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FLORY-HUGGINS INTERACTION PARAMETERS OF LCP/THERMOPLASTIC BLENDS MEASURED BY DSC ANALYSIS

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Abstract

Liquid crystalline polymer/polyamide 66 (LCP/PA66) and LCP/poly(butyl terephthalate) (LCP/PBT) blends were compounded using a Brabender Plasticorder equipped with a mixing chamber. The LCP employed was a semi-flexible liquid crystalline copolyesteramide based on 30 mol% of *p*-amino benzoic acid (ABA) and 70 mol% of poly(ethylene terephthalate) (PET). The Flory–Huggins interaction parameters (χ_{12}) of the LCP/ PA66 and LCP/PBT blends are estimated by melting point depression from DSC measurement. The results indicate that χ_{12} values all are negative for LCP/PA66 and LCP/PBT blends, and when the LCP content in these blends is more than 10 mass%, the absolute value of χ_{12} decreases. Thereby, we can conclude that LCP/PA66 and LCP/PBT blends are fully miscible in the molten state, the molecular interaction between the LCP and PA66 is stronger than that between LCP and PBT. As the LCP content in LCP/PA66 and LCP/PBT blends is more than 10 mass%, the molecular interaction between LCP and matrix polymer decreases.

Keywords: Flory–Huggins interaction parameter, miscibility, polyamide 66, poly(butyl terephthalate), semiflexible liquid crystalline copolyesteramide

Introduction

The in-situ composites based on conventional thermoplastic polymers and liquid crystalline polymers (LCPs) have attracted considerable attention. However, the immiscibility and poor interfacial adhesion between LCP dispersed phase and the thermoplastic matrix generally result in the LCP/thermoplastic composites having low tensile strength and impact toughness. A number of attempts have been made by polymer scientists to improve

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the miscibility and the interfacial adhesion between these two distinct phases. The method widely used by them involves the addition of a suitable compatibilizer [1–6]. Another approach to increase the interfacial adhesion involves the modification of LCP structures. For example, the introduction of a long flexible spacer in the main chain of LCP can enhance the adhesion between LCP and polymer matrix [7–9].

More recently, the authors studied the composites of semiflexible LCP with polyamide, polyester and the blend of polyamide and polyester [10–12]. The semiflexible LCP is a copolyesteramide based on *p*-aminobenzoic acid (ABA) and poly(ethylene terephthalate) (PET). They found that the optimum content of LCP is 5–10%, where the mechanical properties of these composites are the highest. These results should be associated with the interactions between the LCP macromolecules and the thermoplastic matrix. There are several different ways of obtaining an estimate of the interaction between two polymers [13]. These include heat of mixing measurements, inverse gas chromatography, solvent vapor absorption, various scattering techniques and viscosity measurements. In the case of crystalline materials, measurement of melting point depression by a technique such as DSC can also be used. In the present study, we use DSC measurement to estimate the Flory–Huggins interaction parameters (χ_{12}) of the LCP/polyamide 66 (PA66) and LCP/poly (butyl terephthalate) (PBT) blends.

Experimental

Materials

LCP used in this work consisted of 30 mol% of ABA and 70 mol% of PET. It was synthesized following the procedures reported earlier [14]. Its intrinsic viscosity was 0.57 dL g^{-1}. The glass transition and melting temperatures were 100 and 256°C, respectively. PA66 pellets (Novamid) were supplied by Mitsubishi Engineering-Plastics Corp. (Taiwan). PBT pellets (Lumicon 1401) were purchased from Toray Industries Inc. (Japan). All the materials were dried in an oven at 120°C for 48 h before mixing.

Sample preparation

LCP/PA66 and LCP/PBT blends containing different content of LCP were prepared in a Brabender Plasticorder equipped with a mixing chamber of 50 cm^3, and operated at 275°C and 75 rpm for 5 min. The blends produced were cut into small pellets for further measurements.

Differential scanning calorimetry (DSC)

DSC measurements were conducted in a Perkin Elmer DSC-7 instrument at a heating rate of 10°C min^{-1} under dry nitrogen atmosphere. Prior to DSC recording, the sample (about 8 mg) was added into an aluminum pan and heated to 280°C, then kept at this temperature for 3 min in order to eliminate the influence of their previous thermal histories. The sample in the Al pan was substantially quenched to an ambient temperature at the rate of 200°C min^{-1}. For the measurements of melting point and heat of fusion, the experimental temperature range was from 50 to 280°C. The onset melting temperature (T_m) and heat of fusion (ΔH_m) of the sample were determined according to the melting peaks.

In order to analyze the phase behavior of LCP/ PBT blends in the molten state, the PBT/LCP blends were molten, and then, quenched rapidly in the liquid nitrogen. The glass transition in LCP/PBT blend was investigated in a Perkin Elmer DSC-7 instrument at a heating rate of 20°C min^{-1} under dry helium atmosphere. The experimental temperature range was from –50 to 130°C. The glass transition temperature (T_g) of the sample was determined according to the DSC curve.

Results and discussion

Figures 1 and 2 show that DSC heating curves for LCP/PA66 and LCP/ PBT blends. PA66 and PBT are known as a highly crystalline polymers, and they exhibit two crystalline structures, which can undergo a reversible transformation at low level of applied stress [15, 16]. The appearance of two melting endotherms can be interpreted reasonably as the results of the sequential melting of the two different crystalline structures. The melting temperature (T_m) and heat of fusion (ΔH_m) of these samples determined from these curves are listed in Tables 1 and 2. It is apparent that T_m of PA66 phase and PBT phase in their blends tends to decrease with increasing LCP content.

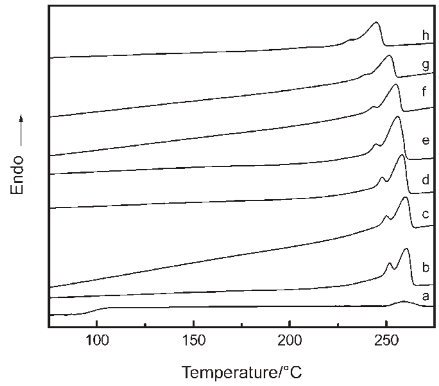

Fig. 1 DSC heating scanning curves of PA66 and blends a – LCP; b – PA66; c – LCP(2.5)/PA66(97.5); d – LCP(5)/PA66(95); e – LCP(10)/PA66(90); f – LCP(15)/PA66(85); g – LCP(25)/PA66(75); h – LCP(35)/PA66(65)

Table 1 Thermal properties of LCP/PA66 blends

m_{LCP}/m_{PA66}	0/100	2.5/97.5	5/95	10/90	15/85	25/75	35/65	100/0
T_m/°C	251.9	250.8	248.4	245.2	244.7	240.8	234.9	256.00
ΔH_m^*/J g^{-1}	66.4	58.5	58.0	50.7	50.0	43.7	38.9	3.40

*Corrected for per gram of PA66 in the blends

Table 2 Thermal properties of LCP/ PBT blends

$m_{\mathrm{LCP}}/m_{\mathrm{PBT}}$	0/100	2.5/97.5	5/95	10/90	15/85	25/75	35/65
T_m/°C	220.17	217.79	216.20	214.31	214.61	212.86	211.95
ΔH_m^*/J g^{-1}	48.42	52.01	55.02	517.71	60.15	64.61	69.82

*Corrected for per gram of PBT in the blends

For crystalline polymer/amorphous polymer blending system, the Nishi–Wang theory [17] can be used to investigate the intermolecular interaction between blending components according to the melting point depression of crystalline polymer in blending system. From Table 1, we can see that the ΔH_m of LCP is rather smaller than those of PA66 and PBT, we can assume the LCP is a non-crystallizable component in the LCP/PA66 and LCP/PBT blends.

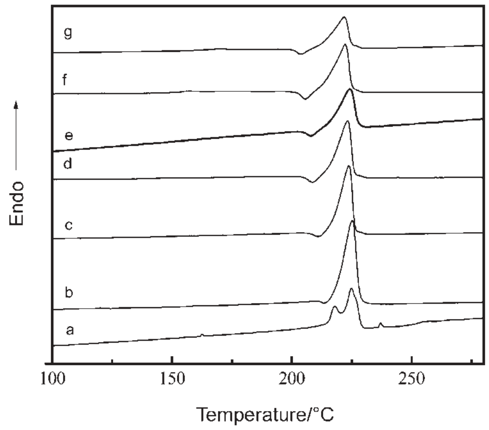

Fig. 2 DSC heating scanning curves of PBT and its blends a – PBT; b – LCP(2.5)/PBT(97.5); c – LCP(5)/PBT(95); d – LCP(10)/PBT(90); e – LCP(15)/PBT(85); f – LCP(25)/PBT(75); g – LCP(35)/PBT(65)

For the LCP/PA66 blends, according to the Nishi–Wang theory, the following equation for the melting point depression of PA66 in the blends can be determined from:

$$T_m = T_m^0 + T_m^0 \left(\frac{V_2}{\Delta H_2} \right) B \phi_1^2 \tag{1}$$

$$T_m = T_m^0 + T_m^0 \left(\frac{V_2}{\Delta H_2} \right) B (1-\phi_2)^2 \tag{2}$$

where ϕ_1 and ϕ_2 are the volume fractions of LCP and PA66, respectively; and $\phi_1+\phi_2=1$. Moreover, B is the polymer-polymer interaction energy density, and $B=\chi_{12}RT/V_1$; T_m^0 and T_m are the melting temperatures of pure PA66 and PA66 in blends respectively; $\Delta H_2/V_2$ is the heat of fusion of 100% crystalline PA66 per unit volume; V_1 is the molar volume of LCP; χ_{12} is the Flory–Huggins interaction parameter. Accordingly, ϕ_1 should be the volume fraction of LCP in the blending system.

Table 3 Values of the interaction energy density (B) and the interaction parameter (χ_{12}) for LCP/PA66 blends at 270°C

LCP concentration	B/J cm^{-3}	χ_{12}
<10 mass%	–7.65	–0.210
>10 mass%	–0.49	–0.014

For the LCP/PBT blends, the density of PBT is estimated to be 1.26 g cm^{-3}. The variation of the melting point of PBT with the square of the volume fraction of LCP is shown in Fig. 4. Similarly, the plots yield two straight lines with different slopes. The value of χ_{12} determined at 270°C accordingly is listed in Table 4. It is apparent that χ_{12} is $-4.07\cdot10^{-4}$ for the blends containing LCP content <10 mass%. However, χ_{12} value become to $-1.97\cdot10^{-5}$ accordingly, when the LCP content reaches 10 mass% or above.

Table 4 Values of the interaction energy density (B) and the interaction parameter (χ_{12}) for LCP/PBT blends at 270°C

LCP concentration	B/J cm^{-3}	χ_{12}
<10 mass%	$-1.46\cdot10^{-2}$	$-4.07\cdot10^{-4}$
>10 mass%	$-7.06\cdot10^{-4}$	$-1.97\cdot10^{-5}$

According to the group additive estimation [18], the densities of PA66 and the LCP are estimated to be 1.085 and 1.35 g cm^{-3}, respectively. From these data, we can convert the mass fractions into the volume fractions. The variation of the melting

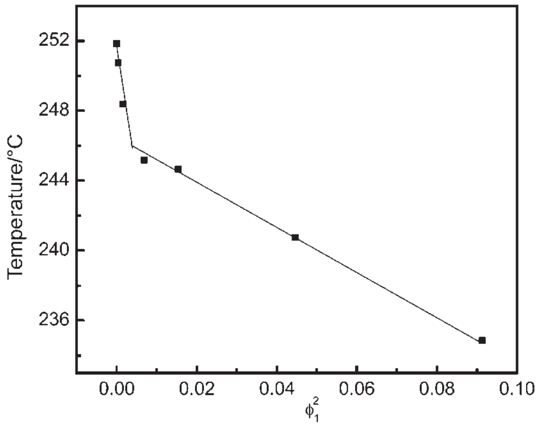

Fig. 3 Variation of T_m of PA66 phase in LCP/PA66 blends with the square of volume fraction of LCP

temperature of PA66 with the square of the volume fraction of LCP is shown in Fig. 3. It is apparent that the plots yield two straight lines with different slopes. In other words, the intermolecular interaction between LCP and PA66 is different when the LCP content in LCP/PA66 blend is different. Because the melting temperature of LCP/PA66 blend is lower than 270°C, the LCP/PA66 blend is in molten state at 270°C. From the slope value, the value of χ_{12} in the molten state is estimated accordingly, and listed in Table 3. It is apparent that χ_{12} is –0.21 for the blends containing LCP content <10 mass%. However, χ_{12} value become to –0.014 accordingly, when the LCP content reaches 10 mass% or above.

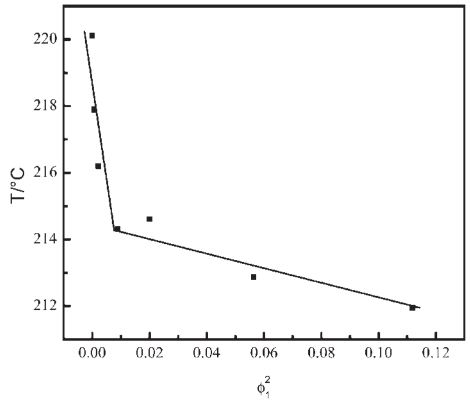

Fig. 4 Variation of T_m of PBT phase with the square of volume fraction of LCP in LCP/PBT blends

Figure 5 shows DSC heating curves for the LCP/PBT blends quenched rapidly into liquid nitrogen from melting state. It can be seen that there is only one single

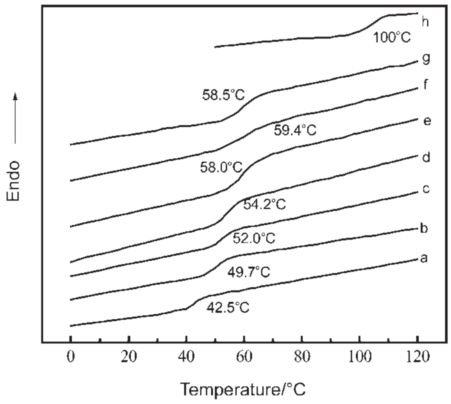

Fig. 5 DSC heating scanning curves of PBT and its blends quenched in liquid nitrogen from molten state
a – PBT; b – LCP(2.5)/PBT(97.5); c – LCP(5)/PBT(95); d – LCP(10)/PBT(90); e – LCP(15)/PBT(85); f – LCP(25)/PBT(75); g – LCP(35)/PBT(65); h – LCP

glass-transition for each LCP/PBT blend. Moreover, the glass-transition temperature of the LCP/PBT blends tends to increase with increasing the LCP content, and approaches to a relative steady value when LCP is up 15 mass%. These results prove that LCP and PBT phases in LCP/PBT blends are miscible in the molten state.

In general, the trans-amidation or trans-esterification reaction [19], which occurs at relative high temperature or during long-time mixing [20–23], can lead to a depression of the melting temperature of blending component. As mentioned above, the mixing time for the LCP/PA66 and LCP/PBT blends at 270°C is 5 min, so the possibilities for the occurrence of trans-amidation and trans-esterification reaction are rather small. Thus, we can conclude that the miscibility of polymer components in LCP/PA66 and LCP/PBT blends owes to the intermolecular interaction. It is well-known that the more negative the χ_{12} value is, the more miscible of the blend components is. As χ_{12} shows negative value in the present study, thus the LCP appears to be miscible with PA66 and PBT in the melting state. The miscibility of LCP/PA66 and LCP/PBT blends may be arisen from the amide and the PET flexible chain segments of the LCP interact with PA66 or PBT chains via hydrogen bond and physical entanglements, respectively. And the miscibility between the LCP and PA66 is better than that between the LCP and PBT due to that the molecular interaction between the LCP and PA66 is stronger than that between the LCP and PBT. Moreover, the χ_{12} value for the blends with LCP content <10 mass% is more negative than that for the blends with LCP content >10 mass%. Subsequently, the miscibility and the interfacial adhesion between the LCP and PA66 or PBT become poorer compared with those of the blends with lower LCP concentration. This is because the LCP content is increased above 10 mass%, the number of LCP domains increases, thereby forming interlocked domains which link themselves via hydrogen bonding. Thus the less interactions occur between the LCP domains and PA66 or PBT matrix, i. e. the intermolecular bonding to link between LCP molecules themselves prevails over the LCP-PA66 or LCP-PBT interaction.

Conclusions

The Flory–Huggins interaction parameters of the LCP/PA66 and LCP/PBT blends are estimated by melting point depression from DSC measurement. The χ_{12} values of these blends indicate that LCP/PA66 and LCP/PBT blends are fully miscible in the molten state, the molecular interaction between the LCP and PA66 is stronger than that between the LCP and PBT. As the LCP content in LCP/PA66 and LCP/PBT blends is more than 10 mass%, the molecular interaction between the LCP and matrix polymer decreases.

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