BUTTERWORTH HEINEMANN

Polymer Vol. 36 No. 20, pp. 3963–3967, 1995

0032-3861/95/$10.00 + 0.00

polymer communications

Miscibility of ethylene terephthalate–caprolactone copolyester blends with polycarbonate

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(Received 9 June 1994; revised 4 August 1994)

The miscibility of ethylene terephthalate (ET)–caprolactone (TCL) copolyester blends with polycarbonate has been studied by differential scanning calorimetry (d.s.c.). When ET content in the copolyesters is less than 60%, they are miscible with polycarbonate. Such a miscibility window cannot be predicted by the Flory–Huggins theory. The ratio of the glass transition temperatures T_{g_A}/T_{g_B} has been used to characterize some non-combinatorial entropic contribution which is connected with interaction parameter χ_1. Using the method suggested by Coleman, the total interaction parameter $\chi = \chi_0 + \chi_1$ (χ_0 is the Flory–Huggins interaction parameter) is plotted against the molar volume fraction of ester groups in the TCL copolyesters. The miscibility range determined in this way conforms with the results of d.s.c. experiments.

(Keywords: miscibility window; copolyesters; polycarbonate)

Introduction

The blends of several polyesters with the polycarbonate of bisphenol-A are of considerable scientific and industrial interest. It has been suggested that melt-processed mixtures of poly(ethylene terephthalate) (PET) and polycarbonate (PC) exhibit significant intermolecular mixing[1–3]. A single glass transition temperature (T_g) was observed for compositions containing more than 60–70% PET by weight, while compositions below this range showed two glass transitions[1]. Chen and Bireley[4] have shown from differential scanning calorimetry (d.s.c.), dynamic mechanical analysis and infra-red spectroscopy that extruder-mixed blends with a small extent of transesterification have an inhomogeneous amorphous phase. Hanrahan *et al.*[5] demonstrated the immiscibility of PC and PET by d.s.c. and dielectric loss spectroscopy for solvent-cast blends using two kinds of solvents, 1,1,1,3,3,3-hexafluoro-2-propanol and a mixed solvent of phenol and tetrachloroethane in a 40/60 ratio by weight. Suzuki *et al.*[6] have confirmed that PC and PET are immiscible over the whole composition range studied for both extruder-mixed and solvent-cast blends; the PC/PET blends are homogenized only by transesterification between PC and PET above the melting temperature of PET. Li-Hui Wang *et al.*[7] also reported the same kind of results as Suzuki *et al.*

Simultaneously, Paul and co-workers[8–10] have indicated that poly(ϵ-caprolactone) (PCL) is miscible with polycarbonate of bisphenol-A in the amorphous state. This blend exhibits lower critical solution temperature (*LCST*) behaviour of phase separation. Furthermore, these workers emphasize the existence of physical interaction between the polyester carbonyl moieties and the polycarbonate molecule. Coleman *et al.*[11] have proved the presence of specific chemical interactions between PCL and PC in the amorphous state, which infers miscibility. However, Jonza and Porter[12] have shown convincingly that a single glass transition was found across the compositional diagram of PCL/PC blends, but no depression was observed in the melting points of either PC or PCL. Therefore the Flory interaction parameter (χ) must be zero or slightly positive for these blends.

It is of interest to discover whether or not the ethylene terephthalate–caprolactone (TCL) copolyester is miscible with PC. How does the miscibility between the copolyester and PC depend on the composition of the copolyesters and blends? How can we predict the window of miscibility between the copolyester and PC? How can the miscibility of such blends be understood?

Experimental

A list of the polymers used in the present work with their ethylene terephthalate (ET) contents, intrinsic viscosity values ([η]) and glass transition temperatures (T_g) is given in *Table 1*. The copolyesters were synthesized in our laboratory[13,14] and purified by precipitation in a large amount of methanol from a 5% (w/v) chloroform solution. Their ET contents were determined by nuclear magnetic resonance spectroscopy as described previously[15]. The bisphenol-A polycarbonate was provided by Idemitsu Petrochemical Co. (Idemitsu Polycarbonate N2200, $M_n = 14\,400$, $M_w = 29\,000$ $M_w/M_n = 2.02$; tetrahydrofuran as solvent at 40°C).

The blend films were prepared by solution-casting from chloroform solution at room temperature. The blend samples were further dried in a vacuum oven at a temperature of 323 K until they reached constant weight.

The glass transition temperatures of the copolyesters and their blends with PC were measured using

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Table 1 Description of synthesized TCL copolyesters

Acronym	ET content[a] (wt%)	T_g[b] (K)	$[\eta]$[c] ($dl\,g^{-1}$)
TCL82	82	306.0	0.8369
TCL72	72	291.0	0.9554
TCL62	62	269.7	0.9941
TCL58	58	261.7	0.8508
TCL48	48	245.6	0.8651

[a] ET content determined by n.m.r
[b] T_g determined by d.s.c. at a heating rate of 20 K min^{-1}
[c] $[\eta]$ measured in *m*-cresol at 30 C

Table 2 Thermal properties of the PCL/PC blends

TCL copolyesters	PC content (wt%)	T_g (K)
TCL82	0	306
	10	312 421
	20	312 420
	50	319 415
	80	320 417
	90	320 415
	100	427
TCL72	0	219
	30	294 414
	50	300 410
	70	298 406
	100	427
TCL62	0	270
	10	275
	20	285 416
	50	295 418
	80	332 393
	90	399
	100	427
TCL58	0	262
	30	273
	50	293
	70	371
	100	427
TCL48	0	246
	10	249
	20	256
	50	284
	80	355
	90	397
	100	427

a Perkin–Elmer DSC-2C with Intracooler-II. The temperature at the half-height of the corresponding heat capacity jump was defined as T_g. The temperature was calibrated with ultrapure indium. In the d.s.c. apparatus the samples were first heated at a rate of 20°C min^{-1} to 530 K, maintained for 1 min and quenched to 190 K. The quenched samples were then reheated from 190 K at a rate of 20°C min^{-1} to 530 K (first scan) to measure the T_g.

A blend sample is considered miscible if its thermogram at each composition exhibits a single T_g intermediate between those of the individual components. Thus, a sample exhibiting two T_gs at a given composition is considered immiscible, even if the possibility of observing a single T_g at other compositions is not excluded.

Phase separation was investigated by d.s.c. with the following annealing cycle. The sample was first cooled to 190 K and maintained at that temperature for 5 min. A first scan was made at a heating rate of 160°C min^{-1} up to an annealing temperature close to the highest T_g of the components considered. After annealing at that temperature for 3 min, it was quenched again to 190 K, then a second scan was made with a heating rate of 20°C min^{-1} to an annealing temperature 10°C above the annealing temperature of the previous scan. Such a post-annealing heating–cooling cycle was repeated up to the annealing temperature of 550 K to detect whether phase separation occurred at a high temperature.

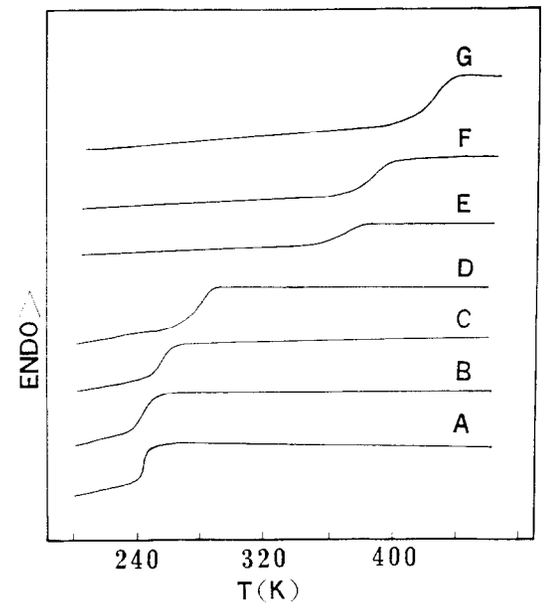

Figure 1 D.s.c. thermograms of TCL48/PC blends with different compositions quenched from 530 K to 190 K: (A) TCL48, (B) 90/10, (C) 80/20, (D) 50/50, (E) 20/80, (F) 10/90, (G) PC

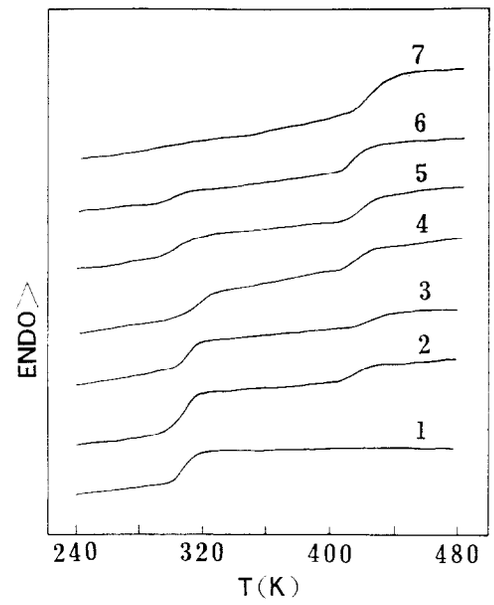

Figure 2 D.s.c. thermograms of TCL82/PC blends with different compositions quenched from 530 K to 190 K: (1) TCL82, (2) 90/10, (3) 80/20, (4) 50/50, (5) 20/80, (6) 10/90, (7) PC

Results and discussion

Miscibility of TCL/PC blends. *Table 2* lists the thermal analysis results of PC blends with copolyesters having different ET contents. The blends of PC/TCL48 and PC/TCL58 exhibit only one T_g in their thermograms for all compositions. In *Figure 1* the thermograms of blends PC/TCL48 are shown. The T_g of these blends changes with composition regularly and can be described by the Gordon–Taylor equation. This means that the blends of TCL48/PC and TCL58/PC are miscible. When ET contents in copolyesters transcend 60 wt%, the blends of copolyesters with PC show different behaviour. The blends of TCL62, TCL72 and TCL82 copolyesters with PC exhibit two T_gs in their thermograms for all compositions. The thermograms of TCL82/PC blends are shown in *Figure 2*. Such results prove that TCL62, TCL72 and TCL82 copolyesters are immiscible with PC. It can be seen that in these blends the two T_gs have slightly different values from the T_gs of the respective parent components. This indicates the formation of two phases in these blends: a PC-rich phase containing small amounts of copolyester, and a copolyester-rich phase with small amounts of PC. It is also found that the T_g values of the two phases become closer to those of the respective parent components with increasing ET content in the copolyesters. Therefore from such experimental results it can be concluded that pure PET must be immiscible with PC. The annealing experiments have shown that for blends TCL48/PC and TCL58/PC, phase separation cannot be observed at any annealing temperature; at the same time, blends TCL62/PC, TCL72/PC and TCL82/PC do not exhibit a tendency to homogenize on annealing without any transesterification.

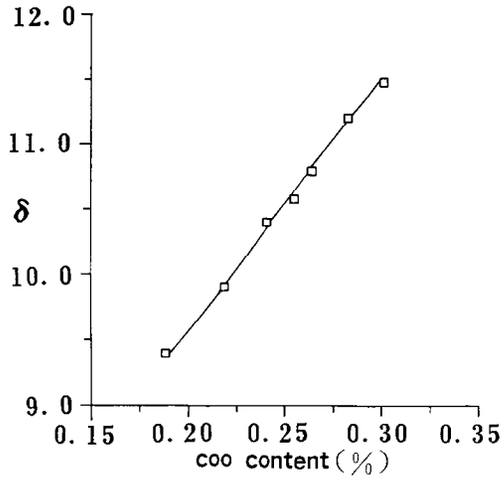

Figure 3 Relationship between solubility parameter and molar volume fraction of ester groups in TCL copolyesters

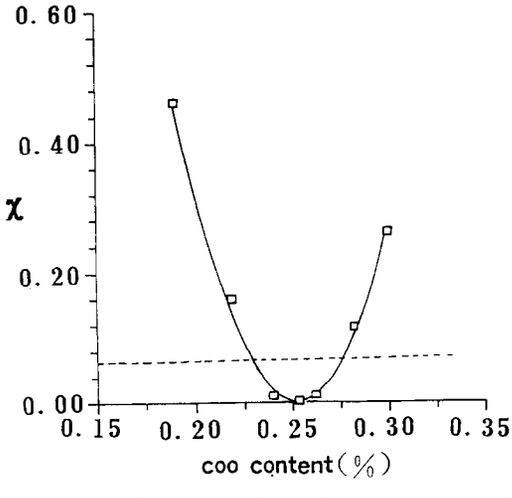

Figure 4 Relationship between interaction parameter in TCL/PC blends and molar volume fraction of ester groups in TCL copolyesters

Explanation of the window of miscibility. In order to understand the miscibility of blends of TCL copolyester/PC with TCL contents less than 60 wt%, we have tried to utilize the method suggested by Coleman *et al.*[16]. In this method, the free energy of mixing was described by the equation:

$$\Delta G/RT = \phi_A \ln \phi_A/N_A + \phi_B \ln \phi_B/N_B + \phi_A\phi_B\chi + \Delta G_H/RT \quad (1)$$

ϕ_A and ϕ_B, N_A and N_B are the volume fractions and degrees of polymerization of A and B component, respectively; χ is the polymer–polymer interaction parameter. This is the well known Flory–Huggins relationship, but with an added term, $\Delta G_H/RT$ to account for the presence of favourable intermolecular interactions. In the absence of favourable intermolecular interaction (i.e. when $\Delta G_H/RT = 0$), the interaction parameter χ is positive and its critical value is:

$$\chi_{crit} = [(N_A)^{-1/2} + (N_B)^{-1/2}]^2/2 \quad (2)$$

If we are dealing with weak interactions (van der Waals force), χ can be related to the Hildebrand solubility parameters of the two polymers:

$$\chi = V_r(\delta_A - \delta_B)^2/RT \quad (3)$$

Here V_r is a reference volume; the solubility parameters δ can be calculated by the group contribution method with sufficient accuracy.

The solubility parameter of TCL copolyester changes linearly with increasing ET content, as shown in *Figure 3*. The abscissa of the figure is the molar volume fraction ϕ_{coo}, which means that the molar volume of ester groups in the copolyester is divided by the molar volume of the copolyester sample. The solubility parameters (ordinate) of the copolyesters are calculated using the values provided by Coleman *et al.*[16]. From equation (3), the interaction parameters between copolyesters and PC can be computed. The numerical results of the solubility and interaction parameters are listed in *Table 3*. The values used in the calculation were PC molar volume $V_r = 191\ cm^3\ mol^{-1}$ and PC solubility parameter $\delta_{PC} = 10.6$. The interaction parameters are plotted against the molar volume fraction of ester groups as shown in *Figure 4*. On the basis of the molecular weights of copolyester and PC, the critical value of χ should be equal to 0.02. From such a critical value the predicted miscibility window is very narrow. Referring to data of PC/PCL blends in the literature[9–12] a value of $\chi_{crit} = 0.08$ is postulated, but the estimated miscibility window ($\phi_{coo} = 0.235$–0.275 or 47 wt%–82 wt%) still

Table 3 Calculated δ and $\chi_{PC/TCL}$ of TCL with different ET contents using Coleman's method[a]

ET content (mol%)	ϕ_{coo}	δ	$\chi_{PC/TCL}$
100	0.299	11.5	0.262
80	0.282	11.2	0.116
60	0.263	10.8	0.013
50	0.252	10.6	0
40	0.241	10.4	0.013
20	0.218	9.9	0.158
0	0.192	9.4	0.465

[a] $\delta_{PC} = 10.6$ (cal cm^{-3})$^{0.5}$

Table 4 Calculated δ and $\chi_{PC/TCL}$ of TCL with different ET contents using our method[a]

ET content (mol%)	ϕ_{coo}	T_g (K)	δ	χ_0	χ
100	0.299	348	11.5	0.262	0.237
80	0.282	318	11.2	0.116	0.072
60	0.263	289	10.8	0.013	−0.064
50	0.252	274	10.6	0	−0.106
40	0.241	260	10.4	0.013	−0.133
20	0.218	231	9.9	0.158	0.138
0	0.192	202	9.4	0.465	−0.198

[a] $\delta_{PC} = 10.6$ (cal cm^{-3})$^{0.5}$. T_g calculated from the Fox equation

Table 5 Calculated δ and $\chi_{PC/PnL}$ of aliphatic polyesters using our method[a]

CH_2/COO	ϕ_{coo}	T_g (K)	δ	χ_0	χ
1	0.543	288	11.9	0.549	0.470
2	0.373	251	10.7	0.003	−0.177
3	0.284	223	10.0	0.116	−0.250
4	0.229	203	9.7	0.262	−0.382
5	0.192	202	9.4	0.465	−0.198
6	0.165	202	9.2	0.633	0.030
7	0.145	202	9.0	0.827	0.164

[a] $\delta_{PC} = 10.6$ (cal cm^{-3})$^{0.5}$. The T_g of PC is 427 K. The T_g of PnL (aliphatic polyesters) is obtained from Ref. (23)

deviates from experimental results (i.e. the blends are miscible when the ET content is less than 60 wt%). This means that the Flory–Huggins theory cannot predict the miscibility window of PC/TCL copolyester blends correctly; postulating the existence of specific molecular interaction cannot improve the situation either. It is necessary to find a new way to explain the miscibility window of PC/TCL copolyester blends.

Schweizer and Curro[17,18] have developed an integral equation theory of polymer blends which is based on the 'reference interaction site model' (RISM) theory. Applying RISM theory to various athermal mixtures, it has been shown that structural asymmetry in the polymer components can lead to a negative χ parameter with an approximate linear composition dependence. The local structural asymmetry on a monomer scale or a radius of gyration length scale can lead to significant non-combinatorial entropy of mixing effects. Using small-angle neutron scattering (SANS), Ito *et al.*[19] have recently determined the effective χ parameter of high molecular weight blends of poly(methyl methacrylate) (PMMA) and poly(ethylene oxide) (PEO). This mixture was found to be miscible with a negative χ parameter of the order of −0.002 (for 50% PMMA monomer fraction). Moreover, when the temperature was increased from 25 to 80°C, no change in the measured χ parameter was detected. This implies that the miscibility is not associated with favourable attractive intermolecular interactions but rather derives from a stabilizing non-combinatorial entropic contribution to the free energy of mixing. Such a non-combinatorial entropic contribution should be initiated from the obvious difference between PEO and PMMA in both their monomer volumes and statistical segment lengths[20]. The result of SANS is consistent with previous melting-point-depression data, despite small values of depression.

In the literature, the PCL/PC blends have been proved to be miscible. The interaction parameters in the blends determined by different authors are different, but the source of the differences is uncertain. However, the common result appears to be that the interaction parameter χ in PCL/PC blends is small, close to zero, and it is difficult to prove the existence of specific intermolecular interaction. Moreover, it is found elsewhere[21] that the free volume and the volume extension index are different in PC and PCL. Therefore in such blends the miscibility should also be determined by some non-combinatorial entropic contribution, for example the difference between local structures in each blend component, the difference in statistical segment length, and so on. Such non-combinatorial entropic contribution factors should be divided into two kinds: favourable and unfavourable. In blends such as PEO/PMMA and PCL/PC, favourable non-combinatorial entropic contributions certainly exist. In PC/TCL copolyester blends, the favourable non-combinatorial entropic contributions may play a role in mixing for the compositions of blends with ET content less than 60 wt%.

How can we predict the miscibility window for PC/TCL copolyester blends? In fact, both local structural asymmetry and statistical segment length must be related to the glass transition of macromolecules. Generally the T_g of miscible blends is connected with molecular interaction between the components in the blends. Here it is proposed that the ratio of the T_gs can be used to characterize some non-combinatorial entropic contribution. The ratio T_{g_A}/T_{g_B} can be considered as some 'average one-dimensional structural parameter' (i.e. the distance between different asymmetry structural units). It has the following relationship with the interaction parameter:

$$\chi_1 = K(T_{g_A}/T_{g_B})^6 \tag{4}$$

Here it is simulated as the van der Waals interaction energy and depends on the distance between different asymmetry structural units (like the London formula $\epsilon_{12} \sim a_1 a_2 / r^6 + \cdots$). χ_1 represents some non-combinatorial entropic interaction in PC/TCL copolyester blends. K is a constant, T_{g_A} and T_{g_B} are the glass transition temperatures of components A and B in the blends. This new interaction parameter is considered as an additional term to the Flory–Huggins interaction parameter χ_0. Then all interaction parameters χ should be represented by the following formulae:

$$\chi = \chi_0 + \chi_1 \tag{5}$$

$$= V_r(\delta_A - \delta_B)^2/RT + K(T_{g_A}/T_{g_B})^6 \tag{6}$$

The constant K was calculated by using the interaction parameter between PC and PCL from the literature[22]

($\chi_{PC/PCL} = -0.189$, and $K = -7.43 \times 10^{-3}$). On the basis of equation (6), a series of interaction parameters χ for blends of PC/TCL copolyesters have been calculated and are given in *Table 4*. If the critical interaction parameter calculated from equation (2), $\chi_{crit} = 0.02$, is used then the range of the molar volume fraction of ester groups ϕ_{coo} (from $\phi_{coo} = 0.273$, corresponding to an ET content of 80 wt%, to $\phi_{coo} = 0.192$ for pure PCL) should be responsible for the miscibility window of PC/TCL copolyester blends. Although the upper limit is higher than the experimental value, the predicted results basically conform to the measured range of miscibility. Simultaneously, the blends of PC with a series of aliphatic polyesters containing different numbers of COO groups are treated by the method described above. The data are listed in *Table 5*. Taking the same χ_{crit} value, the miscibility window of PC/aliphatic polyester blends ranges from $\phi_{coo} = 0.415$ (upper limit) to $\phi_{coo} = 0.175$ (lower limit). The corresponding values of the ratio CH_2/COO are 1.7 and 5.6. Such results also conform to experimental data in the literature[23].

Acknowledgement

This research has been supported by 'National Basic Research Project—Macromolecular Condensed State' Foundation of China.

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