ELSEVIER

Polymer 43 (2002) 1805–1811

polymer

www.elsevier.com/locate/polymer

Miscibility and crystallisation behaviour of poly(ethylene terephthalate)/polycarbonate blends

Y. Kong, J.N. Hay*

Plastic Materials Laboratory, School of Metallurgy and Materials, The University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

Received 11 July 2001; received in revised form 28 August 2001; accepted 2 November 2001

Abstract

Poly(ethylene terephthalate)/polycarbonate blends were produced in a twin-screw extruder with and without added transesterification catalyst, lanthanum acetyl acetonate. The miscibility of the blends was studied from their crystallisation behaviour and variation in glass transition temperature with composition using differential scanning calorimetry, scanning electron microscopy and change in mechanical properties. The blends prepared without the catalyst showed completely immiscible over all compositions, while those prepared in the presence of the catalyst showed some limited miscible. The presence of PC inhibited the crystallisation of PET but this was much greater in the blends prepared in the presence of catalyst suggesting that some reaction had taken place between the two polyesters. The tensile properties showed little differences between the two types of blends. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Miscibility; Poly(ethylene terephthalate)/polycarbonate blends; Crystallisation

1. Introduction

Polymer blends are of considerable scientific and industrial interest since blending is an effective way to tailor the properties of polymers. Both poly(ethylene terephthalate) (PET) and bisphenol-A polycarbonate (PC) are important engineering plastics, in particular, PC has high impact strength and its solvent resistance is improved by mixing with PET. Both are polyesters and can react by transesterification in the molten state to form block or random copolymer, which will greatly alter the blend phase behaviour and morphology [1–5]. PET/PC blends have been extensively studied over the past two-decade [6–15]. Some authors [6,7] have found that the blends were miscible in PET content above 60–70 wt% and immiscible below this range. On the other hand, others [8–10] found that the blends were immiscible at all composition range. Others [16,17] have reported that PET/PC blends are partially miscible from 10 to 90% composition. These discrepancies may result from a variety of factors such as the use of solvents in their preparation, ester exchange reactions, molecular weight differences and the analytical techniques used to analyse and define compatibility.

In this paper, two different sets of blends have been prepared with a twin-screw extruder in the presence and absence of a transesterification catalyst, lanthanum acetylacetonate hydrate [15] in order to determine what effect this reaction has in improving the material properties of the PET/PC blends.

2. Experimental

PET was provided by DuPont Co. Ltd as moulding pellets. It has a number average molecular weight of 19.6 kg mol^{-1} and weight average molecular weight of 36.4 kg mol^{-1}. ECP Enichem Polimeri, Italy, supplied the PC. It has a number average molecular weight of about 20 kg mol^{-1}. Lanthanum acetylacetonate hydrate was purchased from Aldrich Chemical Co. Ltd and used as obtained. Pellets of the two polymers were dried at 125 °C for at least 10 h prior to blending in a twin-screw extruder, manufactured by APV, at 100–150 rpm and 50–70% torque. The zone temperatures varied from 295 to 305 °C. The extruded blends were quenched into cold water and pelletised. The catalyst was mechanically dispersed throughout the PC pellets at a concentration of 0.075 wt%.

The blends were dried in a vacuum oven at 100 °C for 12 h and pressed at 280 °C for 2 min at pressure of 7.5 MN m^{-2} on $100 \times 100 \times 0.8$ mm^3 plaque. Amorphous plaques were obtained by quenching into ice/water. Tensile dumbbell specimens were cut directly from the plaques.

---

* Corresponding author. Tel.: +44-121-414-4544; fax: +44-121-414-5232.

E-mail address: j.n.hay@bham.ac.uk (J.N. Hay).

0032-3861/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(01)00772-8

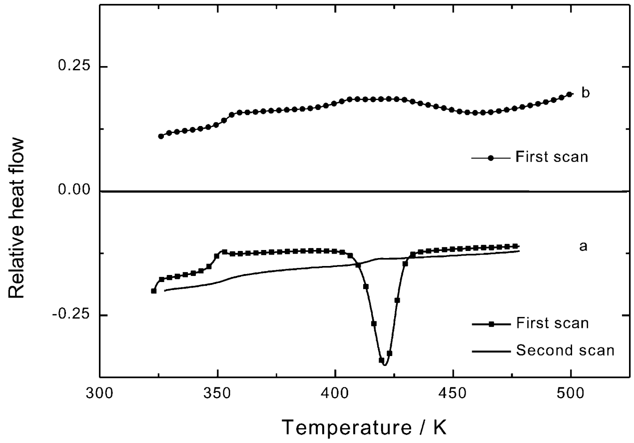

Fig. 1. DSC responses of PET/PC blends at different scans under a heating rate 10 K min^{-1}: (a) PET/PC 70/30 without added catalyst; (b) PET/PC 50/50 added catalyst.

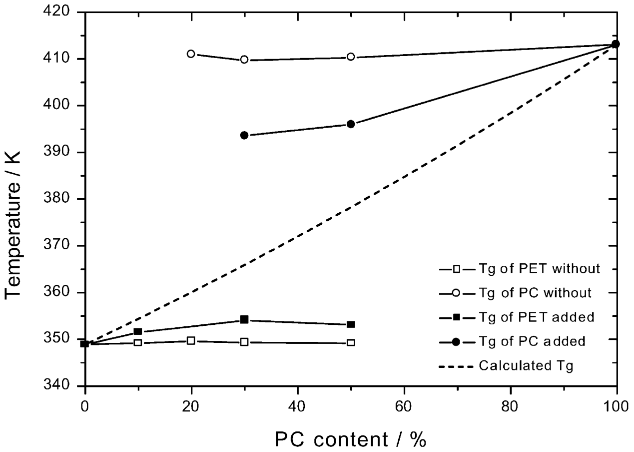

Fig. 2. The effect of PET/PC blend composition on T_gs, dash line is the T_g calculated by Fox equation.

A Perkin–Elmer differential scanning calorimetry, DSC-2, interfaced to a PC was used to measure the thermal properties of the blends. The calorimetry was operated under nitrogen flow of 20 cm^3 min^{-1}. The temperature was calibrated by the mp of ultra-pure materials: stearic acid, indium, tin and lead under different heating rates, corrections being made for thermal lag in the specimens. The glass transition temperature was determined as the midpoint of the step change in specific heat, ΔC_p, at different heating rates and extrapolated to zero heating rate to correct for thermal lag. For the isothermal crystallisation the samples were melted at 550 K for 5 min to erase the previous thermal history and then cooled to predetermined temperature at 160 K min^{-1}. A constant weight of 10.0 ± 0.2 mg was used throughout these measurements.

A scanning electron microscopy (SEM), Joel 5410, was used to examine the extent of phase separation in the blends by examination of their fracture surface. The samples were fractured at liquid nitrogen temperature and etched with diethylene triamine (DETA) for about 1 min at ambient temperature to remove the PC. The specimens were rinsed by distilled water and coated by gold to eliminate surface changing. Silver paint was used to form a conducting pathway between the sample and the mounting block.

Tensile properties were measured on an Instron, model 5566 interfaced to a PC. The crosshead speed was 2 mm min^{-1}. Standard dumbbell-shaped specimens were cut directly from moulded plate. An average of at least five specimens were measured for each determination. The energy to failure at high strain rate (3.5 m s^{-1}) was also investigated using a Zwick impact tester. Dumbbell shaped specimens used were identical to those used in Instron test. An average of at least eight specimens were used. All these tests were carried out at constant temperature of 296 ± 1 K and constant relative humidity of 35 ± 1%.

3. Results and discussion

3.1. Glass transition temperature

Since the glass transition temperature, T_g, depended on the rate at which the glass was formed, a standard quench rate was adopted and corrections were made for thermal lag by linear extrapolation to zero heating rate at constant sample weight. By this method, the T_gs of PET and PC were measured as 349 and 413 K, respectively.

On heating in the DSC, the amorphous blend samples prepared without added catalyst only showed one glass transition at the temperature close to that of PET. This was followed, as can be seen in Fig. 1(a), by an exotherm due to the crystallisation of PET. The size of the exotherm varied with PET composition. No glass transition could be observed in the region of that of PC since it was masked by the crystallisation of PET. However, the second glass transition, close to that of PC, was detected in the second DSC scan of the blend sample once the PET crystallisation was complete. The two T_gs did not vary substantially with blend composition.

However, differences were observed with the blends prepared in the presence of the transesterification catalyst. As can be seen in Fig. 1(b), two T_gs are observed, one close to that of PET which can be attributed to PET-rich phase and the other to that of PC which can be attributed to PC-rich phase, during the first DSC scan above a heating rate of 10 K min^{-1}. The crystallisation of the PET is inhibited and occurs at a much higher temperature, above 425 rather than 400 K. This takes it out of the temperature region of the second glass transition, enabling it to be observed. This is a kinetic effect and at lower heating rates the T_g of PC is hidden by the crystallisation of the PET.

The variation in the T_gs with composition is shown in Fig. 2, where the dash line represents the compositional variation in T_g for a miscible blend system and assuming

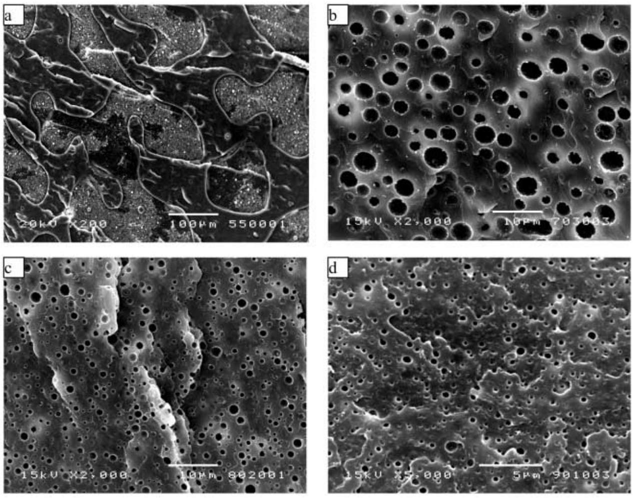

Fig. 3. SEM micrographs of cryo-fracture surface of PET/PC blends prepared without added catalyst etched by DETA for 1 min: (a) PET50/PC50; (b) PET70/P30; (c) PET80/PC20 and (d) PET90/PC10.

that the Fox equation [18] applies. It can be seen that for the blends without added catalyst, both T_gs are almost independent of composition. For the blends with added catalyst, two T_gs could be observed in the 50/50 and 70/30. The T_g of PET-rich phase is slightly higher than that of 100% PET and increases with PC content increasing while the T_g of PC-rich phase is some what lower than that of PC and also increases with PC content increasing. The values of T_gs suggest that there is only 0.5–0.7% PC in the PET-rich phase for 50/50 and 70/30 blends prepared without added catalyst while there is 8–10% PC in the PET-rich phase for corresponding blends added catalyst. This clearly indicates that the blends prepared without added catalyst is immiscible, on the other hand, these blends prepared in the presence of catalyst shows a partial miscibility. The T_g values also confirm that there is more PET contained in the PC-rich phase rather than PC in the PET-rich phase [11].

3.2. Morphology of the blends

The morphology of the blends was investigated by SEM from the appearance of the fracture surfaces after etching with DETA. DETA has a good selectivity to etch PC without attacking PET [19]. The SEM micrographs of the blends prepared without added catalyst are shown in Fig. 3. All the blends exhibited a binary structure and at 50/50 composition a co-continuous morphology was observed. At lower blend compositions, spherical PC particles were distributed uniformly throughout a continue PET matrix. The etched spherical cavities had sharp boundaries and there was no evidence of an interfacial layer between the PET matrix and PC domains. The PC particles decreased in size from about 3–5 μm in 70/30 to 1–2 μm in 90/10 PET/PC blends.

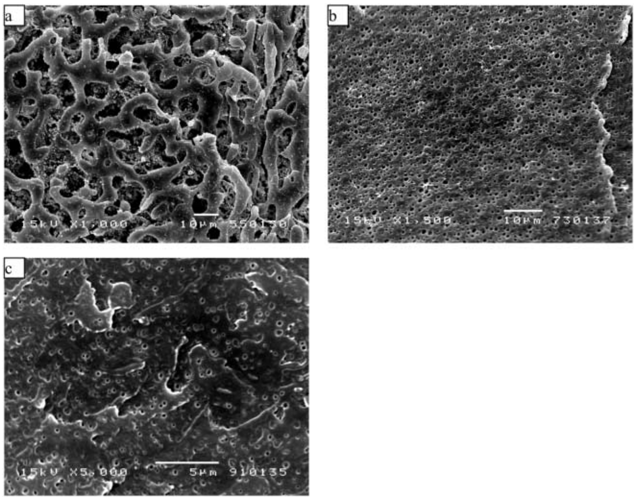

Fig. 4. SEM micrographs of cryo-fracture surface of PET/PC blends in the presence of catalyst etched by DETA for 1 min: (a) PET50/PC50; (b) PET70/P30 and (c) PET90/PC10.

In the blends prepared with added catalyst it can be seen from Fig. 4 that the 50/50 blend shows a co-continuous morphology and a similar trend with increasing PET composition from 70/30 to 90/10 of small PC particles embedded in a PET matrix. However, the PC particles are significantly smaller than observed previously with the blends prepared without the catalyst. The particle sizes are sub-micron and much more dispersed. It is difficult to accept that 30 and 10% of the sample is present as the dispersed phase. The SEM analysis is in agreement with DSC result that the PET/PC blends prepared without added catalyst being completely immiscible and exhibiting a clear two-phase structure. While the blends prepared in the presence of added catalyst show partially miscibility due to much smaller phases. These demonstrate that two materials appear to be more compatible as a result of the treatment with the transesterification catalyst.

3.3. Crystallisation behaviour of the blends

PET crystallises readily at temperature about 40 K above

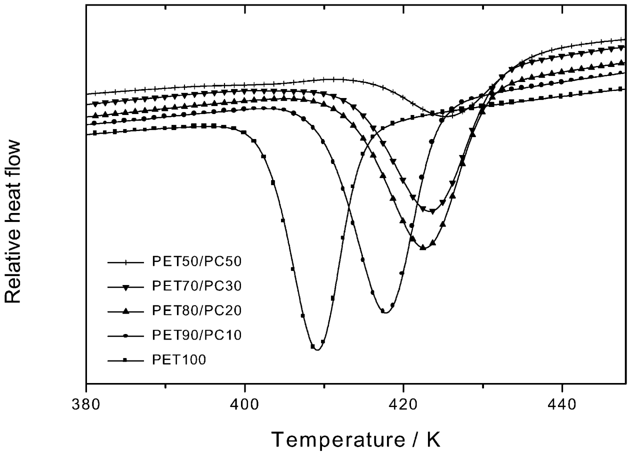

Fig. 5. DSC traces of cold crystallisation of PET and its blends without added catalyst under heating rate 10 K min^{-1}.

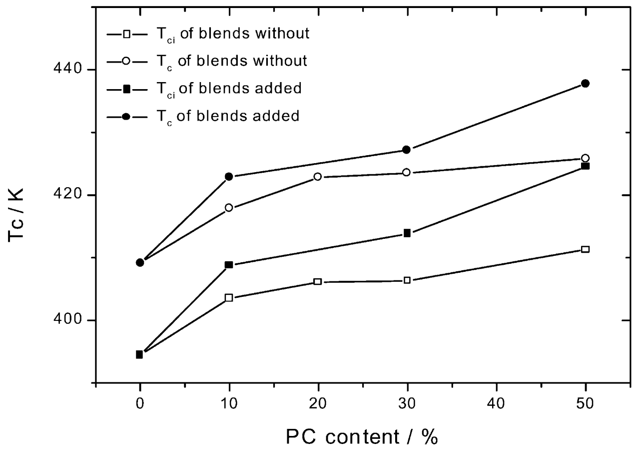

Fig. 6. The crystallisation temperatures of onset and maximum rate point for cold crystallisation of PET and its blends change with composition.

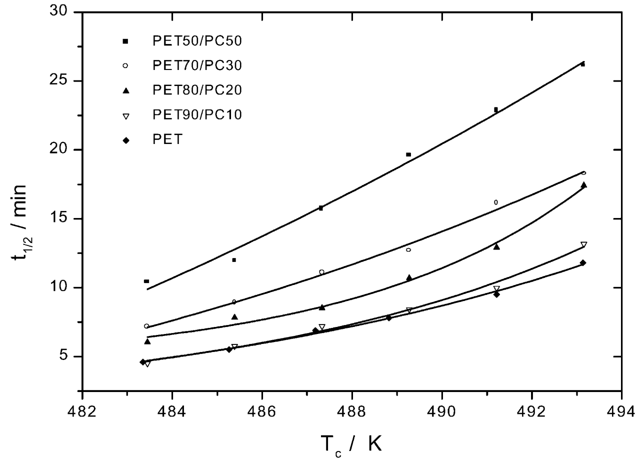

Fig. 8. The half-life, $t_{1/2}$ vs. T_c for PET and its blends without added catalyst.

its T_g, cold crystallisation, or about 60 K below its T_m, hot crystallisation. The cold crystallisation of PET in the blends, without added catalyst, is shown in Fig. 5 as measured by DSC at a heating rate of 10 K min^{-1}. The temperatures of initial onset of crystallisation, T_{ci}, and the temperature of maximum rate of crystallisation, T_c, for the blends are plotted in Fig. 6. These occur at higher temperature than those of PET, and increase with PC content. The corresponding T_{ci} and T_c values for the blends prepared with added catalyst are higher than those without added catalyst. This demonstrated that the PET crystallisation rate is reduced by the presence of PC and the effect is greater in the blends with added catalyst.

Isothermal crystallisation rates were also studied by DSC as a function of temperature in order to understand the nature of this inhibition of the crystallisation of PET by PC. In analysing, the isothermal crystallisation the fractional crystallinity, X_t, developed up to time t was defined to be the ratio of the areas between the heat flow–time curve and baseline of the sample [20,21], i.e.

$$X_t = \frac{\int_0^t \frac{dH}{dt}dt}{\int_0^{t_\infty} \frac{dH}{dt}dt} \tag{1}$$

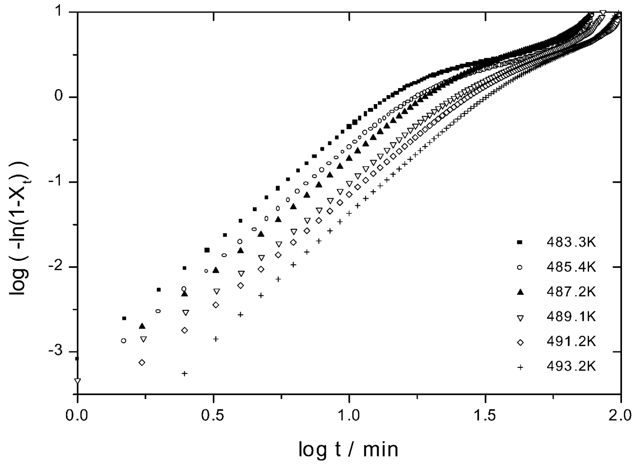

Fig. 7. Avrami analysis for PET isothermal crystallisation.

The degree of crystallinity against time was analysed using the Avrami equation [22–24], i.e.

$$1 - X_t = \exp(-Zt^n) \tag{2}$$

in which X_t is the volume fraction degree of crystallinity, Z is a composite rate constant and n is an Avrami exponent. The equation can also be converted to

$$\log(-\ln(1 - X_t)) = \log Z + n \log t \tag{3}$$

Plots of $\log(-\ln(1 - X_t))$ vs. $\log t$ plots are linear with slope n as is shown in Fig. 7.

The rate constant, Z, was calculated from half-life of the crystallisation, $t_{1/2}$, and the value of n at $t_{1/2}$

$$Z = \frac{\ln 2}{t_{1/2}^n} \tag{4}$$

As can be seen from Fig. 7, there are obvious changes in the slope of each isotherm at about 70% conversion. This is usually interpreted as due to the presence of primary and secondary crystallisation processes. Only the primary process was analysed. The rate parameters obtained from the Avrami equation as a function of crystallisation temperature are listed in Table 1 for PET and both sets of blends.

The n values within experimental error were essentially constant at ± 0.3 consistent with growth of spherulites from heterogeneous nuclei. For each sample the $t_{1/2}$ increased, and Z decreased, with increasing crystallisation temperature but PET crystallised at a faster rate than the blends at the same crystallisation temperature. PC inhibits the crystallisation of PET. A similar conclusion can be discerned from a plot of the half-life, $\ln(t_{1/2})$ vs. T_c, in Figs. 8 and 9. The effect

Table 1
Avrami parameters for PET and its blends molten-crystallisation

Sample	Temperature (K)	$t_{1/2}$ (min)	$n \pm 0.1$	Z ($\times 10^{-4}$ min^{-n})
PET	483.4	4.6	3.0	71.2
	485.3	5.5	3.0	41.7
	487.2	6.9	3.1	17.4
	488.8	7.8	3.0	14.6
	491.2	9.5	3.0	8.11
	493.1	11.8	3.0	4.2
PET/PC 50/50 without catalyst	483.4	10.4	2.7	12.4
	485.4	11.9	2.7	5.2
	487.3	15.8	2.8	3.1
	489.3	19.6	2.8	1.7
	491.2	22.9	2.9	1.5
	493.2	26.1	2.7	1.0
PET/PC 70/30 without catalyst	483.4	7.1	3.1	15.7
	485.4	8.9	3.1	7.9
	487.3	11.1	3.0	5.1
	489.3	12.7	2.9	4.4
	491.2	16.2	2.9	2.2
	493.2	17.9	2.8	2.1
PET/PC 90/10 without catalyst	483.4	4.5	3.1	65.4
	485.4	5.8	3.1	29.8
	487.3	7.2	3.3	10.3
	489.3	8.4	3.1	9.4
	491.2	10.0	3.2	4.4
	493.2	13.2	3.2	1.8
PET/PC 50/50 added catalyst	469.9	9.6	2.9	9.8
	471.8	11.7	3.0	4.3
	473.8	13.4	3.0	2.9
	475.3	15.3	2.9	2.5
	477.6	18.0	2.9	1.6
	479.5	20.2	3.0	0.84
PET/PC 70/30 added catalyst	471.8	12.0	3.0	4.0
	473.8	14.0	3.1	1.9
	475.7	16.0	3.2	0.97
	477.6	19.0	3.1	0.75
	479.5	21.6	3.0	0.65
	481.4	25.0	3.0	0.44
PET/PC 90/10 added catalyst	477.6	13.4	3.0	2.9
	479.5	15.3	3.1	1.5
	481.4	17.7	3.0	1.2
	483.1	21.6	3.0	0.69
	483.3	22.6	3.0	0.60
	485.3	29.8	3.0	0.26
	487.2	34.8	3.0	0.16

is more marked with the blends prepared with added catalyst than those without and indeed the later blends crystallised over a similar temperature range to that of PET but with half-lives which were reduced in proportion to the content of PET in the blend, see Table 1. Thus the 50/50 blends have half-lives which are approximately double those of PET, and similarly with the other blends. The reduction in crystallisation rate in these blends is considered to occur from a physical restriction to the growth by the PC domains.

Very different temperature dependences are observed with the crystallisation half-lives of the blends prepared with added catalyst, see Fig. 9(a), in which they crystallise at much lower temperatures and the displacement to lower crystallisation temperatures is disproportional to the amount of PC present. 10% PC in the blend had a greater effect proportionally than 30 or 50%.

The temperature dependence of the crystallisation half-lives of PET and the 50/50 blends were analysed using the Mandelkern equation [25],

$$\ln(1/t_{1/2}) = A - (4\sigma\sigma_{\mathrm{e}}/R\Delta H_v)\Big[T_{\mathrm{m}}^0/T_{\mathrm{c}}\Big(T_{\mathrm{m}}^0 - T_{\mathrm{c}}\Big)\Big] \tag{5}$$

in which A is a constant, σ and σ_{e} are the surface free energy of substrate and fold surface free energy, respectively, ΔH_v is the heat of fusion of per monomer mole and R is the gas constant. From Fig. 10 it can be seen that the plots of $\ln(1/t_{1/2})$ vs. $T_{\mathrm{m}}^0/(T_{\mathrm{m}}^0 - T_{\mathrm{c}})T_{\mathrm{c}}$ were approximately linear and parallel indicating that the slopes

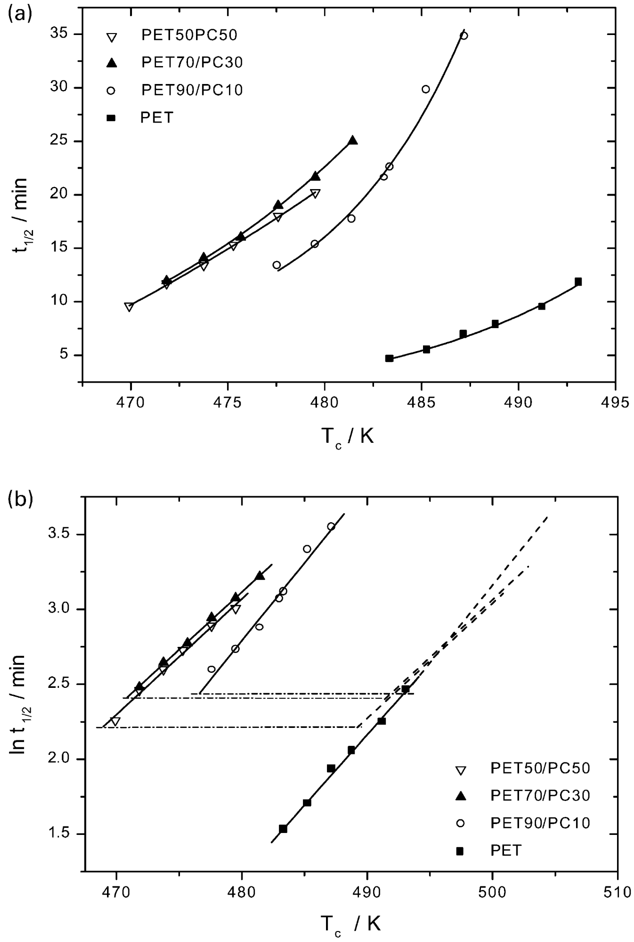

Fig. 9. (a) The half-life, $t_{1/2}$ vs. T_c for PET and its blends added catalyst. (b) $\ln(t_{1/2})$ vs. T_c for PET and its blends added catalyst, the dash lines indicate the shift of each blend.

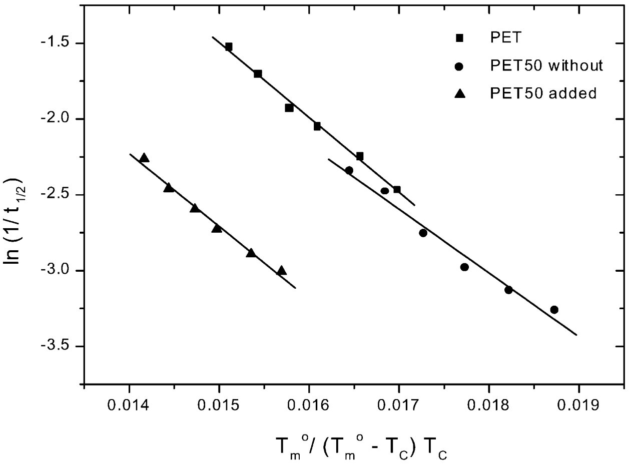

Fig. 10. Temperature dependence of crystallisation rate for PET and 50/50 blends, for PET $T_m^0 = 560$ K, PET/PC 50/50 blend without added catalyst $T_m^0 = 554$ K and PET/PC 50/50 blend in the presence of catalyst $T_m^0 = 546$ K.

represent the term $4\sigma\sigma_e/R\Delta H_v$ were similar. Assuming [26] that $\sigma = 0.1\Delta H_v$, the values of σ_e were calculated to be 10.3, 10.0 and 9.0 ± 1.5 kJ mol^{-1} for PET and the two 50/50 blends prepared with and without added catalyst, respectively. Although it can be seen that PC inhibits the crystallisation of PET this cannot be due to the small changes observed in the fold surface free energy, which would be expected if PC were soluble and being rejected during crystallisation.

It is apparent for Eq. (5) that $\ln(t_{1/2})$ is also a function of the degree of super-cooling, $\Delta T = T_m^0 - T_c$. Plots of $\ln(t_{1/2})$ against T_c, see Fig. 9(b), for each blend could be superimposed onto the PET data by a lateral shift along the temperature axis equivalent to a ΔT value for each blend. These were 15, 19 and 20 K for the 90/10, 70/30 and 50/50 blends added catalyst consistent with a marked lowered of the equilibrium mp in these blends and to the presence of a soluble impurity.

T_m^0 values were measured by the Hoffman and Weeks procedure [27] as 560 and 546 K for PET and the 50/50 blend in the presence of catalyst, respectively. The values do indicate a marked reduction in T_m^0 of the blend from the PET value and so would account for the observed crystallisation behaviour. The behaviour is consistent with partial miscibility of the PC in PET.

3.4. The mechanical properties of the blends

In the tensile tests, all the amorphous blends exhibited ductile failure with a yield point followed by the development of a neck and strain hardening before finally failing. The tensile properties of both sets of blend are listed in Table 2. The elastic modulus increased progressively with PC content in the blends prepared with catalyst and

Table 2
Mechanical properties of PET and PC and their blends

Sample	Young's modulus (GPa)	Ultimate strength (MPa)	Elongation at break (%)	Tensile impact (MJ m^{-2})
PC	1.10 ± 0.01	50.9 ± 3.0	91 ± 16	0.89 ± 0.26
PET50 added	1.39 ± 0.01	46.4 ± 4.8	174 ± 53	0.51 ± 0.13
PET70 added	1.42 ± 0.01	59.4 ± 3.5	389 ± 24	0.33 ± 0.08
PET90 added	1.40 ± 0.02	57.6 ± 3.9	477 ± 32	0.36 ± 0.07
PET50 without	1.18 ± 0.02	45.2 ± 1.5	164 ± 12	0.44 ± 0.09
PET70 without	1.19 ± 0.01	47.1 ± 3.0	288 ± 27	0.36 ± 0.08
PET90 without	1.23 ± 0.02	54.9 ± 4.3	460 ± 37	0.36 ± 0.09
PET	1.29 ± 0.04	52.3 ± 5.2	498 ± 50	0.34 ± 0.04

decreased in the blends without catalyst. The greatest increase in modulus was obtained at 10% composition. The ultimate strength was also greater in these blends although the trend was not so clear. An initial increase was observed with composition followed by a decrease as the co-continuous morphology developed.

In both blend systems the elongation at break decreased gradually with increasing PC content and little differences were observed between the two systems. The tensile impact results changing with PC composition are displayed in Table 2. The tensile impact strength increased limitedly with increasing PC content for both sets of blends with almost identical values at each composition.

4. Conclusions

Blends produced without added catalyst have two T_gs independent of composition and a binary morphology. The blends are completely immiscible over the composition range studied. However, for the blends prepared with added catalyst, two T_gs close to each other are observed over a limited concentration range. Where there are two glass transitions the morphology is of a much more finely divided phase separation and some limited solubility of PC in PET.

The Avrami model was applied to analyse the crystallisation kinetics of PET and both sets of blends where the PET crystallisation is inhibited by the presence PC, particularly for the blends prepared with added catalyst. For blends without added catalyst the main reason is that of PC domains physical constraining the development of the PET crystallisation while for the other blends it is due to the limited soluble PC in PET depression its equilibrium mp.

The tensile and impact properties of the blends are also consistent with this limited solubility.

Acknowledgements

One of the authors, Y.K., acknowledges receipt of a scholarship from ORS Committee during the tenure of this study. Thanks are also due to Mr F. Biddlestone for his technical support.

References

[1] Kotliar AM. J Polym Sci, Macromol Rev 1981;16:367.
[2] Pilati F, Marianucci E, Berti C. J Appl Polym Sci 1985;30:1267.
[3] Godard P, Dekoninck JM, Devlesaver V, Devaux J. J Polym Sci, Polym Chem 1986;24:3301.
[4] Godard P, Dekoninck JM, Devlesaver V, Devaux J. J Polym Sci, Polym Chem 1986;24:3315.
[5] Montaudo G, Puglisi C, Samperi F. Macromolecules 1998;31:650.
[6] Nassar TR, Paul DR, Barlow JW. J Appl Polym Sci 1979;23:85.
[7] Murff SR, Barlow JW, Paul DR. J Appl Polym Sci 1984;29:3231.
[8] Chen XY, Bireley AW. Br Polym J 1985;17:347.
[9] Hanrahan BD, Angeli SR, Runt J. Polym Bull 1986;15:455.
[10] Suzuki T, Tanaka H, Nishi T. Polymer 1989;30:1287.
[11] Zheng WG, Wan ZH, Qi ZN, Wang FS. Polym Int 1994;34:301.
[12] Zheng WG, Qi ZN, Wang FS. Polym Int 1994;34:307.
[13] Tan Q, Ma DZ. J Appl Polym Sci 1993;48:747.
[14] Ignatov VN, Carraro C, Tartari V, Pippa R, Scapin M, Pilati F, Berti C, Toselli M, Fiorini M. Polymer 1997;38:195.
[15] Ignatov VN, Carraro C, Tartari V, Pippa R, Scapin M, Pilati F, Berti C, Toselli M, Fiorini M. Polymer 1997;38:201.
[16] Kim WN, Burn CM. J Polym Sci, Polym Phys 1990;28:1409.
[17] Wang L, Huang Z, Hong T, Porter RS. J Macromol Sci, Phys 1990;B29:155.
[18] Fox TG. Bull Am Phys Soc 1956;1:123.
[19] Hobbs SY, Dekkers MEJ, Watkins VH. J Mater Sci 1988;23:1219.
[20] Booth A, Hay JN. Polymer 1969;10:95.
[21] Hay JN, Mills PJ. Polymer 1982;23:1380.
[22] Avrami M. J Chem Phys 1939;8:212.
[23] Avrami M. J Chem Phys 1939;9:177.
[24] Evans UR. Trans Faraday Soc 1945;41:365.
[25] Mandelkern L, Fatou JG, Howard C. J Phys Chem 1964;68:3386.
[26] Beech PR, Booth C, Hillier ZH, Pickles CJ. Eur Polym J 1972;8:799.
[27] Hoffman JD, Weeks JJ. J Res Natl Bur Stand 1962;66A:13.