by pressure moulding at 150°C of blends previously obtained by the solution/precipitation method.

RESULTS AND DISCUSSION

Before presenting the results obtained in this work, we would like to remark that all the d.s.c. data that will be shown here correspond to blends prepared by the solution/precipitation method. Although blend films prepared by casting from dioxane were also analyzed, results were not affected by the blend preparation method. Consequently, we will only show the results concerning the samples prepared by the first method.

Polylactide/poly(methyl methacrylate) blend

In order to simplify the study of the polylactide/PMMA blend, amorphous polylactide (PDLA) was first used. PDLA/PMMA blends covering all the composition range were analyzed by d.s.c. *Figure 1* shows the glass transition temperature of the blends as a function of composition. The T_g values correspond to those measured at the midpoint of the glass transition, and the error bars represent the transition width. As can be seen, only one T_g is detected for each sample in the whole composition range, the T_g value being a function of blend composition.

Among the theories described in the literature to study the T_g-composition dependence in a polymer blend, the Gordon–Taylor equation[36] has been one of the most frequently used. As is known, it includes an adjustable parameter k which has often been interpreted as a miscibility measure since it has been related to the interaction strength between the components in a blend. However, Prud'Homme *et al.*[37,38] pointed out that the value of this parameter cannot be used to compare two totally different blend series but elements of a series where the interaction strength varies with the element considered[39–41] within the same series.

We can rewrite the original Gordon–Taylor equation as:

$$T_g^b = T_g^1 + k\left(\frac{\omega_1}{\omega_2}\right)\left(T_g^2 - T_g^b\right) \qquad (1)$$

where ω_i refers to the weight fraction and the 1, 2 and b denote the pure components and the blend, respectively. If

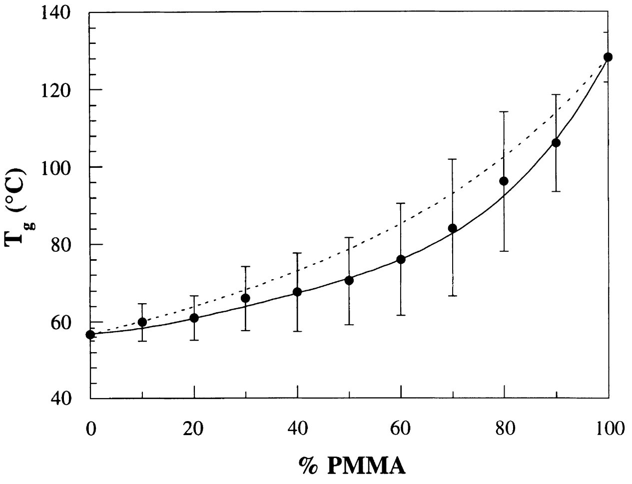

Figure 1 $T_{g(\mathrm{midpoint})}$ *versus* composition in PDLA/PMMA blends. (●) Experimental results. (- - -) Fox equation prediction. (———) Gordon–Taylor equation prediction for $k = 0.25$. The error bars represent the glass transition width

we apply equation (1) to the experimental results of the PDLA/PMMA blend, a value of $k = 0.25$ is obtained. The solid line represented in *Figure 1* corresponds to the T_g-composition Gordon–Taylor prediction for this system with $k = 0.25$ whereas the dotted line corresponds to the Fox equation prediction (equation (2))

$$\frac{1}{T_g^b} = \frac{\omega_1}{T_g^1} + \frac{\omega_2}{T_g^2} \tag{2}$$

As mentioned above, it is difficult to interpret this value unless we compare it with the behaviour of an adequate system. If we consider PMMA and PMA as polymers of a same family of acrylic polymers with the same alcoholic *R* moiety we will be able to, somehow, understand and explain the value of this parameter. As will be shown later, the value of the Gordon–Taylor parameter that best fits the experimental data for the PDLA/PMA blend is $k = 0.87$. This value is considerably higher than that of the PDLA/PMMA blend which could be interpreted as a more favourable trend of PMA to form miscible blends with PDLA than PMMA does. In spite of the uncertainty of this statement, it is true that, as will also be shown later, the glass transitions of the PDLA/PMA blends are narrower than those of the PDLA/PMMA blend, and this is undoubtly clear evidence of a higher blend homogeneity. In relation to this, it must be said that, in fact, the PDLA/PMMA blends with PMMA contents around 70–80% present very broad glass transitions as shown by the error bars in *Figure 1*, and this is a typical feature of systems close to the miscibility limit.

In order to clarify the miscibility of this blend we also studied the system by DMTA. Thus, *Figure 2* shows the dynamic mechanical spectra of the homopolymers and the blends at three different compositions. As can be seen, in agreement with the d.s.c. results, the loss tangents of the blends present only one maximum which, in addition, is blend composition dependent.

Physical aging of polymer blends has also been extensively used to establish polymer–polymer phase behaviour. As is well known, after annealing an immiscible blend (previously quenched into the glassy state at an adequate temperature below the glass transition of both homopolymers), each polymer relaxes toward equilibrium. The relaxation process results in a decrease in thermodynamic quantities such as enthalpy and volume, and can be identified as an enthalpy recovery peak during a second d.s.c. run. The fact that each polymer has its own specific aging behaviour, manifested by the position and magnitude of the enthalpy recovery peak, can be used to determine polymer–polymer miscibility. The method is particularly useful when the polymers in question have similar glass transition temperatures which makes them difficult to distinguish separately during a conventional d.s.c. run. This should not be the case for the PDLA/PMMA blend, as the T_gs of the corresponding homopolymers are separated by almost 70°C, but if we assume that there is partial miscibility between the components of the blend and we have two phases of similar composition, these phases will have very close T_gs, so physical aging of the blend might afford additional information related to the phase behaviour.

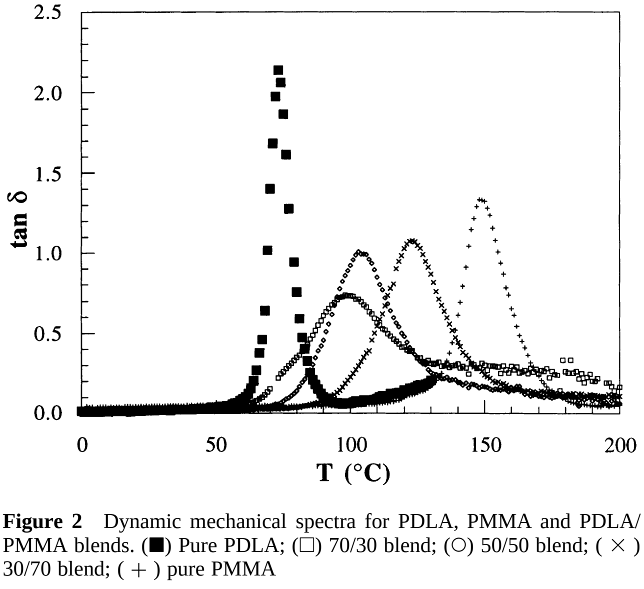

Figure 2 Dynamic mechanical spectra for PDLA, PMMA and PDLA/PMMA blends. (■) Pure PDLA; (□) 70/30 blend; (○) 50/50 blend; (×) 30/70 blend; (+) pure PMMA

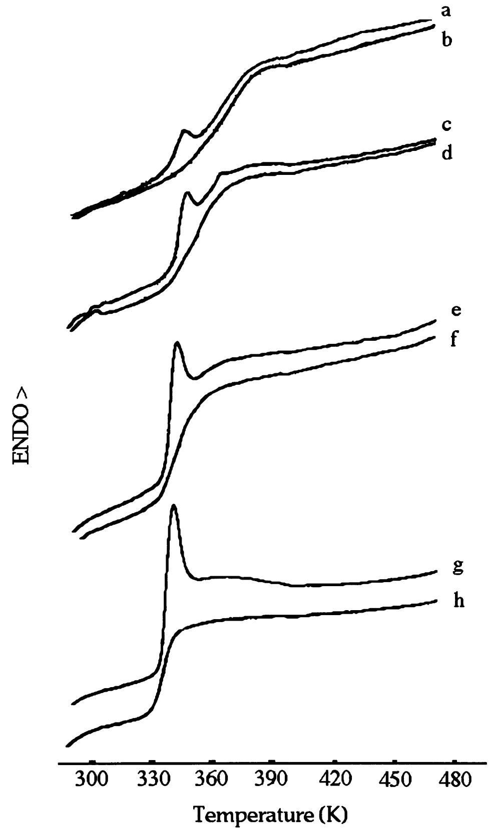

Figure 3 DSC thermograms for PDLA/PMMA blends. The first scan is recorded after annealing the samples at 20°C for 6 months. (a) and (b) 20/80 blend, 1st and 2nd scans, respectively; (c) and (d) 40/60 blend, 1st and 2nd scans; (e) and (f) 60/40 blend, 1st and 2nd scans; (g) and (h) 80/20 blend, 1st and 2nd scans

Let us start with a fortuitous result we obtained analyzing samples whose thermal history had been previously destroyed and had been stored at room temperature for long time. Thus, *Figure 3* shows the thermograms (1st and 2nd runs) of samples of different composition after 6 months at 20°C. As can be seen, the samples with a high PDLA content present typical relaxation phenomena and only one peak is observed; however, those rich in PMMA, and especially the blend 20/80 PDLA/PMMA, exhibit a clear peak separated from the rest of the transition. Although this could be first understood as the relaxation phenomenon of an immiscible blend where, due to an inadequate annealing temperature only the relaxation process of one of the components is observed, the experiments we show below demonstrate that this observation corresponded to an intermediate state of a single relaxation process that had

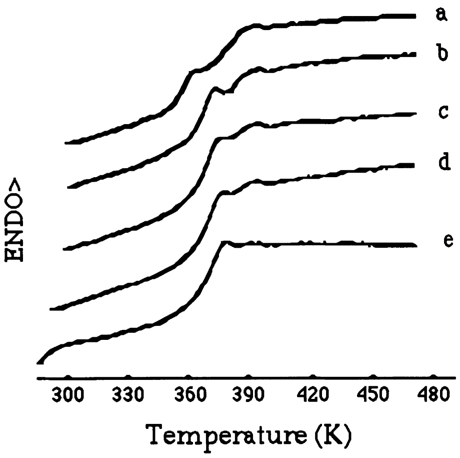

Figure 4 DSC thermograms for PDLA/PMMA 20/80 blend after annealing for 30 min at several temperatures. (a) 60°C; (b) 74°C; (c) 76°C; (d) 78°C; (e) 80°C

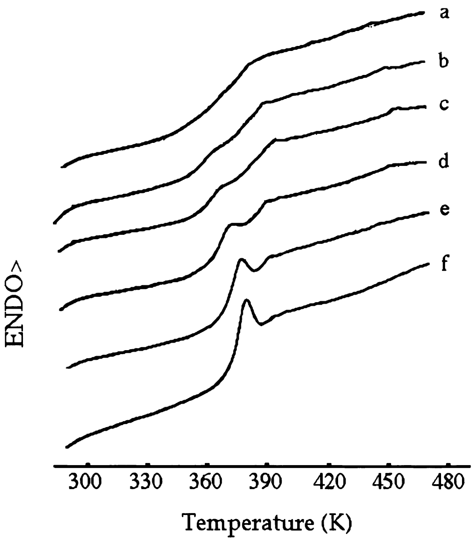

Figure 5 DSC thermograms for PDLA/PMMA 20/80 blend after annealing at 70°C for several periods of time. (a) Without any treatment; (b) 5 min; (c) 15 min; (d) 2 h; (e) 24 h; (f) 4 days

been extremely slowed down by the big difference between the annealing temperature (20°C) and the T_g of the blend ($T_{\text{g-midpoint}} = 96°C$; $T_{\text{g-onset}} = 73°C$).

Therefore, *Figure 4* shows the d.s.c. thermograms of the 20/80 blend obtained with the aging procedure described in the experimental section for an annealing time of 30 min at different aging temperatures. As shown in this figure, higher annealing temperatures seem to accelerate the relaxation process and shift the emerging relaxation peak to higher temperatures. This is better observed in *Figure 5* where the effect of annealing time is represented at constant aging temperature: it is clear that increasing treatment time increases the magnitude of the peak and shifts its position to higher temperatures. The system changes towards a unique relaxation peak in such a way that its temperature is a linear function of log *t*, *t* being the aging time (*Figure 6*). The shift is as large as 19°C, but this is a well-established feature of physical aging: changes of the same order are, for example, observed for PVC[42] when aged at 60°C, and this reflects how far the aged blend is from the thermodynamic equilibrium.

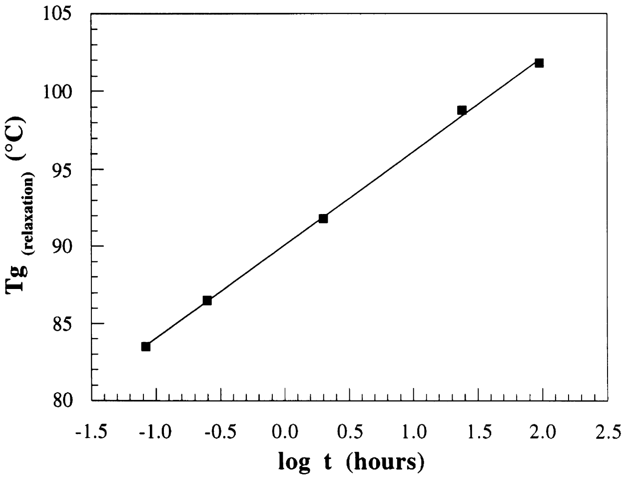

Figure 6 Semi-logarithmic plot of $T_{g(\text{onset})}$ *versus* annealing time (log *t*) for the enthalpy relaxation of PDLA/PMMA 20/80 blend at 70°C

Table 1 PLLA/PMMA glass transitions and melting temperatures at different compositions

Sample	T_{g1} (°C) (onset)	T_{g2} (°C) (onset)	T_m (°C) (peak max.)
PMMA	—	115	—
PLLA/PMMA 10/90	—	108	—
PLLA/PMMA 20/80	—	105	175
PLLA/PMMA 30/70	77	105	175
PLLA/PMMA 40/60	79	107	176
PLLA/PMMA 50/50	77	103	178
PLLA/PMMA 60/40	78	105	180
PLLA/PMMA 70/30	79	104	180
PLLA/PMMA 80/20	80	108	182
PLLA/PMMA 90/10	81	—	181
PLLA	81	—	181

In conclusion, the enthalpic recovery peak experiments do not allow us to confirm the existence of well separated phases in PDLA/PMMA blends. Therefore, the broad glass transitions observed (*Figure 1*) could be the result of a deficient intime mixing as a consequence of the preparation method and the very different melt viscosities of the components.

When we analyzed the blends of semicrystalline polylactide (PLLA) with PMMA by d.s.c., it was seen that, independently of the preparation method, the blends exhibited a multiphase structure, that is, they were phase separated. As shown in *Table 1*, the thermograms corresponding to the first scan after preparation showed two T_gs, one around 77°C and another one around 107°C, along with an endothermic peak about 178°C (maximum of the peak). Both T_gs are slightly different from the T_g of the homopolymers in the pure state probably due to the presence of each of the components in the amorphous phase of the other one. The increase of the T_g of the PLLA phase could also be contributing to the 'stiffening' effect of the PLLA crystalline phase, which would act as crosslinking points.

The situation is, however, completely different after running the system up to 200°C followed by a fast cooling: once the crystalline phase has been melted, the high temperature allows the mixing of both polymers and as a result, only one T_g is observed during the second run, its value increasing when the PMMA contents increases. Furthermore, the T_g-composition dependence is similar to

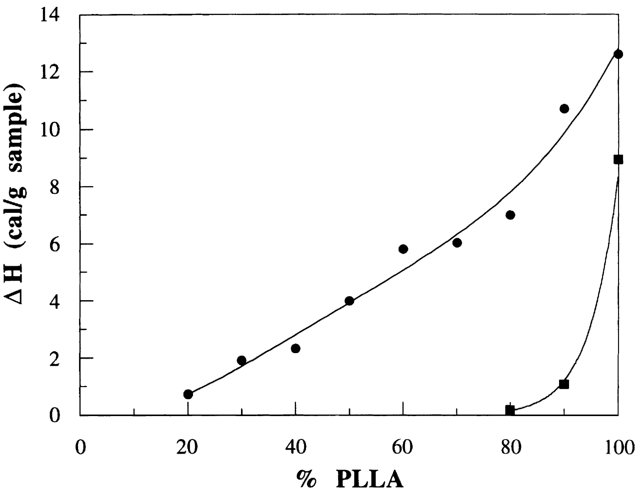

Figure 7 Heats of fusion *versus* composition for PLLA/PMMA blends. (●) 1st scan; (■) 2nd scan. The lines are the best fits to the experimental results

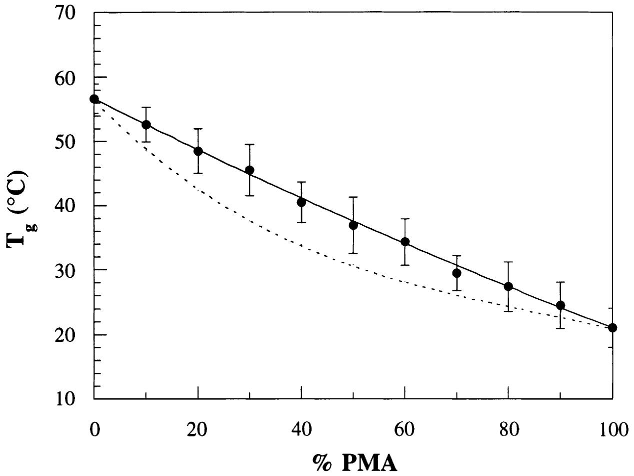

Figure 8 $T_{g(\mathrm{midpoint})}$ *versus* composition in PDLA/PMA blends. (●) Experimental results. (- - -) Fox equation prediction. (———) Gordon–Taylor equation prediction for $k = 0.87$. The error bars represent the glass transition width

that shown by the PDLA/PMMA blend. It must also be said that the T_gs of the PLLA/PMMA blends when the PMMA content is 70–80% are also broad. In addition, PLLA is only able to crystallize to a significative extent during the second run when its content in the blend is very high. In fact, it is only possible to observe the crystallization and melting of the PLLA crystals during the second run, when PLLA contents in the blend are higher than 80%. This could be considered as a typical example of a miscible blend in the amorphous state with a T_g higher than that of the semicrystalline component; as a result it is observed that crystallization kinetics decrease dramatically. *Figure 7* shows the melting enthalpies (referred to total blend weight) measured after the first and second runs. As can be seen, PMMA prevents the crystallization of PLLA in such a way that, for instance, the PLLA contents in the blend must be about 90% to achieve a degree of crystallinity, during the second run, similar to that obtained in the first run with 20% PLLA.

The melting point depression of the semicrystalline component is further evidence of some degree of miscibility between the components of a blend. When the PLLA melting temperatures in the PLLA/PMMA blend were measured, the trend depicted in *Table 1* was seen. The highest decrease is about 7°C. This is not a large depression but is significant enough considering the conditions under which the melting temperatures have been measured: when the melting temperatures are determined under non-equilibrium conditions, as has been done in this work, the melting point depression does not correspond to that derived theoretically from pure thermodynamical considerations[43]. Several morphological factors contribute negatively to the melting temperature decrease and thus, any experimental decrease is always lower than the theoretically expected. As a consequence, any melting point depression of the semicrystalline component in a blend should be understood as, at least, partial miscibility between the components.

Polylactide/poly(methyl acrylate) blend

Traditionally, the Hildebrand solubility parameter concept[44] has been used to estimate the miscibility of two liquids. According to this concept, two materials with matched solubility parameters will be miscible. However, some difference between them is allowed if there is any favourable intermolecular interaction such as dipolar interactions, or even better, hydrogen bonding. Neither PDLA/PMMA blend nor PDLA/PMA blend can be considered to be systems where strong specific interactions can take place, but some kind of weak dipolar interaction should not be discarded owing to the chemical structure of both homopolymers. A rough calculation of the critical difference between the solubility parameters of two components in a blend, assuming that there are, at least, dipole–dipole interactions, establishes[45] that this difference must not exceed 0.5. If we calculate the solubility parameters by means of the group contribution method[45], the following results are obtained for the polymers used in this work: $\delta_{\mathrm{PDLA}} = 10.1\ (\mathrm{cal\,cm^{-3}})^{1/2}$, $\delta_{\mathrm{PMA}} = 9.61\ (\mathrm{cal\,cm^{-3}})^{1/2}$, $\delta_{\mathrm{PMMA}} = 9.06\ (\mathrm{cal\,cm^{-3}})^{1/2}$. It is clear that according to these data only in the case of the PDLA/PMA should some miscibility be expected, however, there is experimental evidence that PDLA/PMMA is apparently miscible. The question is whether the calculation made to estimate the critical difference between the solubility parameters is very approximate, and whether only average interaction energies have been considered. Maybe in this particular case there are stronger interactions than the ones considered in the calculations, and even if they were weak, but correctly quantified, they might have 'allowed' the difference between the solubility parameters of PDLA and PMMA. In any case, taking into account the experimental evidence of miscibility in the PDLA/PMMA blend and the similar chemical nature of the groups present in PMA and PMMA, it would be reasonable to predict the miscibility of the PDLA/PMA blend considering the lower difference between the solubility parameters of PDLA and PMA compared with the case of PDLA and PMMA. Certainly, thermal analysis of PDLA/PMA blends shows, in the whole composition range, a unique composition dependent T_g. *Figure 8* shows the change in the T_g with blend composition as well as the predictions based on the Fox and Gordon–Taylor equations for $k = 0.87$. A noticeable feature of this figure is the T_g widths that have been represented by error bars: compared with those in the PDLA/PMMA blend, the T_gs of the PDLA/PMA blend are considerably narrower. As mentioned in the discussion of the PDLA/PMMA behaviour, this difference can be undoubtly

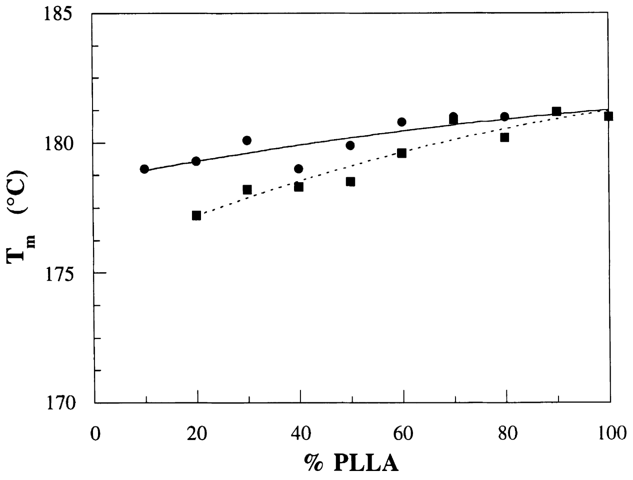

Figure 9 Melting temperatures (peak max.) *versus* composition for PLLA/PMA blends. (●) 1st scan; (■) 2nd scan

attributed to a higher homogeneity of the PDLA/PMA blend.

The behaviour of the PLLA/PMA blend resembles that of the PLLA/PMMA blend. Independently of blend preparation, the first scans always show two T_gs and an endothermic peak, corresponding to the melting of the PLLA crystalline phase. However, both T_gs become unique during the second run, that is, once the thermal history of the blend has been completely destroyed. According to this, it can be said that both polymers are miscible in the melt, although it must be pointed out that these unique T_gs are much broader than the T_gs observed in the blends with the amorphous polylactide.

Comparing with the PLLA/PMMA blend, it must be remarked that PMA does not disturb the crystallization of PLLA during the second run as much as PMMA does. Thus, it is possible to detect (but not measure accurately) an small melting peak even in blends with just 10% of PLLA. The reason relies on the low T_g of PMA compared with that of PDLA (40°C lower); once both polymers are mixed at high temperature, then during the second run the mobility of the PLLA chains is enhanced by the presence of intimately blended PMA chains. As a result, crystallization is favoured.

Finally, and as expected, the PLLA melting point depression is also observed (*Figure 9*). Now, the decrease in T_m is lower than in the case of the PLLA/PMMA blend (7°C against 4°C approximately); nevertheless, this small difference does not allow one to come to the relevant conclusions because, as was mentioned before, several factors different from the purely thermodynamic considerations may determine the magnitude of the experimental melting point depression.

CONCLUSIONS

In conclusion, and based on the results obtained by means of the different techniques used in this study, we can say that PMA is, undoubtly, miscible with PDLA: only one blend-composition dependent T_g is observed, which means that the molecular mobility of the chains of each homopolymer is mutually affected. On the other hand, a PDLA/PMMA blend can, in principle, also be considered as a miscible blend even though the enlargement of the T_g width, observed at high PMMA contents, could suggest that we are dealing with a system which is in the miscibility limits. Nevertheless, additional experimental data obtained by means of DMTA and enthalpy relaxations, do not contradict the d.s.c. results—what is more, they seem to confirm them.

The application of the Gordon–Taylor equation to both blends also shows another difference between them: while the value of the parameter k that best fits the experimental results for the PDLA/PMA blend is 0.87, in the PDLA/PMMA blend $k = 0.25$. This difference is interpreted as an increased tendency of PMA to form miscible blends with PDLA than PMMA. This seems to be congruent with the differences in the T_g widths of both blends as discussed earlier.

Concerning the behaviour of the blends of semicrystalline polylactide, we can say that both blends PLLA/PMA and PLLA/PMMA, behave as blends that present some degree of miscibility in the melt; but after cooling, if an adequate thermal treatment is applied, the crystallization tendency of PLLA acts as the driving force for phase separation and the formation of segregated crystalline micro-domains. In addition, in both cases the shape and size of the crystals are presumably affected as shown by the melting point depression observed. As a remarkable difference between these two blends, the crystallization of PLLA during the second d.s.c. run is almost prevented when blended with PMMA, but largely favoured with PMA. The different T_g of the second components accounts for this effect.

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