Thermochimica Acta, 187 (1991) 185-200
Elsevier Science Publishers B.V., Amsterdam

INFLUENCE OF PBT CRYSTALLIZATION ON MISCIBILITY DEGREE OF AMORPHOUS PHASE IN PC/PBT MELT BLENDS

G.POMPE, E.MEYER, H.KOMBER, H.HAMANN
Institute of Polymer Technology, Box 411, O-8012 Dresden, Germany

Abstract

Melt blends of bisphenol-A-polycarbonate (PC) with poly-(butyleneterephthalate)(PBT) were studied by DSC and DMA. Variation of crystallinities and consequently of amorphous phase states was achieved by changing cooling conditions from the melt and by addition of nucleating agents. Our results suggest that the system PC/PBT is miscible in the melt state and also in solid state if it is possible to suppress PBT crystallization. In the case of PBT crystallization we found that it is rather the crystallite size than the degree of crystallinity which determines the homogeneity/heterogeneity of amorphous phases.A hypothesis was formulated to explain the change of the state of amorphous phase owing to the presence of crystalline regions. We also studied the influence of transesterification on crystallinity and amorphous phase behaviour.

1.INTRODUCTION

The miscibility and morphology of blends are important for their properties. Although the PC/PBT melt blends are commercially applied there are still open questions on miscibility behaviour. Conflicting results on these problems have been reported in the literature. Some authors (Wahrmund

0040-6031/91/$03.50

et al [1], Birley and Chen [2], Hobbs et al [3], Pratt and Smith [4]) concluded partial miscibility of these blends from measurements of the glass transition temperature. Other authors, as Hanrahan et al [5], who studied solution-cast blends, characterize PC and PBT as immiscible polymers.

Wahrmund et al [1], who found even three amorphous phases in some samples, assumed that the location of glass transition may be affected by the level and nature of crystallinity. However,as far as we know, further studies concerning the relationship between PBT crystallinity and miscibility have not been published.

The purpose of our investigations is to find a correlation between crystallinity and miscibility. We changed the crystallinity by variation of the cooling conditions from melt and investigated the amorphous phase state. Additionally, the nucleating agent Ca-stearate was used to vary the crystallite size at a constant blend composition 60PC/40PBT.

It is known [6,7] that polyesterblends may undergo three types of exchange reactions during melt processing: acidolysis, alcoholysis and direct transesterification. The transesterification is the most likely mechanism [6] of interchange reactions in PC/PBT blends. The transesterification complicates the characterization of miscibility behaviour [5,6]. Devaux et al [6] believe that a small content of copolymers may cause the glass transition temperature change observed in melt blends. However, Hobbs et al [3] demonstrated by calorimetric studies that small contents of copolymers are not predominant for the change of glass transition temperature T_g. In further investigations we tried to produce a defined degree of transesterification. We wanted to compare the so-formed amorphous phase state with the amorphous phase behaviour in blends without copolymers.

It must be pointed out that the samples for the investigations in chapter 3.1 show a non-provable copolymer content.

On the basis of our results we were able to formulate a hypothesis on a correlation between level and kind of PBT crystallinity and homogeneous/heterogeneous phase state.

2. EXPERIMENTAL

- Materials

The melt blends were prepared from commercial Poly(butylene-terephthalate) PBT (Grisuplast U, supplied by the man-made fibre plant, Premnitz, Germany) ($\overline{M}_w$ = 34000) and Bisphenol-A-Polycarbonate PC designated as Lexan (General Electric Plastics, Netherlands). For studies dealing with variation of cooling conditions (chapter 3.1) we used a blend system produced with PC of type Lexan 124R/112 ($\overline{M}_w$ = 21500). The PC-type Lexan 161 ($\overline{M}_w$ = 29500) was applied to the mixture 60PC/40PBT with different concentrations of nucleating agent (chapter 3.1 and also 3.2).

Compounding was carried out on a double screw extruder with the jet temperature of about 240 ^{0}C. After extrusion the pelletized material was dried 4h at 120 ^{0}C in a vacuum oven prior to processing in the injection moulding machine. The maximum temperature of the temperature regime of injection moulding is 260 ^{0}C for PC-rich systems and 245 ^{0}C for blends with PC contents ≤ 50 m%. A similar extrusion regime was used for compounding of 60PC/40PBT melt blends with nucleating agent (Ca-stearate). A change of drying conditions (4h, 60 ^{0}C, in air) and a reduction of the injection moulding temperature (Tmax = 215 ^{0}C) was chosen to prevent thermal degradation to a large extent.

In dependence on PC-content the optical impression of the injection moulding samples reaches from opaque (≤ 50 m% PC) to transparent (≥ 90 m% PC). It is remarkable that samples of the same composition may be opaque, translucent up to transparent when varying cooling rate (observed at 70PC/30PBT) and Ca-stearate content (observed at 60PC/40PBT).

- Comments to the use of nucleating agent

Different nucleating agents were tested to change the crystallite size. Ca-stearate, whose content varied from 0 to 0.2 m%, was the most efficient type with respect to our purpose.

The crystallite size could be strongly diminished (see chapter 3.1). It is known that efficient nucleating agents cause a displacement of $T_{c,0}$ to higher temperatures [7,8,9]. $T_{c,0}$ is the onset-temperature of crystallization upon cooling from melt. In contradiction to the usual behaviour we observed a displacement of $T_{c,0}$ to lower temperatures by Ca-stearate in sample system 60PC/40PBT. Legras, Mercier et al [9,10,11] proved that nucleating agents of the kind of alkali metal salts of organic acid accelerate the nucleation via a chemical reaction. These salts react with the molten macromolecules and produce ionic end groups, which are the true nucleating species. Legras et al [11] found that the chemical attack of these alkali metal salts on different polyester macromolecules (e.g. PC,PET) is not the same. Additionally, Ca-stearate also influences the transesterification rate (see chapter 3.2). We could not separate the complex chemical attack of Ca-stearate on the blend components, but we only recorded the effect on PBT crystallization and degree of transesterification. In this connection further investigations are necessary for a detailed explanation.

- Comments on the transesterification

The transesterification rate depends on the concentration of residual catalyst,e.g. Ti-compounds used in PBT processing and of organic salt content as discussed in [12] and as we observed when using the nucleating agent Ca-stearate. Both the enthalpy of fusion ΔH_f and the melting peak temperature T_m decrease with progressive transesterification [13 - 16]. Both values were used as a qualitative indicator of transesterification degree. The observed PBT crystallinity is caused by decreasing average length of PBT segments . With further progressive interchange reaction, the melting peak dissapears and infrared data show a new band at 1070 cm^{-1} with increasing intensities [13,16]. We used the ^1H-NMR-spectroscopy to prove directly the existence of copolyesters for a selected sample .

It is interesting that the formed copolyesters strongly depress the onset-temperature $T_{c,0}$ of crystallization. (At 60PC/40PBT without Ca-stearate we observed a decrease from 471 K to 454 K after a thermal treatment at 250°C.) Consequently, the crystallizibility is strongly influenced (see chapter 3.2).

- Differential scanning calorimetry

The DSC experiments were carried out under nitrogen using a Perkin Elmer DSC-2 coupled with an off-line computer recording data for the following calculation of enthalpies. The DSC-2 was calibrated with metal standards (indium, lead). In an initial set of experiments, the as-prepared specimens (5 - 8 mg) were heated in DSC from 293 K to 523 K, then cooled to the starting temperature at various rates (5 or 80 K/min) and reheated. The heating rate was always 10 K/min.

The crystallinity degree α of the PBT-content can be calculated with following equation

$$\alpha = \frac{\Delta H_f - |\Delta H_{cc}|}{\Delta H_f^0}$$

with ΔH_f - the enthalpy of fusion, ΔH_{cc} - the enthalpy of cold crystallization during heating scan (both enthalpies were related to PBT content) and $\Delta H_f^0 = 142$ J/g as the enthalpy of fusion of 100% crystalline PBT [5].

- Dynamic mechanical analysis

Dynamic mechanical investigations were done by means of a DMA 981 of Du Pont (resonance type) to characterize the glass transition behaviour of blends. The averaged frequency in the transition regions is about 12 Hz. The measurements were carried out with a heating rate of 5 K/min.

Three cooling rates were applied in our experiments (rapid, medium and low). The medium cooling rate corresponds the cooling condition in the injection moulding process. For the rapid and low cooling rates the as-prepared samples were externally melted at 240°C and were quenched with liquid nitrogen or very slowly cooled in oven.

- NMR spectroscopy

^{1}H-NMR-spectrum was recorded by a Bruker AC 250 NMR spectrometer, operating at 250 MHz for ^{1}H. The selected sample (about 15 mg) was solved in a 1:1 $CDCl_3$ / trifluoroacetic acid - d_1 . The amount of triads BP - T - BP and BP - T - B formed by transesterification was determined from signal intensities of the T-centred triads in the ^{1}H-NMR-spectrum (B - butylene-unit, BP - bisphenol-unit, T - terephthalate-unit).

3. Results and discussion

3.1 Influence of cooling rate and nucleating agents on PBT-crystallinity and amorphous phase state

Figures 1 and 2 show the effect of cooling rate on the amorphous phase state characterized by form and temperature shift of glass transitions of selected blend compositions.

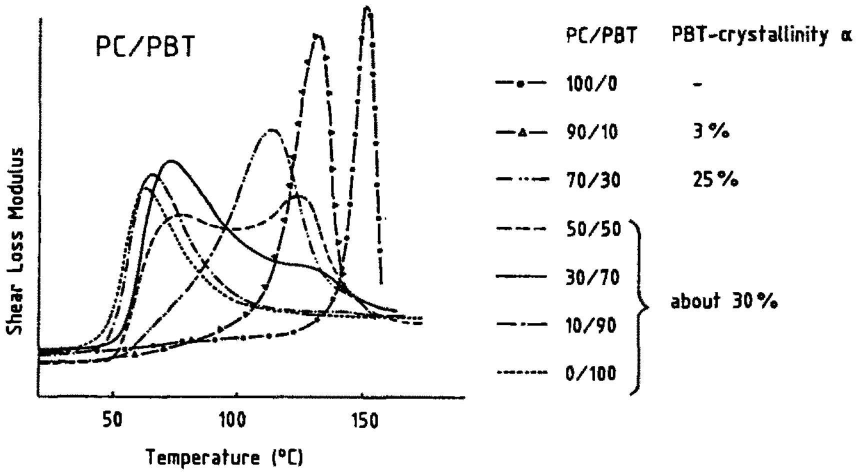

Fig. 1. Shear loss modulus versus temperature of selected PC/PBT melt blends cooled from melt at medium cooling rate

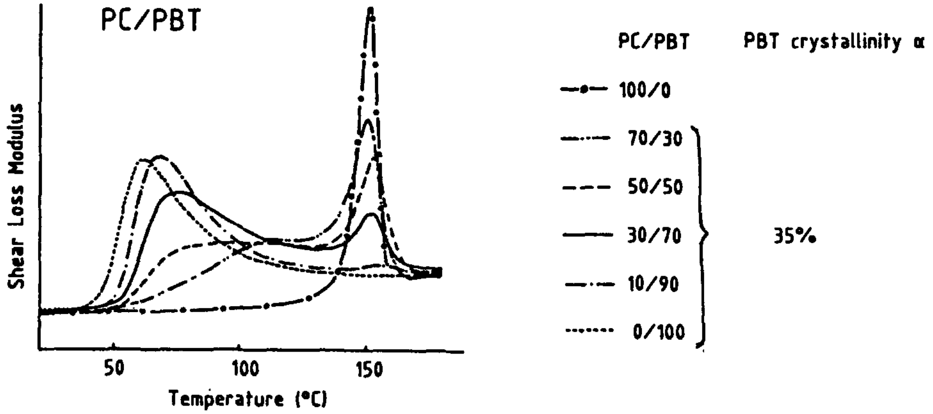

Fig. 2. Shear loss modulus versus temperature of selected PC/PBT melt blends cooled from melt at low cooling rate

The corresponding PBT-crystallinity α, determined from the enthalpy balance (Fig.3), are listed in the table (accurate values of crystallinity were difficult to determine because the cold crystallization already starts in the glass transition range and hence can only be estimated).

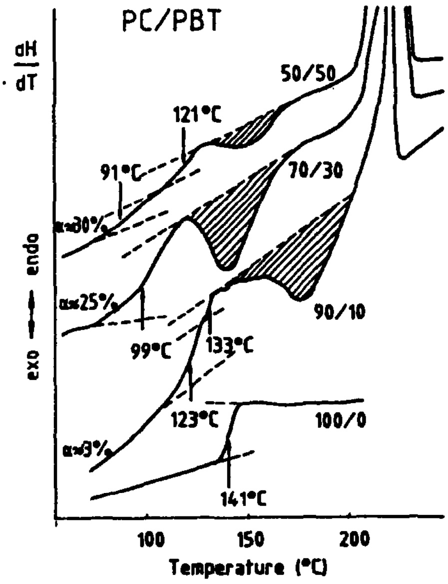

Fig. 3.

DSC-heating scans for selected PC/PBT melt blends cooled from melt at medium cooling rate

The change of cooling rate causes different amorphous phase states and, correspondingly, the degrees of miscibility. A medium cooling rate (injection moulding process) leads to blends with a rather high degree of miscibility in some cases (Fig.1). Lower cooling rates effect broadenings and shifts of glass transitions to higher temperatures and cause even the appearance of pure PC phase regions (Fig.2). The comparison of crystallinities in Fig.1 and 2 shows that all blend compositions achieve a rather high degree of crystallinity at low cooling rates. For higher cooling rates the degree of crystallinity of PC-rich samples is dependent on the PC content, because PC hinders the PBT-crystallization (see Fig.3).

It seems that the crystallinity mainly determines the miscibility. To support this assumption we tried to vary the crystallinity in samples with constant composition.

The PC-rich sample 70PC/30PBT was appropriate for changing the crystallinity from 3 to 39% (Fig.4).

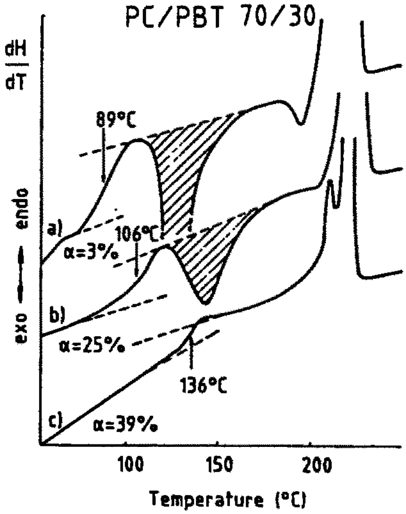

Fig. 4. DSC-heating scans of sample PC/PBT 70/30 with different cooling conditions from melt

a) low cooling rate (cooling at 5 K/min from melt)

b) medium cooling rate (as-prepared state)

c) rapid cooling rate (cooling at 80 K/min from melt)

Fig.5 shows that a low crystallinity (rapid cooling) implies a sharp glass transition which represents a high degree of miscibility. Lower cooling rates lead to higher crystallinities and to formation of so- called microheterogeneous amorphous phases, whereby samples with high crystallinities always show pure PC phase content.

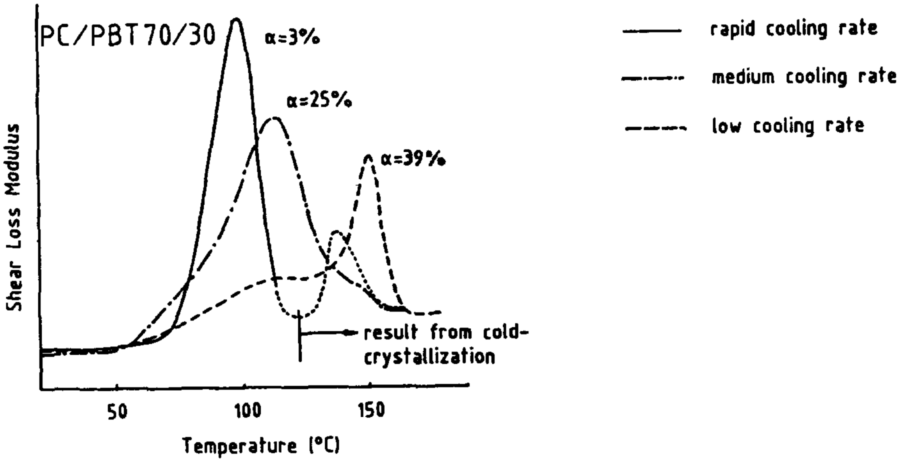

Fig. 5. Shear loss modulus versus temperature of PC/PBT 70/30 at different cooling conditions

However, we also observed changes of glass transition in samples with nearly the same degree of crystallinity produced at various cooling rates (Fig.6).

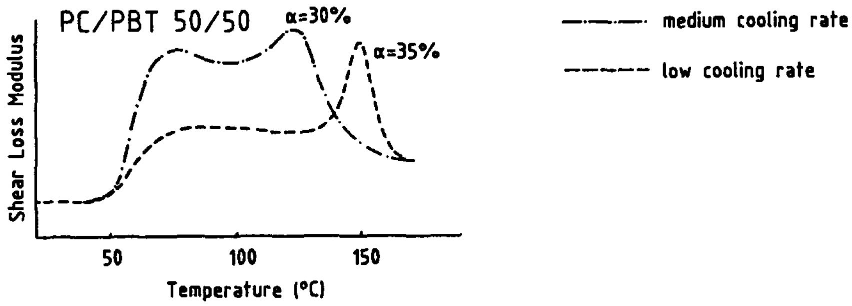

Fig. 6. Shear loss modulus versus temperature of PC/PBT 50/50 at different cooling conditions

We suppose that these changes are mainly due to differences in crystalline region sizes, which can be influenced by cooling conditions.

In further studies we tried to control the crystallite size by addition of nucleating agents [8]. We used Ca-stearate (0 - 0.2 m%) as additive in processing of 60PC/40PBT. Samples without Ca-stearate are opaque. With increasing nucleating agent content the blends become more translucent. After addition of 0.2 m% Ca-stearate the material appears transparent, and shows no crystalline reflections in WAXS investigations. That means that the extent of crystalline regions is smaller than 5 nm. We used the degree of transparency as a qualitative measure for the crystallite size because the PBT crystallinity was nearly the same for all samples (α ≈ 26%). Fig.7 shows a rather high degree of miscibility for the blend with small crystallites (0.2m % Ca-stearate) whereas with increasing size of crystallites the so-called microheterogeneous phases arise.

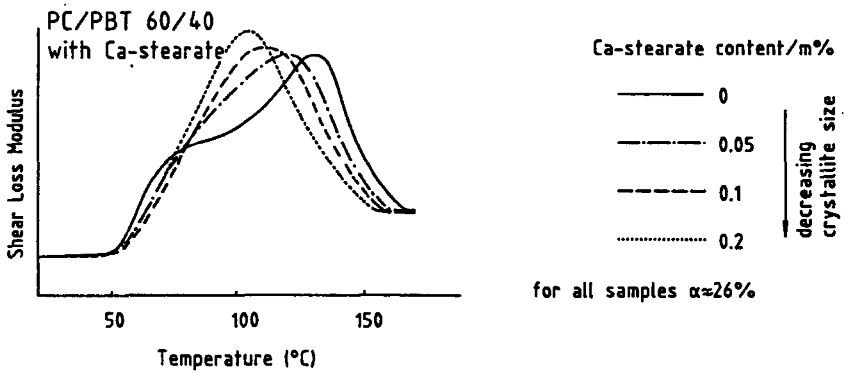

Fig. 7. Shear loss modulus versus temperature for PC/PBT 60/40 with different Ca-stearate contents

Our results suggest that the system PC/PBT is miscible in the melt state and that this state can be maintained in the solid state if it is possible to suppress PBT crystallization or to reduce the crystallite size.

We explain the occurence of microheterogeneous phases and the existence of pure PC phases with the growth process of the crystallites which causes a depletion of PBT in its surroundings. The arising concentration gradient of composition of amorphous phases leads to broadenings of glass transition and its shifts to higher temperatures.

3.2 Influence of transesterification on PBT crystallization and amorphous phase state in PC/PBT melt blends

As mentioned above we observed that the used nucleating agent Ca-stearate apparently supports the transesterification . The samples of the composition 60PC/40PBT with Ca-stearate content from 0 to 0.2 m% were thermally treated in the DSC oven for 40 minutes at 250°C and cooled to 20°C at 10K/min. Fig.8 shows

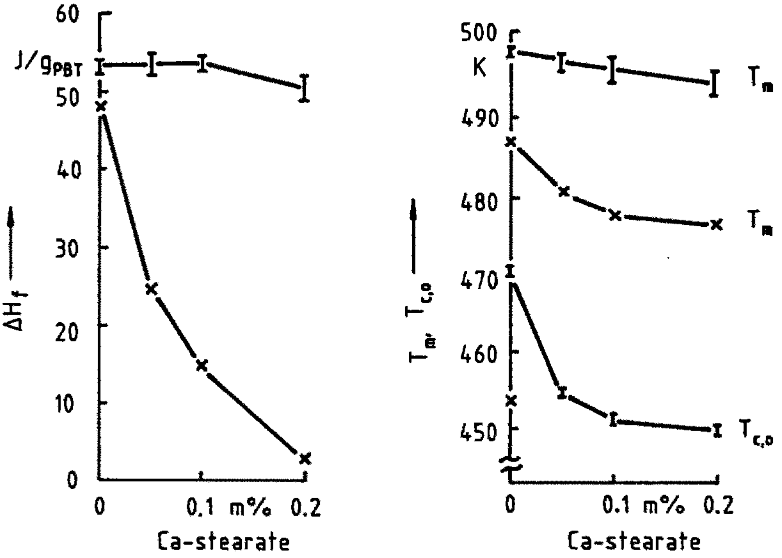

Fig. 8. Enthalpy of fusion ΔH_f and temperatures T_m and $T_{c,0}$ of sample PC/PBT 60/40 versus Ca-stearate content

I range of value before thermal treatment

x value after a thermal treatment at 250°C for 40 minutes

ΔH_f and T_m before and after thermal treatment in dependence on the Ca-stearate content. Both values decrease with increasing Ca-stearate content as a consequence of transesterefication taking place during thermal treatment in the melt.

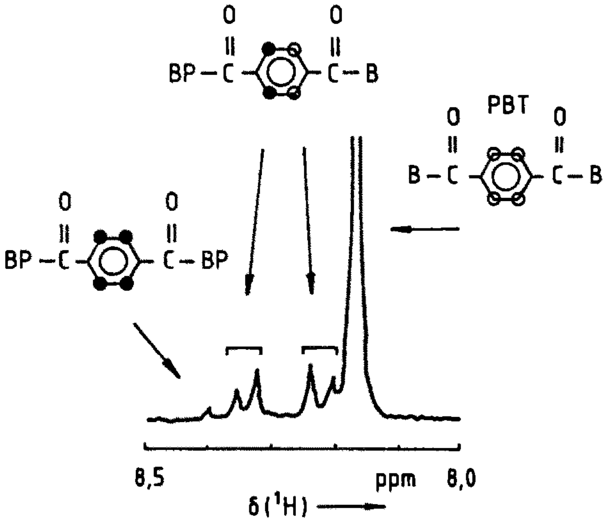

Fig. 9. ^{1}H-NMR spectrum of sample PC/PBT 60/40 with 0.2 m% Ca-stearate after a thermal treatment at 250°C

A ^{1}H-NMR spectrum (Fig. 9) was recorded for the sample with 0.2m% Ca-stearate, whose enthalpy of fusion was only about 1 J/g_{PBT}. The signals represent the different types of the terephthalate-centred triads. The amount of BP - T - B and BP - T - BP triads is about 21 %. This is a direct proof for the transesterification. The DSC heating scans (Fig. 10) of so-treated samples show that characteristics and temperature position of the glass transition are nearly independent of the degree of transesterification. The crystallinity decreases more rapidly than the enthalpy of fusion as a measure of the transesterification degree. Comparing the samples without and with 0.05 m% Ca-stearate, we have found that ΔH_f decreases by a factor of 1.4, but the crystallinity α (produced upon the cooling) decreases by a factor of 10 due to the thermal treatment.

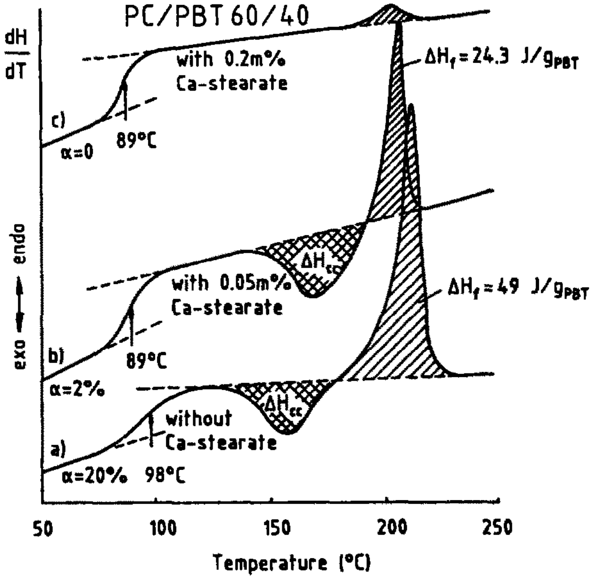

Fig. 10. DSC-heating scans of PC/PBT 60/40 with different Ca-stearate contents after a thermal treatment at 250°C for 40 minutes

In this connection it is interesting that the onset-temperature $T_{c,0}$ of crystallization was depressed to the same value by the copolyesters as well as the Ca-stearate additivies (see Fig.8). That means that not only the number of crystallizable PBT segments is reduced by transestrification but that also the crystallization of the residual crystallizable PBT segments is strongly hindered by small contents of transestrification products themselves.This explains the relatively small influence of the transesterification degree on the glass transition temperature.

We confirm this conclusion with the DSC heating scans of the sample 60PC/40PBT with 0.2 m% Ca-stearate at three different sample state (Fig.11). The crystallinity of the as-prepared state is about 25 % (curve a). The other states (curves b,c) produced in different ways are almost completely amorphous.

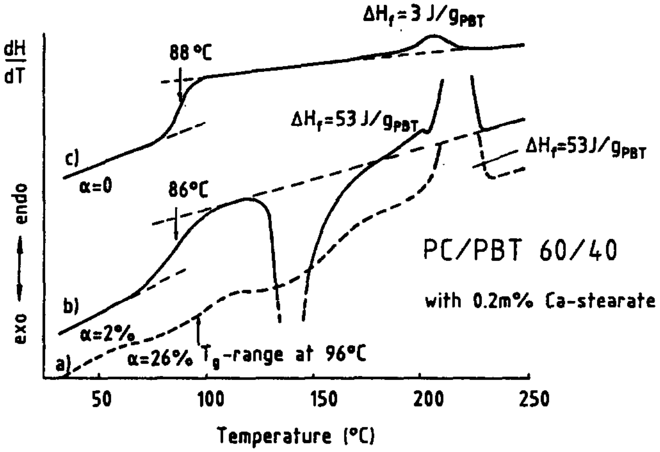

Fig. 11. DSC-heating scans of PC/PBT 60/40 with o.2 m% Ca-stearate in three different states

a) as-prepared

b) after heating to 250^{0}C and rapid cooling

c) after thermal treatment at 250^{0}C for 40 minutes and cooling at 10 K/min

Since the crystallite size in the as-prepared state, which represents a physical mixture, is very small, we observed only a small difference of T_g of states with 25 % and zero crystallinity. Nearly the same glass transition of a homogeneous phase was found at the physical mixture with very small crystallinity (Fig.11, curve b) and the same mixture with either a higher (Fig.11, curve c) or a lower (Fig.10, curve b) degree of transestrification .

The results confirm that this homogeneous amorphous phase state is determined by strongly reduced crystallinity independent of whether it has been produced by additives or by copolymers.

SUMMARY

The PBT-crystallization is regarded as the main factor which determines the miscibility of PC/PBT melt blends. The crystallinity was varied by cooling conditions from melt, nucleating agents and transesterification products . Our results suggest that the system PC/PBT is miscible in the melt state and also in the solid state if it is possible to suppress the crystallization of PBT. The investigations showed that at arising PBT-crystallization it is not the degree of crystallinity but the crystallite size which affect the formation of various amorphous phase states. We explain this fact with the growth process of crystallites which causes a depletion of PBT in its surroundings. The arising concentration gradient of the composition of the amorphous phase leads to the broadenings of glass transitions and its shifts to higher temperatures.

Additionally, we also investigated the effect of transesterification on the amorphous phase state. We found that the copolyesters determine the miscibility only via its influence on the PBT-crystallization.

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