

MONOMERIC INTERACTION BETWEEN ETHYLENE— TEREPHTHALATE AND CAPROLACTONE

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ABSTRACT

The miscibility of poly(ethylene terephthalate (ET)—caprolactone (CL) (TCL)/poly(ethylene terephthalate) (PET) blends were examined by Differential Scanning Calorimeter (DSC). In these blends, a miscibility limit specified by ET content in the TCL was found to be about 70(wt%). In the blends of TCL/TCL with different ET contents, a miscibility window defined by ET content was also found to range from 82 to 58(wt%). Based on the experimental miscibility limits and the mean field binary interaction model, the interaction parameter between monomeric units of ET and CL was obtained.

INTRODUCTION

Recently, there has been considerable scientific and industrial interest in the miscibility of polymer blends^[1]. From the thermodynamical analysis, the importance of specific interactions in yielding a negative heat of mixing ΔH_m is obviously due to the negligible contribution of the entropy of mixing ΔS_m for high molecular weight polymers^[2-4]. However, some miscible binary polymer blends, especially those involving random copolymers, do not exist evidently intermolecular specific interaction^[5-10]. In these polymer blends, the intramolecular interaction between different monomeric units rather than specific intermolecular

interaction has been considered to be an important factor controlling themiscibility. A mean-field binary interaction model was proposed to describe this miscibility behavior^[10-12]. The simplest cases of these blends are the mixture of a homopolymer(A) with a random copolymer (AB) (denoted as A/A_xB_{1-x}), and a mixture of two copolymers containing the same segments but with different compositions(A_xB_{1-x}/A_yB_{1-y})^[13,14]. In these cases, the miscibility windows can be determined by monomeric interaction of the segment A and B, and the relationship between the miscibility limits and monomeric interaction parameter can be described by the mean-field binary interaction model.

In our laboratory, a series of ethylene terephthalate (ET)-caprolactone (CL) random copolyesters(TCL) with different ET contents has recently been synthesized^[15,16]. It is interesting to investigate the effect of monomeric composition of the copolyesters on the miscibility of blends of TCL and PET. In this work, the miscibility of the blends of PET with TCL copolyesters and the blends between TCLs with different ET contents were examined by thermal analysis, and the miscibility windows defined by ET contents in the TCL copolyesters were obtained. Based on these experimental miscibility limits and the mean field binary interaction model, the interaction parameter between monomeric units of ethylene terephthalate and caprolactone was discussed.

EXPERIMENTAL

A list of the copolyesters used in the present work with their ET contents, intrinsic viscosity $[\eta]$ and glass transition temperature (T_g) is given in Table 1. The synthesized random copolyesters^[15,16] were purified by precipitation in large amount methanol from a 5% (w/v) chloroform solution. The molecular weight values of the copolyesters were about 10^4 as measured by dynamic light scattering^[17]. ET content was determined by nuclear magnetic resonance spectroscopy as described previously^[15]. PET with M_v 42,000 ($[\eta]=4.68 \times 10^{-4} M_v^{0.68}$) was purchased from Beijing Changzheng Chemical Factory.

Blend samples were prepared by coprecipitation in methanol from a 2% (w/v) tetrachloroethane solution at room temperature. The blend samples were further dried in a vacuum oven at 50°C until they reached constant weight.

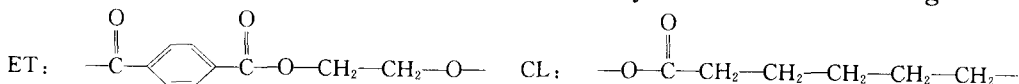


Table 1 Description of the polymers used in this study

TCL Copolyesters	ET content ^b (wt %)	$[\eta]^a$ (dl g ⁻¹)	T_g (K)
TCL91	91	0.617	328
TCL82	82	0.837	306
TCL72	72	0.955	291
TCL62	62	0.994	270
TCL58	58	0.851	262
TCL48	48	0.866	246
TCL13	13	1.987	208

a. Measured in m-cresol at 30°C, b. ET content determined by NMR method

The glass transition temperatures (T_g) of the copolymers and their blends were measured using a Perkin-Elmer DSC-2C. The sample weight used in thermal analysis is about 10–15 mg. The temperature at the half height of the corresponding heat capacity jump was defined as T_g . The temperature was calibrated with ultra-pure indium. In the DSC apparatus, the samples were first heated at a rate of 40K/min to 540K, maintained at that temperature for 1 minute and quenched to the temperature at 200K. They were then heated from 200K at a rate of 20K/min to 500K to measure their glass transition temperatures of the blend samples. A sample is considered miscible if it gives at each composition a single T_g intermediate between those of the individual components, while a sample exhibiting two T_g s at a given composition is considered immiscible.

RESULTS AND DISCUSSION

Fig. 1 gives the DSC thermograms of some typical PET/TCL blend samples. A series of PET/TCL with different compositions were measured and the related miscibility results were summarized in Table 2. The blends of PET with TCL copolyesters change from miscible to immiscible with the decrease of ET contents in the TCL. For the blends containing TCLs with ET contents higher than about 70(wt%), one T_g was observed which means that these blends are miscible. When ET contents of the TCL copolyesters are lower than 70 (wt%), immiscibility of PET with TCL which show two T_g s in the DSC thermograms can be obtained.

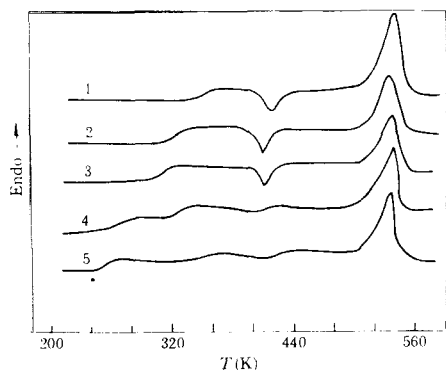


Fig. 1 DSC thermograms of PET/TCL having different ET contents quenched from 530K to 200K

1. PET/TCL91(5;5)
2. PET/TCL82(5;5)
3. PET/TCL72(5;5)
4. PET/TCL62(5;5)
5. PET/TCL48(5;5)

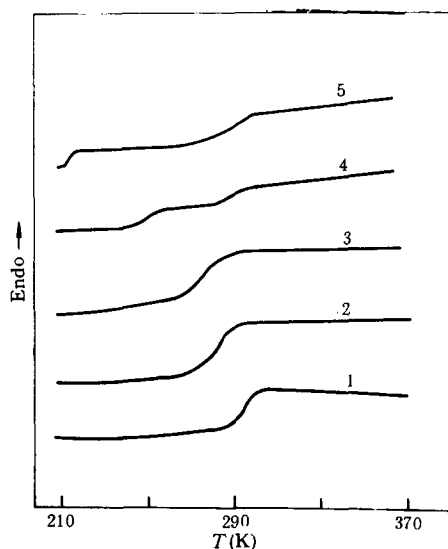


Fig. 2 DSC thermograms of TCL82/TCL having different ET contents quenched from 530K to 200K

1. TCL82/TCL72(5;5)
2. TCL82/TCL62(5;5)
3. TCL82/TCL58(5;5)
4. TCL82/TCL48(5;5)
5. TCL82/TCL28(5;5)

Table 2 Miscibility of TCL copolyesters/PET blends shown from DSC curves

TCL	TCL91	TCL82	TCL72	TCL62	TCL58	TCL48	TCL13
PET	M	M	M	IM	IM	IM	IM

M=miscible

IM=immiscible

PET/TCL mixture is a typical A/A_xB_{1-x} blend system. In the mean-field binary interaction model, the thermodynamics of this system is described by the well-known relations^[11,12]:

$$\Delta G = RT(\phi_1 \ln \phi_1 / N_1 + \phi_2 \ln \phi_2 / N_2 + \phi_1 \phi_2 \chi) \quad (1)$$

where for the A/A_xB_{1-x} system,

$$\chi = (1 - x)^2 \chi_{AB} \quad (2)$$

and for the A_xB_{1-x}/A_yB_{1-y} system

$$\chi = (x - y)^2 \chi_{AB} \quad (3)$$

Here ΔG is the free energy of mixing per unit volume. χ_{AB} is the segmental interaction parameter between A and B. N_1 and N_2 are respectively the number of monomeric units per chain of A and A_xB_{1-x} and x is the volume fraction of the A in A_xB_{1-x} molecules. and are respectively the volume fractions of A and A_xB_{1-x} in blend system. The phase behavior of the system is determined by:

$$f(\chi) = \chi - \chi_c \quad (4)$$

where χ is the critical interaction which can be arisen from the Flory-Huggins theory in the usual way and is formulated as:

$$\chi_c = (N_1^{-1/2} + N_2^{-1/2})^2/2 \quad (5)$$

when $f(\chi) \leq 0$, i. e. $\chi \leq \chi_c$, miscibility will be obtained. If the actual molecular weight and miscibility limits are available, the interaction parameter between two monomeric units can be obtained by equation (2), (4), (5). For the PET/TCL blends, molar mass of two components are about 10^4 ^[17], and the miscibility limit of those blends specified by ET content is about 70(wt%). Thus, the approximate value of χ_{AB} of ET/CL can be estimated, which is about 0.21.

As we know, for the polymer blends without specific intermolecular interaction, the simplest method to estimate the interaction parameter between two components is based on the solubility parameter theory. Applying the notions of Scott^[18]:

$$\chi = V_r[\delta_A - \delta_B]^2/RT = |\Delta\delta|^2/RT$$

the χ_{AB} of PET/PCL, i. e. the monomeric unit interaction parameter of ET/CL, can be estimated to be 0.75. This value is much higher than the estimated value based on the mean-field binary interaction model.

Table 3 Miscibility of TCL/TCL blends shown from DSC curves

TCL	TCL91	TCL82	TCL72	TCL62	TCL58	TCL48	TCKL13
TCL82	M	M	M	M	M	IM	IM

M=miscible

IM=immiscible

The binary blends between TCL copolyesters with different compositions were also measured by DSC. The results (Fig. 2, Table 3) showed that the

miscibility window described by ET content of TCL in these mixtures was ranging from 82 to 58(wt%). TCL/TCL is a typical A_xB_{1-x}/A_yB_{1-y} blend system. Based on the mean-field binary interaction model and the miscibility limit obtained from DSC measurement, the monomeric interaction parameter of ET/CL χ_{AB} , can be estimated from equation (3) and equation (4), which is about 0.29. This value is close to the χ_{AB} obtained from PET/TCL blend systems.

Keywords:

Polymer blends; Miscibility; Interaction parameter; Copolyester; Ethylene terephthalate; Caprolactone

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