Journal of Thermal Analysis, Vol. 40 (1993) 597-604

CALORIMETRIC STUDY OF BLENDS OF POLY(BUTYLENE TEREPHTHALATE) AND LIQUID CRYSTALLINE COPOLYESTER

*S. Mehta** *and B. L. Deopura*

DEPARTMENT OF TEXTILE TECHNOLOGY, INDIAN INSTITUTE OF TECHNOLOGY, NEW DELHI-110016, INDIA

A calorimetric study of blends of poly(ethylene terephthalate-co-p-oxybenzoate), PET/PHB, with poly(butylene terephthalate), PBT has been carried out in the form of as-spun and drawn fibres. DSC melting and crystallization results show that PBT is compatible with LCP and the crystallization of PBT decreases by the addition of LCP in the matrix. The crystallization behaviour of blend fibres is investigated as a function of temperature of crystallization. A detailed analysis of the crystallization course has been made utilizing the Avrami expression. The isothermal calorimetric measurements provide evidence of decrease of rate of crystallization of PBT on addition of the liquid crystalline component up to about 50% by weight. The values of the Avrami exponents change in the temperature range from 200° to 215°C. Dimensionality changes in crystallization could be due to LCP mesophase-transition.

Keywords: DSC, liquid crystalline copolyesters

Introduction

Thermotropic liquid crystalline main chain polymers, with their peculiar structure and unique properties, offer new opportunities for the preparation of blends with commercial thermoplastics. Various investigators have reported that the rate and degree of crystallization of flexible-coil polymers was increased by the addition of an LCP [1–5]. Joseph *et al.* [1, 2] studied the thermal behaviour of blends of poly(ethylene terephthalate) (PET) and a liquid crystalline copolyester

---

* National Institute of Immunology, Aruna Asif Ali Marg, J.N.U. complex, New Delhi-110067.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

based on 60 mole percent *p*-hydroxybenzoic acid (PHB) and 40 mole percent PET (40 PET/60 PHB). The rate of crystallization increased as the LCP content increased in the blend, which was attributed to nucleation of the PET crystallization by the LCP. The degree of crystallinity also increased with the addition of the LCP. Similarly Misra and co-workers [3, 4] studied blends of PET with two different LCPs: one, a commercial LCP based on 6-hydroxy-2-naphthoic acid (HNA) and PHB, and the other a copolymer of PET and PHB. Like Joseph and coworkers, they also found that the crystallization rates for the blends were higher than that of pure PET. Takayanagi *et al.* [5] studied blends of wholly aromatic polyamides with aliphalic polyamides, and they suggested that the surface of the rigid polyamide acts as a nucleating agent for the crystallization of the matrix polymer.

Isothermal crystallization kinetics studies of blends of poly(butylene terephthalate) (PBT) and liquid crystalline poly (biphenyl-4,4'-ylene) sebacate (PB8) were reported by Paci *et al.* [6]. They found that the two polymers were not immiscible in the isotropic state, and they showed that the degree of crystallinity of PBT increased on addition of the liquid crystalline component up to about 35–50% by weight.

In the present paper, we discuss the calorimetric data for the blends of PBT and LCP (PET/60PHB) in the form of as spun and drawn fibres.

Experimental

The poly(butylene terephthalate) (PBT) used in these experiments was provided by LML, India. Its intrinsic viscosity in phenol-tetrachloroethane 60:40 weight fraction solution was 0.77 dL/g at 25°C. Liquid crystalline copolyester (LCP) was a copolyester of ethylene terephthalate and hydroxy benzoic acid (PHB), provided by Mitsubishi Kasei Corp. Japan. Its intrinsic viscosity in the above solvent blend was 0.67 dL/g. All samples were dried in a vacuum oven at 110°C for 24 hours before use to minimize moisture effect. Dry blends were prepared in the range of concentration from 5 to 50 weight percent of LCP in PBT. Melt spinning of PBT, LCP and their blends was carried out at 260°C and at a take up speed of –250 m/min.

A differential scanning calorimeter (DSC) model DSC-7 (Perkin Elmer) was employed to evaluate phase behaviour and transitions of homopolymers and blend fibres. Heating and cooling was carried out at 10 deg·min^{-1} and under the nitrogen atmosphere.

Results and discussion

The DSC heating scans of the as-spun blend fibres presented in Fig. 1 show single melting endotherm, corresponding to PBT crystallites in all the blend compositions. Table 1 shows that the end temperature of melting endotherms and peak temperature of as spun blend fibres show a slight decrease upto 50 wt% LCP content. It was believed that this could be associated with the dissolution of PBT phase in the PET rich phase of PET/60PHB.

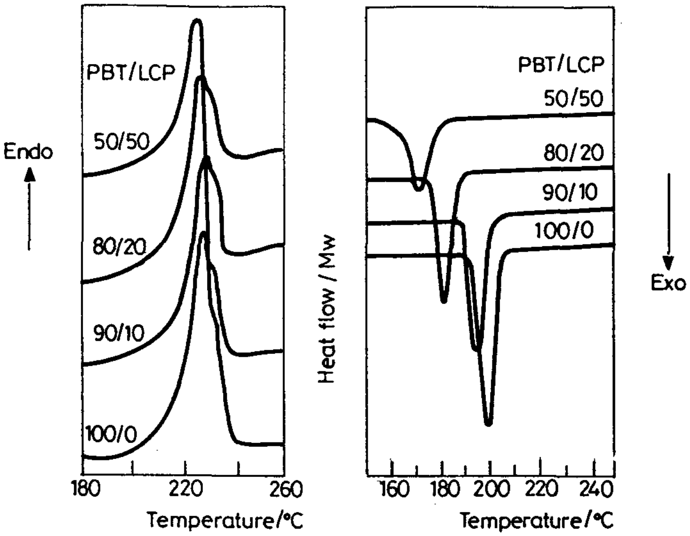

Fig. 1 Heating and cooling DSC scans of PBT/LCP as spun blend fibres

Table 1 Thermal properties of PBT/LCP blend fibres

PBT/LCP	Melting (endotherm)			Cooling (exotherm)	
	T_p/°C[a]	T_f/°C[b]	X_c/%[c]	T_{cp}/°C[d]	X_c/%
100/0	226	238	43	196	39
90/10	225	237	43	193	39
80/20	224	235	45	179	40
50/50	223	234	46	170	42

[a] Peak temperature of melting endotherm in as-spun blend fibres
[b] end temperature of melting endotherm
[c] %crystallinity in drawn blend fibres
[d] crystallization peak temperature

DSC cooling traces of as-spun blend fibres (Fig. 1 and Table 1) showed that crystallization temperature (T_{cp}) of PBT was affected dramatically by the addition of LCP. The initiation of crystallization occurred at 201°C for PBT, but was delayed for the blends, the crystallization peak temperature was also lowered. This was because when PBT started to crystallize, the LCP was in a supercooled mesophase state, and it restricted the mobility of PBT chains. The 50/50 blend was noteworthy in the depression of T_c and showed a larger half time for PBT crystallization.

Table 1 illustrates that percent crystallinity (X_c) of PBT component in the drawn blend fibres was not affected much by the presence of LCP. This was in agreement with one previous result in PET/LCP blend fibres [7].

Isothermal crystallization

The crystallization isotherms of PBT and PBT/LCP 80/20 blends are shown in Figs 2 and 3 respectively. These plots show the fraction of uncrystallized material, Q_a as a function of time. All of the isotherms have a sigmoidal shape typical of polymer crystallization.

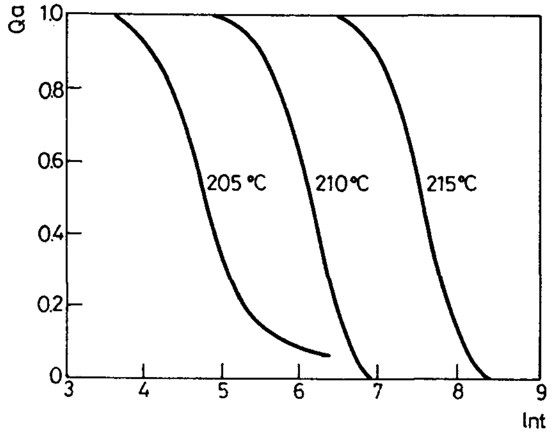

Fig. 2 Crystallization isotherms of PBT at various temperatures

The crystallization kinetics of polymers was analysed in terms of the Avrami expression given in Eq. (1).

$$Q_a = e^{-kt^n} \tag{1}$$

where, Q_a is the fraction of uncrystallized material, k is the kinetic rate constant, t is the time, and n is the Avrami exponent describing the mechanism of crystallization. The mathematical formulation of the kinetic phase change and the deviation of the Avrami equation can be found in many sources [8–10]. In the Avrami expression, the kinetic rate constant, *k*, is a function of the nucleation and the growth rates. The Avrami exponent provides qualitative information on the nature of nucleation and the growth process.

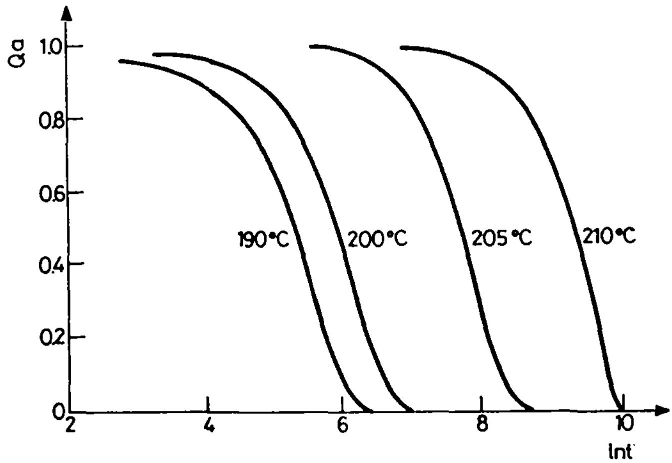

Fig. 3 Crystallization isotherms of PBT at various temperatures

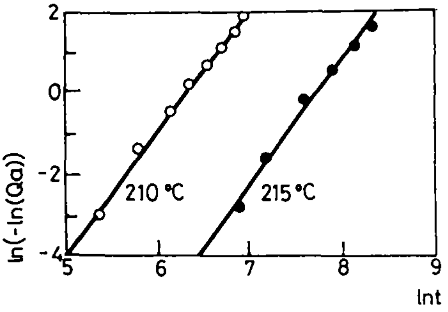

Fig. 4 Avrami plot of crystallization behaviour of PBT at various temperatures

The kinetic parameters are obtained by plotting the data according to Eq. (2).

$$\ln(-\ln Q_a) = \ln k + n \ln t \tag{2}$$

Therefore, a plot of $\ln(-\ln Q_a)$ *vs.* $\ln t$ yields a straight line, the slope is equal to *n*, and the intercept is equal to $\ln k$. Typical Avrami plots for the crystallization behaviour of 100% PBT and PBT/LCP (80/20) blend are given in Figs 4 and 5 respectively. A summary of the n, k and $t_{1/2}$ values for the crystallization behaviour of the various blend samples is given in Table 2.

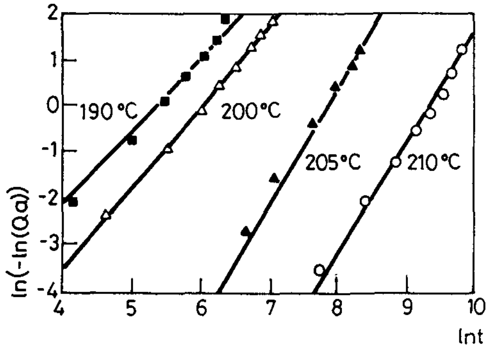

Fig. 5 Avrami plot of crystallization behaviour of PBT/LCP 80/20 blend at various temperatures

Table 2 Half time and Avrami exponents n for the isothermal PBT crystallization in PBT-LCP blends

PBT/LCP	T_c/°C	$t_{1/2}$/°C	n
100/0	210	501	2.1
	215	2261	3.0
90/10	205	375	1.66
	210	1708	2.76
	215	9364	3.13
80/20	200	367	1.68
	205	2440	2.46
	210	10522	2.54
50/50	190	109	1.63
	200	1259	3.11

The half time of crystallization $t_{1/2}$, is taken as a measure of the overall rate of crystallization. The shorter the $t_{1/2}$, the faster will be the rate of overall crystallization. The half time of crystallization is obtained from Eq. (3).

$$t_{1/2}=\left(\frac{0.693}{k}\right)^{1/n} \tag{3}$$

It can be seen from Table 2 that with the increase in LCP content, the half time of crystallization increases. For example the half time of crystallization increased from about 500 s to about 10000 s, with the addition of 20% LCP content at 210°C, crystallization temperature. Thus, the rate of PBT crystallization decreases markedly with the increase of LCP content, as could be anticipated in view of the retardation of crystallization of PBT chains due to PHB rigid units in LCP system.

In order to understand the difference in isothermal crystallization kinetics between PBT and the blends of PBT and LCP, let us examine the Table 2. At the same crystallization temperature, for example 210°C, with the increase in LCP content, the crystallization exotherms slow down and shift to higher side on time axis scale. The values of the Avrami exponents change, with blend composition, in the temperature range 200° and 215°C. Dimensionality changes in crystallization could be due to LCP mesophase-transition. Marrs *et al.* [11] reported Avrami exponent values in the range of 2.6–2.8 in PBT/PB8 blend system.

Conclusions

On the basis of our results, we conclude:

- DSC measurements show that the two polymers are compatible and the LCP restricts the crystallization of PBT.
- The rate of PBT crystallization decreases, with the increase of LCP content.
- The values of *n* change in the temperature range from 200° to 215°C.

References

1 E. G. Joseph, G. L. Wilkes and D. G. Baird, Polymer Liquid Crystals, Ed. A. Blumstein, Plenum Press, NY 1984.
2 E. G. Joseph, G. L. Wilkes and D. G. Baird, Am. Chem. Soc., Div. Polym. Chem., Polym. Prepr., 24 (1983) 304.
3 S. K. Sharma, A. Tendolkar and A. Misra, Molec. Cryst. Liq. Cryst., 157 (1988) 597.
4 S. K. Bhattacharya, A. Tendolkar and A. Misra, Molec. Crsyt. Liq. Cryst., 153 (1987) 501.
5 M. Takayanagi, T. Ogata, M. Morikawa and T. Kai, J. Macromol. Sci., Phys., B17 (1980) 571.
6 M. Paci, C. Barone and P. L. Magagnini, J. Polym. Sci. Polym. Phys. Ed., 25 (1987) 1595.
7 S. Mehta and B. L. Deopura, Polym. Eng. Sci., (under printing).
8 L. Mandelkern, Crystallization of polymers , McGraw Hill, NY 1964.
9 A. Sharples, Introduction to polymer crystallization, Edward Arnold (Publishers), London 1966.
10 P. Meares, Polymers, Structure and Bulk properties, Van Nostrand, London 1966.
11 W. Marrs, R. H. Peters and R. H. Still, J. Appl. Polym. Sci., 23 (1979) 1077.

Zusammenfassung — Es wurde eine kalorimetrische Untersuchung von Gemischen von Poly(ethylen-terephthalat-co-p-oxybenzoat), PET/PHB mit Poly(Butylen-terephtalat), PTB durchgeführt. Die DSC Schmelz- und Kristallisationsergebnisse zeigen, daß PBT kompatibel mit LCP ist und daß die Kristallisation von PBT durch Zusatz von LCP in der Matrix abnimmt. Das Kristallisationsverhalten der Gemischfibern wurde in Abhängigkeit von der Kristallisationstemperatur untersucht. Unter Anwendung der Avrami-Gleichung wurde eine ausführliche Analyse des Kristallisationsweges erstellt. Die isothermen kalorimetrischen Messungen bestätigen die Abnahme der Kristallisationsgeschwindigkeit von PBT bei Zusatz der Flüssigkristallkomponente bis zu 50 Gew %. Im Temperaturbereich variieren die Avrami Exponenten zwischen 200° und 215°C. Dimensionsänderungen der Kristallisation könnten der LCP Mesophasenumwandlung zugeschrieben werden.