Microhardness of condensation polymers and copolymers. 1. Coreactive blends of polyethylene terephthalate and polycarbonates

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Abstract

The microhardness of coreactive blends of polyethylene terephthalate (PET) and bisphenol A polycarbonate (PC) was investigated over the whole range of compositions. The occurrence of one single glass transition temperature (T_g) step in the DSC curves indicated that intensive chemical interactions had taken place during melt blending resulting in formation of copolycondensates with dominating random sequential order. The parallel decrease of microhardness (H) and of T_g with increasing PET content in the blends has been ascribed to the formation of new copolymer molecules enriched in the component characterized by lower H - and T_g -values. It is emphasized that such non-crystallizable copolymers offer the possibility to evaluate the intrinsic contribution of the repeating units to the H - and T_g - characteristics of copolymers with various composition and sequential order.

Introduction

Polymer blends based on a polyester and a polycarbonate have been shown to be immiscible provided no transesterification reaction occurs [1]. Heat treatment of the same blends yielded different degrees of compatibility depending on temperature and time extent of the treatment as well as presence and type of catalyst [1-3]. This method has been successfully used to increase compatibility of different polymers including poly(bisphenol-A-carbonate) (PC)/polybutylene terephthalate (PBT) [3-6], polyethylene terephthalate (PET)/poly(hydroxy ether of bisphenol A) [7], PET/PC [2] and PC/polycaprolactone [8] among others. In this case, induced reactions occurring during melt blending modify the chemical structure of the two, in principle, immiscible polymers to render a final system with a controlled degree of compatibility due to the obtaining of copolymers of the two starting partners [9,10]. In particular, this method has been used to prepare ester-ether copolymers starting from PET and PC [10]. Hardness (H) has been shown to be a promising technique for the microstructural investigation of multicomponent blends and can provide information on the degree of interpenetration of the blend components [11]. The case of blends of low density and high density polyethylene (PE) is an example where H can be described in terms of an additive system of two independent components [12]. However, in systems like PE/polypropylene blends prepared from semidilute solution or PBT/PC blends a deviation from the additivity law is detected [13,14]. In these cases the deviation of H from the additive behaviour of the single components can be related to the changes of crystallinity and to the thickness of the crystals. It is worth mentioning that in case of blends of condensation polymers, in contrast to the polyolefines, the blend partners can interact chemically and form copolymers. For this reason the observed deviation from the additivity law for such systems can be related also to the chemical

changes taking place during blending. In order to distinguish between the contribution of crystallinity factors and chemical changes one has to investigate condensation blends in the glassy state.

The purpose of the present study is to supplement our earlier microhardness studies of blends of condensation polymers [13,15], where evidences for chemical interactions were observed with reference to the microhardness additivity of the two components. In the present work the same chemical reactions are in a more advanced stage and result in a profound change of the chemical composition of the starting blend and eventually its phase state.

Due to its significant commercial interest the PET/PC blend has been investigated rather intensively, particularly, with respect to its miscibility. In preceding studies complete miscibility for all compositions to only partial miscibility has been reported [1]. For example, blends prepared with an extruder at a die temperature of 290°C led to two amorphous phases over the whole composition range, suggesting that neither miscibility nor transreactions take place [16]. On the other hand the exchange reaction in molten PET/PC blends (in the range 240–274°C and in the presence of a transesterification catalyst) gave rise to four-component copolycondensates [17].

More recently it was reported [18,19] that the same system is entirely miscible only after transesterification, as per melt mixing at high temperature (300°C), or under long processing time. It is therefore not surprising that immiscible blends are obtained on blending after a single extrusion due to insufficient time for reaction [20]. Without reaction this pair is immiscible.

Very recently the sequential reordering in copolymers from PET/PC blend was also investigated in detail [21]. In agreement with previous reports [1,22] it was found that

annealing at 280°C for hours (without an extra added catalyst) results in a complete disappearance of crystallization or melting of the blends. Such an amorphization is attributed to the formation of random copolymers. This statement has been confirmed by NMR measurements, by the observation of one glass transition temperature in the range of the initial two Tg's, and by solubility tests.

Experimental

Materials

The blends used in this study were prepared from commercial grades of PET (JELPET, Jelchem S.A., Jelenia Gora, Poland) and poly(bisphenol A carbonate) (BISTAN AW, Zachem S.A., ^{Bydgoszcz}Bydgonor, Poland). The blends were prepared with varying content of PET between 0 and 100 wt.% by means of coreactive mixing. For this purpose PET and PC pellets were mixed in the reactor in the temperature range of 275-290°C and vacuum of 0.1 to 0.2 mm Hg pressure in the presence of magnesium hydrohexabutoxy-O-titanate as a catalyst (1.5 cm³ on 400 gm of the mixture). After 45 minutes the respective blend was extruded and granulated.

For further thermal and mechanical characterization of the blends films were prepared from the pellets via injection molding followed by compression molding. The latter was performed at a pressure of 5 MPa at 220°C for 10 sec. After molding the films were cooled down between two metal blocks for 2 min. The films so prepared, differing in their starting PET/PC ratio, were tested by wide-angle X-ray scattering (WAXS) and found to be completely amorphous. Such a result has been reported earlier [2] for the same blends even without performing intensive chemical reactions between the partners.

Techniques

The calorimetric measurements were carried out in a Perkin Elmer DSC4 differential scanning calorimeter. Scanning rates of 20°C/min; about 10 mg samples were used. Calibration was made by using standard indium samples.

Microhardness (H) was measured at room temperature using a Leitz Tester equipped with a square based diamond indenter. The H-value was derived from the residual projected area of indentation according to the expression

$$H = kP/d^2 \text{ (MPa)} \quad (1)$$

where d is the length of the impression diagonal in meters, P , the contact load applied in N and k is a geometrical factor equal to 1.854. A loading cycle of 0.1 min and loads of 0.5 and 1 N were used. Ten measurements for each sample were averaged.

Results

Fig 1 shows the DSC curves for the homopolymers PET and PC and their blends after coreactive blending and film preparation as described in the experimental part. The homo PET indicates both a well defined glass transition and crystallization peak at around 65°C and 120°C, respectively. The small endothermic peak at 65°C is typical for an aged PET material and is due to an enthalpy relaxation of the glass towards equilibrium as shown previously [23]. The homo PC shows only a glass transition around 130°C. More striking is the observation that all the blends show only one glass transition temperature which increases with the rise of the PC content in the starting blends. There is no sign for crystallization in the interval studied (60-180°C). This last observations supports the conclusion drawn on the basis of the WAXS results and findings reported for the

same blends [2] that the samples are in the glassy state. This peculiarity of the blends is very important for the subsequent microhardness measurements performed at room temperature.

Table 1 summarizes the glass transition temperatures derived from the curves displayed in Fig 1 together with other experimental and calculated data.

Fig 2 shows the dependence of microhardness on the composition of the coreactive blends. The H-values for the two homopolymers are also given. One observes an almost linear decrease of microhardness with the increase of the PET content in the blends, i.e. with increasing concentration of the component with the lower H-value.

The solid straight line on Fig 2 reflects the H-values calculated according to the mechanical parallel model

$$H = wH_a^{PET} + (1 - w)H^{PC} \quad (2)$$

where w and $1-w$ are, respectively, the weight fractions of PET and PC, H_a^{PET} and H^{PC} are the microhardness values for amorphous PET and for PC. Rather good agreement between the experimentally measured and calculated values is observed for the coreactive blends with different compositions (Fig 2).

For crystalline polymers and copolymers it is known that the microhardness depends primarily on crystal characteristics such as size, perfection, chain conformation within the crystals, etc [24]. Dealing with completely amorphous samples these parameters obviously cannot be used. The only quantity left is the glass transition temperature. For this reason an attempt was made to look for a relationship between H and Tg bearing in mind that they should be sensitive in a similar way to the blend composition and the occurrence of chemical reactions leading to formation of copolymers.

In Fig 3 the T_g -values are plotted for the two homopolymers, PET and PC, respectively as well as for their coreactive blends. The data are taken from the DSC curves presented in Fig 1.

In contrast to the microhardness behaviour (Fig 2) the glass transition temperature decreases non-linearly with increasing PET content in the coreactive blends. The T_g value for the PET richest blend deviates from the general trend being even slightly higher than the preceding one (Fig 3). Possibly this difference is related to the effect of certain molecular ordering on T_g [23]. Since only this blend is potentially crystallizable, as shown in the discussion, one can assume that the cooling conditions in the present case did not exclude some preordering. Similarly to the case with the microhardness, the experimentally evaluated T_g values are compared with theoretically derived ones using two equations frequently applied to polymer blends and copolymers. The Fox equation [25] being is close to the parallel model used for the calculation of the microhardness (eq. 2):

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (3)$$

where T_g is the glass transition temperature of the binary blend, T_{g1} and T_{g2} are the glass transition temperatures of polymers 1 and 2, and w_1 and w_2 are the mass fractions of polymers 1 and 2.

The equation of Couchman [26], used mostly for miscible blends, is as follow:

$$\ln T_g = (X_1 \Delta C_{p1} \ln T_{g1} + X_2 \Delta C_{p2} \ln T_{g2}) / (X_1 \Delta C_{p1} + X_2 \Delta C_{p2}) \quad (4)$$

where T_g is the glass transition temperature of the blend, X_i is the mole fraction of the component i , and ΔC_{pi} is the difference in the specific heat between the liquid and glassy states at T_g . While the Fox equation (eq. 3) supposes a linear change of T_g with the

change of the composition, the last equation (eq. 4) predicts a monotonic dependence of T_g upon concentration and when $T_{g2} > T_{g1}$ and $\Delta C_{p2} < \Delta C_{p1}$ the glass transition of the blend T_g will be a concave function of blend composition. The values of T_g for coreactive blends with various composition as derived from eq. 3 and eq.4 are given in Table 1 and plotted in Fig 3 together with the experimental data. One can conclude that the measured T_g values are closer to those derived from the Fox equation (eq. 4).

Fig 4 shows the plot of the relationship between the microhardness depression $\Delta H = H^{PC} - H^{BL}$ and the glass transition depression $\Delta T_g = T_g^{PC} - T_g^{BL}$, for coreactive blends with various composition where H^{PC} and H^{BL} are the microhardness of the PC homopolymer and of the coreactive blend, respectively, and T_g^{PC} and T_g^{BL} are the glass transition temperatures of the PC homopolymer and the coreactive blend, respectively. A linear correlation between ΔH and ΔT_g in Fig 4 is obtained.

Discussion

Chemical Reactions

Considering the reports [17-22] and taking into account the experimental conditions used for the coreactive blending in the present study (275–290°C, treatment time of 45 min, presence of a transesterification catalyst) one has to assume occurrence of intensive chemical interactions. It is also to be expected that these reactions will lead not only to the formation of copolymers but will result in a more or less complete randomization of the sequential order of the repeating units. If this is the case the initially two-components blends should be converted into one-component ones. Even more, the latter will represent also one phase systems so far as randomization, i.e. amorphization is taking place.

This is really the case as can be concluded from the DSC curves shown in Fig 1 - the

blends do not crystallize in contrast to the homopolymer-PET and they exhibit only one glass transition temperature.

The conclusion that the starting PET/PC blends are converted via coreactive blending into one-component material with only one phase (amorphous) has important consequences when the “blend” is characterized with respect of its mechanical properties. Unfortunately, this peculiarity of such “blends” is frequently disregarded or underestimated, which results in erroneous conclusions as for example concerning the miscibility of the starting partners [1].

A second detail concerns the way of expression of the “blend” composition. Dealing with blends of condensation polymers which have been reacted and converted into copolymers, the latter being uniform with respect of the number of components (as well as with respect of the number of phases provided no phase separation via crystallization or dephasing has occurred) it seems more reasonable to express the ratio of the components in mol % rather than in wt %. This reflects more realistically the composition of the system and at the same time, particularly the expression as a mol ratio offers an idea about the character of the sequential order in the chains assuming complete randomization has taken place. For this reason in Table 1 the composition is given in both wt. and mol % as well as in a mol ratio. The fact that the mol ratio reflects the block length when complete randomization is achieved allows one to make direct conclusions about the crystallization ability of the copolymers obtained. For example, in the present case only the richest PET blend (90/10) is potentially crystallizable. For the rest of the blends the PET “blocks” are too short to form lamellae with thickness of 50–60 Å which represents the lowest limit [21]. It should be emphasized that in the case studied the differences between wt% and mol% are not that big because the molecular weight of the two repeating units are

rather close to each other but there are cases when the difference is significant.

Microhardness additivity law

Bearing in mind the outlined peculiarities of blends of condensation polymers and particularly when they consist of one-component and of one-phase (this case is more the exception rather than a general rule since block copolymers usually consist of two, three or more phases) the application of the additive law for evaluation of their characteristics seems not to be completely justified. The observed good agreement between the measured microhardness values and the calculated ones according to eq. (2), (Fig 2) allows one to make an important conclusion in this respect. Basically, the application of the additive law for blends assumes the presence of spacially well defined regions of chemically and structurally uniform moieties which is not the case for the present amorphous PET/PC copolymers since only a single T_g is observed. Then, it follows that the contribution of the two species to the microhardness of the copolymers is transferred via the repeating units constituting the copolymer molecules. Since in the present system there are no crystalline phases which can independently contribute to the microhardness of the copolymer, the observed microhardness can be regarded only as arising from and depending on the chemical composition of the copolymer. Possibly, one can speak about the intrinsic contribution of the two repeating units to the microhardness of the copolymeric solid. One can conclude that the additive law can be applied at the molecular level, i.e. the microhardness of amorphous copolymers differing in their composition obey the additive law based on microhardness of the respective amorphous homopolymers provided no other factors affect the microhardness of the copolymers.

It is important to note here that the additive law is applicable to blends of miscible

pairs of polymers. This was demonstrated for the blends of polymethyl methacrylate and polyvinylidene fluoride [12].

Rather similar is the situation with the dependence of the glass transition temperature T_g on the composition of the “blends”.

Glass transition temperature

For the evaluation of the T_g of polymer blends the commonly used empirical equation is that of Fox [16] (eq.2) suggested for miscible blends (a detail which is often disregarded). There are other equations trying to account for other factors affecting T_g in addition to the mass fraction of components. Such one is used in the present study (eq. 3) and recommended [27] for random copolymers and miscible polymer blends, giving much better correlation of experimental observations than any other similar equation. This fact can be taken as evidence underscoring the importance of the entropy, rather than the volume, as the main factor controlling the onset of glass transition [27]. This equation was claimed to be derived purely from thermodynamic considerations based on the concept of the continuity of the entropy of mixing at the glass transition temperature [27].

Dealing with blends of condensation polymers which are allowed to react to the extent of complete involvement of the starting homopolymers into copolymers new factors affecting T_g appear. Of particular interest is the case when the copolymers obtained are non-crystallizable. Such an amorphous system is very close to a blend of miscible polymers with respect to the number of components and phases. In the same time there is an essential difference – the appearance of new type of chemical bonds. In addition to the effect of the repeating units chemical composition and structure on T_g , which is common for both cases, the generation of new type of chemical linkages will affect the

internal mobility of the groups in a single chain and thus will contribute to the increase or decrease of T_g . For this reason equations accounting for the internal rotation around a single bond seem to be more appropriate for evaluation of T_g of amorphous copolymers obtained from a blend. A good example for such a relation is the following equation [28]:

$$T_g = \frac{2\delta^2}{mR} + C_1 \quad (5)$$

where δ^2 is the cohesive energy density (CED), m is a parameter which describes the internal mobility of the groups in a single chain, R is the gas constant and C_1 is a constant. It is noteworthy that the cohesive energy density provides an integrated measure of the strength of the secondary bonds in a compound; materials with strong secondary bonds show high CED-values. So, the above equation accounts for the two most important factors determining the value of T_g : (i) the possibility for rotation around single bonds and (ii) for formation of secondary bonds with the surrounding atoms. In addition, it offers a link between the glass transition temperature and microhardness of polymer glasses since the cohesion energy is the basic factor in determining also the microhardness as demonstrated earlier [29].

By this common dependence of T_g and H upon cohesion energy one can explain the almost linear relationship between the depressions ΔH and ΔT_g caused by the increasing amount of PET in the copolymers, as shown in Fig 4.

Conclusions

When working with blends of condensation polymers one has always to take into account the possibility for chemical interaction and formation of copolymers. The extent of this reaction is also important because it is possible to obtain one-component as well as one-phase system when the blocky sequential order is converted to a random one.

Such systems are very appropriate for verification of relationships reflecting the effect of composition on various properties since they are free from other factors. Finally, in such cases one deals with copolymers distinguished by creation of new chemical bonds, but not anymore with blends although one mixes two or more homopolycondensates at the very beginning. Systematic studies of microhardness of well defined block copolymers with respect to blocks characteristics and morphological features are now in progress.

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Table 1 Glass transition temperature T_g experimentally measured and calculated according to the Fox equation (eq 3) and Couchman equation (eq 4), the difference in the specific heat ΔC_p between liquid and glassy states at T_g , the microhardness H , and the depressions ΔT_g and ΔH , respectively for homo PET and homo PC as well as for their coreactive blends with various compositions.

Composition (PET/PC)			T _g (°C)			ΔC_p (cal/del)	H (MPa)	ΔT_g (°C)	ΔH (MPa)
wt %	mol %	mol ratio	exp.	calc. eq 3	calc. eq 4				
100/0	100/0	–	70	–	–	0.078	128	58	24
90/10	92.6/7.4	12.50/1	89	72,5	70,8	0.0805	129	39	23
70/30	75.5/24.5	3.08/1	87	80.0	75.5	0.0725	131	41	21
50/50	56.9/43.1	1.32/1	93	89.7	82.6	0.0759	138	34	14
30/70	36.1/63.9	1/1.77	100	101.9	93.7	0.0658	143	28	9
10/90	12.8/87.2	1/6.81	113	117.9	113.0	0.0658	149	15	3
0/100	0/100	–	128	–	–	0.041	152	0	0

Figure captions

Fig 1 DSC curves for homo PET and homo PC and their coreactive blends with various composition as indicated on the respective curves.

Fig 2 Dependence of microhardness H on the composition of coreactive PET/PC blends.

The values of the homo PET and homo PC are also given. The solid line reflects the H -values calculated according to the eq. 2.

Fig 3 Dependence of the glass transition temperature T_g on the composition of coreactive PET/PC blends. The values of the homo PET and homo PC are also given. The experimental data (O) are evaluated from the DSC curves displayed in Fig 1. The dashed line reflects the T_g values calculated according to the eq. 3 ($\square$) and the solid line – according to the eq. 4 ($\bullet$).

Fig 4 Relationship between the microhardness depression ΔH and the depression in the glass transition temperature ΔT_g for coreactive PET/PC blends with various composition.

Fig. 1

Fig. 2

Fig. 3

Fig 6