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THERMAL ANALYSIS OF POLYMER BLENDS. I. POLY(ε-CAPROLACTAM) WITH A SECOND CRYSTALLINE COMPONENT

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ABSTRACT

The thermal properties of some blends of poly(ε-caprolactam) with an elastoplastic semicrystalline block copolymer of the poly(etherester) type and with a homopolyether (poly(ethyleneoxide)) have been studied. The two polymers crystallize separately, but the crystallization kinetic of each component, analyzed via the Avrami equation, is rather strongly influenced by the presence of the other one. In both cases the already crystallized polymer increases the crystallization rate of the second component. The equilibrium melting point is only slightly modified.

INTRODUCTION

Investigations on polymer-polymer mixibility are going to be more and more important as far as polymer blends become relevant materials in several applications.

Thermal analysis is a powerful way of studying polymer-polymer interactions by measuring the phase transition temperatures both of the glassy and of the crystalline state.

The melting and crystallization behaviour, their influence on the morphology and on the final properties of the blend have been investigated by several authors (ref.1,2); so far, the main interest has been devoted to blends containing an amorphous and a semicrystalline component (ref.3) ; however, several papers on blends containing both semicrystalline polymers have been published recently (ref.4,5).

EXPERIMENTALS

Materials

Poly(ε-caprolactam) (PCL) and poly(etherester) (HYT) were commercial products

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supplied by Enichimica and Dupont, respectively. As for the first one, the GPC analysis resulted in $\bar{M}_n = 20.4 \times 10^3$ and $\bar{M}_w = 68.9 \times 10^3$. The second one has the trade name Hytrel 5556; its general formula is $(A_nB_m)_z$, where

hard segment A: $-CO-C_6H_4-CO-O(CH_2)_4-O-$

soft segment B: $-CO-C_6H_4-CO-O(CH_2-CH_2-CH_2-CH_2-O)_x-$

Poly(ethyleneoxide) (PEO) was a Fluka laboratory product ($\bar{M}_v = 15.4 \times 10^3$ in CH_3OH at 20°C).

Specimen preparation

Specimens have been prepared either by isothermal evaporation of dilute solutions of the two polymers in a common solvent (hexafluorobuthanol) or by melt extrusion. In the first case, after a controlled evaporation, the specimens have been dried under vacuum till constant weight.

Measurements and techniques

Thermal scanning and isothermal crystallization have been carried out with a Perkin Elmer DSC 2 calorimeter equipped with a 3500 Data Station apparatus,using heating rates of 20°C/min and cooling rates of 10°C/min. The isothermal crystallizations have been performed by melting the blend for 5 min at 267°C and rapidly cooling down the specimen at the selected temperature.

RESULTS AND DISCUSSION

The comparison of the melting curve of a PCL 75/HYT 25 blend with thermograms obtained from the pure polymers under the same experimental conditions (Fig.1) shows that the fusion of the mixture resembles that of PCL: no remarkable endothermic effect in the range between 175 and 200°C is measured. However, the smoothness and the area of the 210°C peak are strongly modified. Following the model proposed elsewhere (ref.6), the formation of aggregates smaller and less regular than those present in the pure Hytrel is foreseen; the recrystallization is supposed to be more relevant. It can be argued that PCL spherulites are not modified by the second component present in the melt, but the crystallization mode of the copolymer hard segments is rather different when previously crystallized PCL spherulites are present. This conclusion is supported by data obtained from isothermal crystallizations, which can be followed easily since the two com

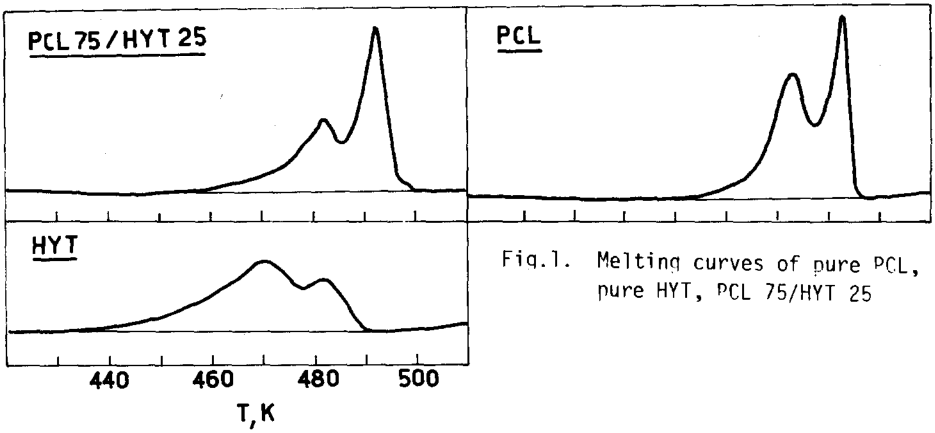

Fig.1. Melting curves of pure PCL, pure HYT, PCL 75/HYT 25

TABLE 1

Kinetic and thermodynamic data for the crystallization of PCL/HYT blends

Sample [a)]	T_c, °C	n	K	T_m^o, °C
PCL, pure polymer	190	3.4	0.75	261.0
PCL 75/HYT 25	190	2.6	0.87	261.0
HYT, pure polymer	182	2.2	0.12	242.1
PCL 25/HYT 75	182	3.3	7.12	241.8

a) sample prepared by evaporation technique

TABLE 2

Kinetic and thermodynamic data for the crystallization of PCL/PEO blends

Sample [b)]	T_c, °C	n	K	T_m^o, °C
PCL, pure polymer	194	4.6	0.01	261.0
PCL 75/PEO 25	194	4.8	0.001	261.0
PEO, pure polymer	40	2.7	0.47	67.0
PCL 25/PEO 75	40	2.5	1.28	71.6

b) sample prepared by melt extrusion

ponents lead to well separated exotermic peak at 184.4 and 166.2°C respectively.

The thermograms have been elaborated according to the well-known Avrami equation; Table 1 collects the calculated values for the overall rate constant K and the index n at the corresponding crystallization temperatures T_c. The values for PCL are of the same order of magnitude both in the pure polymer and in the blend; small differences can be accounted for by the area effect (ref.7). As far as the copolymer is concerned, both n and K are higher in the mixture; K is remarkably different, leading to a faster crystallization and therefore to a larger number of smaller and more irregular aggregates.

The results obtained for the system PCL/PEO are summarized in Table 2. The effect on the crystallization kinetic previously discussed is evident also in this case and actually the value of K for PEO is remarkably increased by the crystallized PCL environment.

Beside this, also the kinetic of PCL is influenced by the melt PEO: at 194°C the crystallization rate of PCL in the mixture 75/25 is smaller of an order of magnitude than in the pure polymer. This effect is not appreciable when the percentage of PEO in the blend is less than 10%. It can be suggested that the whole behaviour is correlated with the mobility of the PEO chains and with the mixibility of the PCL/PEO system as it will be discussed extensively elsewhere(ref.8).

Finally, we would like to point out that the values of the equilibrium melting temperatures, obtained according to the Hoffman - Weeks plot, are unaffected by the second component for PCL and HYT, while a small increase was found for PEO in PCL/PEO blends. This phenomenon was detected in some other systems and reviewed in ref. 9; morphological effects such as increased lamellar thickness or crystal perfection are the possible explanations.

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