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Studies of miscibility, transesterification and crystallization in blends of Poly(ethylene terephthalate) and Poly(ethylene-2,6-naphthalene dicarboxylate*)

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*) *Dedicated with best wishes to Prof. Dr. E.W. Fischer on the occasion of his 65th birthday*

Abstract: Blends of poly(ethylene terephthalate) (PET) and poly(ethylene-2,6-naphthalene dicarboxylate) (PEN) were obtained by coprecipitation from solution followed by melt-pressing for different times t_m and quenching in iced water. When the melt-pressing time was 0.2 and 0.5 min, two glass transition temperatures T_g were observed by means of dynamic mechanical analysis (DMA), indicating that there are two phases present, a PEN-rich phase and a PET-rich phase. The differential scanning calorimetry (DSC) curves show two crystallization peaks and two melting peaks which, according to wide-angle x-ray scattering (WAXS) measurements, can be attributed to PET and PEN, respectively. In the case of $t_m = 2$ min or longer, a single value of T_g and thus a single phase is found to exist. For $t_m = 10$ min and 45 min no crystallization and melting at all is observed during heating with 10°C/min, indicating that a copolyester of PET and PEN has been formed by transesterification during melt-pressing.

Time-resolved WAXS measurements during isothermal crystallization show that, in the blend, the half-time of crystallization of PET is different from that of PEN, and not the same as that which is found in the pure polymer.

Key words: Transesterification – miscibility – crystallization

A. Introduction

Blends of crystallizable polymers are interesting subjects for investigation. Among others, the following questions arise: Are the polymers in the blend miscible or partially miscible? How is the crystallization behavior of each component influenced by the presence of the other component? Do any chemical reactions such as transesterification take place between the two components and how do these reactions influence the miscibility or depend on miscibility?

Extensive investigations of the miscibility and crystallization behavior have been performed, among others, on blends of poly(ε-caprolactone) and polystyrene [1, 2], of poly(ethylene oxide) and poly(methyl methacrylate) [3], of poly (vinylidene fluoride) and polyamide-6 [4] and of isotactic polypropylene with different rubbers [5]. It was shown that the second component influences the crystallization kinetics and morphological structures in many different ways depending on composition and miscibility.

There also exist some studies of miscibility and transesterification, mainly in blends of polycarbonate and poly(butylene terephthalate) [6, 7] as well as of polycarbonate and poly(ethylene terephthalate) (PET) [8–12]. Clear evidence was found that transesterification plays an important role in blending such systems. Neutron scattering experiments have revealed [13, 14] that within a single component system such as PET, above the melting point a large amount of transesterification takes place within a few minutes.

While there exist many studies on the miscibility and on the crystallization, the question of how transesterification is related to miscibility and to crystallization is still not answered. We have investigated this problem using blends of poly(ethylene terephthalate) (PET) and poly(ethylene-2,6-naphthalene dicarboxylate) (PEN). Both materials are able to crystallize. The melting point and glass transition temperatures are 270° and 120 °C, respectively, in the case of PEN, and 268° and 70 °C, respectively, in the case of PET. The crystallization behavior of PET has been extensively investigated by us in previous works [15, 16]. We have also studied the crystallization of PEN [17] and the glass transition and crystallization of statistical copolyesters of PEN and PET [18, 19]. First studies on blends of PET and PEN have indicated that both polymers form a one-phase system when annealed for 2 min in the melt, however, it was not clear to what extent transesterification has taken place. In the present work, the two polymers were mixed by coprecipitation from solution in order to avoid any transesterification and then melt-pressed for different times in order to study the extent of transesterification by means of different methods.

B. Experimental

PET and PEN were synthesized starting from ethyleneglycol together with dimethyl terephthalate and dimethyl-2,6-naphthalene dicarboxylate respectively as described in previous publications [15, 19]. Different catalysts were used in order to study the influence of the catalyst on the transesterification, namely, manganese acetate (Mn), antimony trioxyde (Sb), zinc acetate (Zn) and tetra-n-butylorthotitanate (Ti). The viscosities of the samples were measured in hexafluoroisopropanol. The different materials which were synthesized are listed in Table 1 together with the catalysts and the intrinsic viscosities $[\eta]$. By using the equation $[\eta] = 5.2 \cdot 10^{-4} M_w^{0.695}$, which was found [20] to be valid for PET with $[\eta]$ in dl/g, the molecular weight M_w was calculated. As it is not known how far this equation can also be applied to PEN, the values obtained for this polymer can be only considered to represent an apparent molecular weight. In order to obtain the blends, the two polymers were dissolved in hexafluoroisopropanol and coprecipitated in ethanol. Amorphous films were obtained from the precipitated powder by melt-pressing in vacuo for various times t_m and quenching in iced water. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) measurements were performed on instruments from DuPont (DSC 910, DMA 983). The DMA measurements were performed in the shearing mode on strips having the dimensions 0.8 cm × 1.5 cm × 220 μm. The wide-angle x-ray scattering (WAXS) was measured by means of a Θ–2Θ goniometer from Siemens (D500). Time-resolved measurements were performed on the polymer beamline at HASYLAB in Hamburg, which is described elsewhere [21].

Table 1. Catalysts, intrinsic viscosities $[\eta]$, and molecular weight of the samples investigated in this publication. The amount of catalyst is given in mol%

Sample	Catalyst	$[\eta]$ [dl/g]	M_w [g/mol]
PET	none	0.7454	34800
PET	0.11% Mn/0.023% Sb	1.2213	70800
PET	0.11% Mn/0.023% Zn	0.8569	42500
PET	0.03% Ti	1.2378	72200
PEN	0.11% Mn/0.023% Sb	0.6129	26300
PEN	0.03% Ti	0.6089	26000
PEN	0.03% Ti	1.2087	69800

C. Results

1. *DSC and DMA*

Figure 1 represents the loss modulus G'' and the loss factor $\tan\delta$ as a function of temperature T of blends containing 30 wt.-% PET obtained in the amorphous state by melt pressing at 280 °C for different times t_m and quenching in iced water. Two well-separated maxima of G'' are observed after melting for 0.2 min and 0.5 min. The first maximum appears at 72° and 78 °C, respectively. The temperature of 72 °C corresponds to the temperature position of the glass transition maximum of pure PET [18]. However, the maximum of the blend is broader than the one of pure PET. The second maximum appears at 103° and 105 °C, respectively, which is about 15 °C lower than the glass transition maximum of pure PEN [18]. This

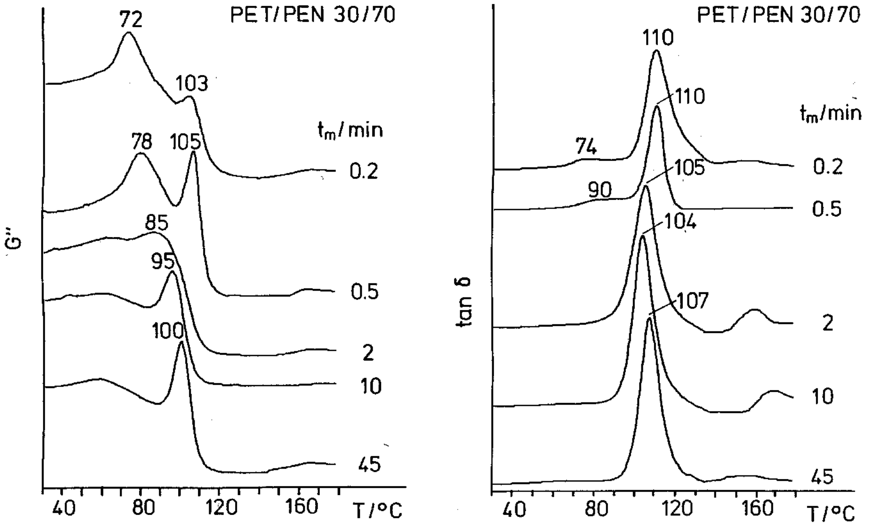

Fig. 1 G'' and tanδ as a function of temperature during heating of blends PET/PEN containing 30 wt.-% PET after different times t_m of melt-pressing at 280 °C

indicates that, after short melting times such as 0.2 and 0.5 min, two different phases coexist, one rich in PET and the other one rich in PEN.

With further increasing melting time, the two maxima approach each other resulting in a broad maximum at about 85 °C, after a melting time of 2 min, and a sharp maximum at 100 °C, after 45 min of melting. This indicates that a single phase is formed during these longer periods of melting. The maximum at 65 °C visible in the two last spectra is the β^* maximum of PEN. The tanδ curves (right side of Fig. 1) correspond to the G'' curves except that, as expected, the temperatures of the maxima are slightly shifted to higher values and the intensity of the maximum at the higher temperature is enhanced with respect to the intensity of the maxima at lower temperature. In some cases the last effect becomes so strong that some peaks appear either only in G'' or in tanδ.

Similar results are obtained on blends containing 44 and 60 wt.-% PET (Figs. 2 and 3, respectively). The two peaks observed after melting times t_m of less than 2 min merge into a single peak after longer melting times. As expected, the peak of PEN becomes weaker with increasing PET content. In the case of 70 wt.-% PET (Fig. 4) the PEN peak completely disappears. The broad peak at 123 °C is caused by crystallization of the PET.

Figure 5 shows the DSC curves of the blends containing 30 wt.-% PET after different times of melt-pressing t_m (as in Fig. 1). The DSC curve of the powder as precipitated ($t_m = 0$) is also presented. The samples molten for 0.2 and 0.5 min show two exothermic peaks, a small one in the region of 140–150 °C which can be attributed to the crystallization of PET, and a larger one at approximately 180 °C attributed to the crystallization of PEN. After melting for 2 min the PET peak is no longer apparent. If the melting time is further increased, the other peak also gradually disappears. The precipitated powder ($t_m = 0$) is already crystallized to some extent at the beginning of the heating in the DSC. Therefore, the crystallization peak is comparatively small.

A melting peak at 266 °C, corresponding to the melting of PEN, with a small shoulder at 251 °C, can be seen in the case of $t_m = 0$, 0.2 and 0.5 min. In agreement with the following results, these peaks can be attributed to the melting of PEN (266 °C) and PET (251 °C). With increasing t_m of previous melting, the melting peak gradually moves to lower temperatures, becomes less intense, and finally disappears. The changes of the temperature positions and the decrease of the intensities of the crystallization and melting peaks with increasing time t_m can be explained by assuming a transesterification process between PET and PEN leading to a random copolyester of these components. It is known from previous investigations [19] that random copolyesters of PET and PEN of compositions investigated here crystallize only to a small extent or not at all.

Similar results are obtained for other compositions of the blend. With increasing amount of

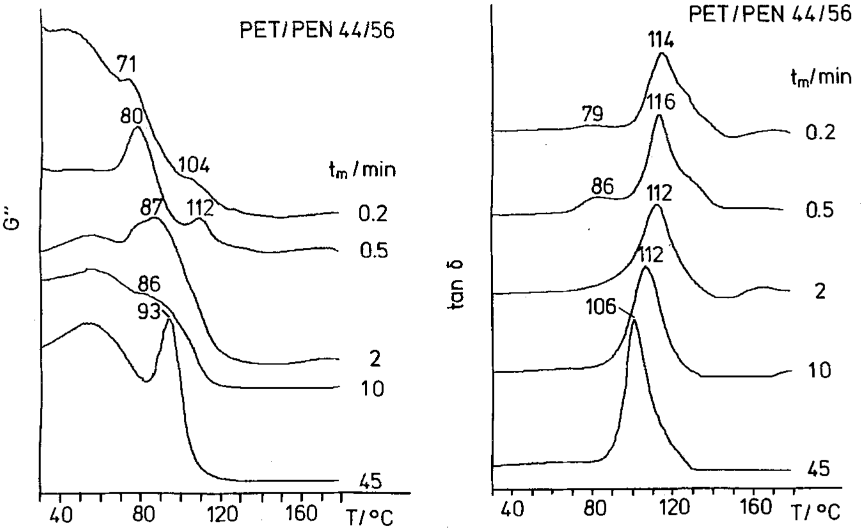

Fig. 2 G'' and $\tan\delta$ as a function of temperature during heating of blends PET/PEN containing 44 wt.-% PET after different times t_m of melt-pressing at 280 °C

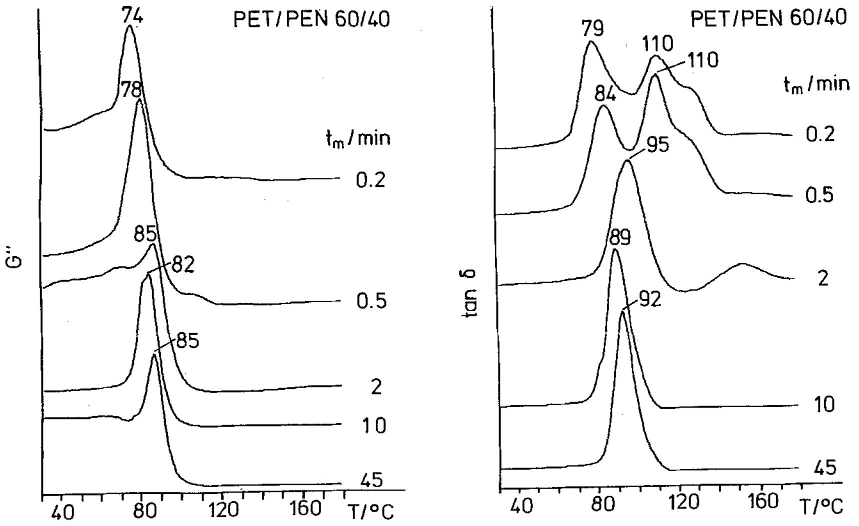

Fig. 3 G'' and $\tan\delta$ as a function of temperature during heating of blends PET/PEN containing 60 wt.-% PET after different times t_m of melt-pressing at 280 °C

PET the crystallization peak at the lower temperature increases while the one at the higher temperature decreases, which justifies the attribution of these peaks to the crystallization of PET and PEN, respectively. No crystallization and melting is observed for $t_m = 45$ min in the samples PET/PEN 30/70 and 44/56 and for $t_m = 10$ min in the samples 60/40 and 70/30 (see for example Fig. 6).

We have also studied the influence of the degree of dispersion of the two phases on the melt-pressing time t_m which is necessary to obtain a one-phase system. It can be assumed that the finest dispersion is obtained by coprecipitation from the solution as it was performed in the experiments relating to Figs. 1 to 6. The less dispersed systems investigated were:

i) a mixture of two powders with 0.5 mm grain diameter
ii) a mixture of two powders with 2 mm grain diameter
iii) a film of PET placed on top of a film of PEN each 0.2 mm thick.

As described before, the samples were melt-pressed at 280 °C for different times t_m, quenched, and then investigated by DMA and DSC. The

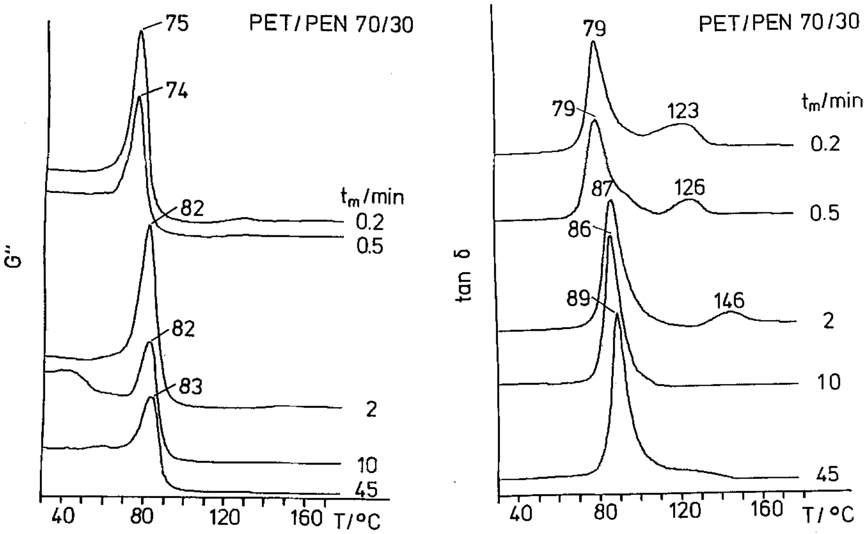

Fig. 4 G'' and tan δ as a function of temperature during heating of blends PET/PEN containing 70 wt.-% PET after different times t_m of melt-pressing at 280 °C

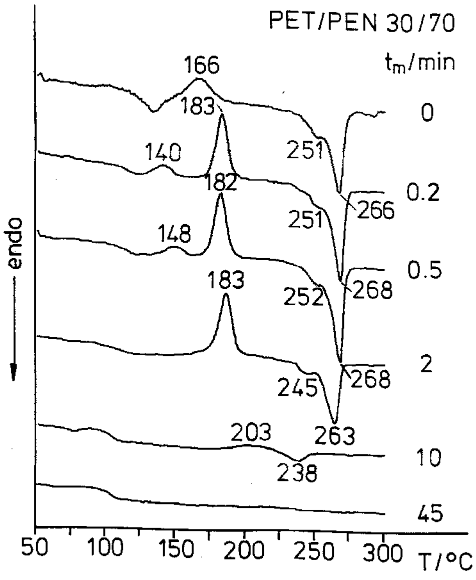

Fig. 5 DSC curves of blends PET/PEN containing 30 wt.-% PET after different times t_m of melt-pressing at 280 °C and quenching in iced water

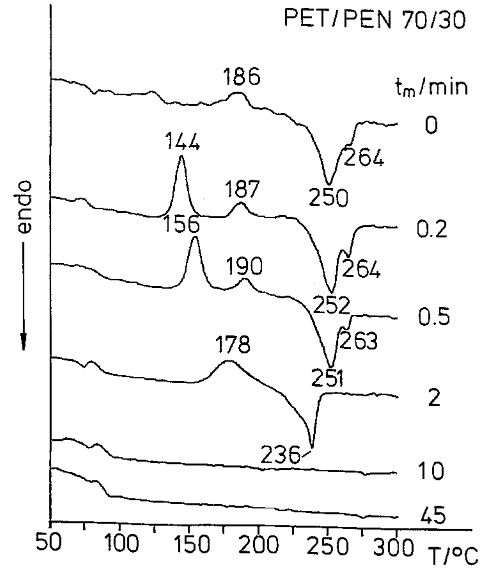

Fig. 6 DSC curves of blends PET/PEN containing 70 wt.-% PET after different times t_m of melt-pressing at 280 °C and quenching in iced water

results are represented in Figs. 7 and 8, respectively, together with the results of the sample obtained by coprecipitation from the solution. In this sample, the one-phase formation seems to be complete after 2 min (see Figs. 7a and 8a). In the mixture of the powder with 0.5 mm grain diameter (Figs 7b and 8b) this occurs after approximately 10 min. In the DSC diagram, in contrast to the results of the coprecipitated mixture, some crystallization and melting can be detected even after 10 min of melting. In the case of the 2 mm grain powder and the layered films, the first changes in the curves occur after $t_m =$ 10 min of melting; even after 45 min of melting one can still observe both peaks in tan δ and both crystallization peaks in the DSC curves.

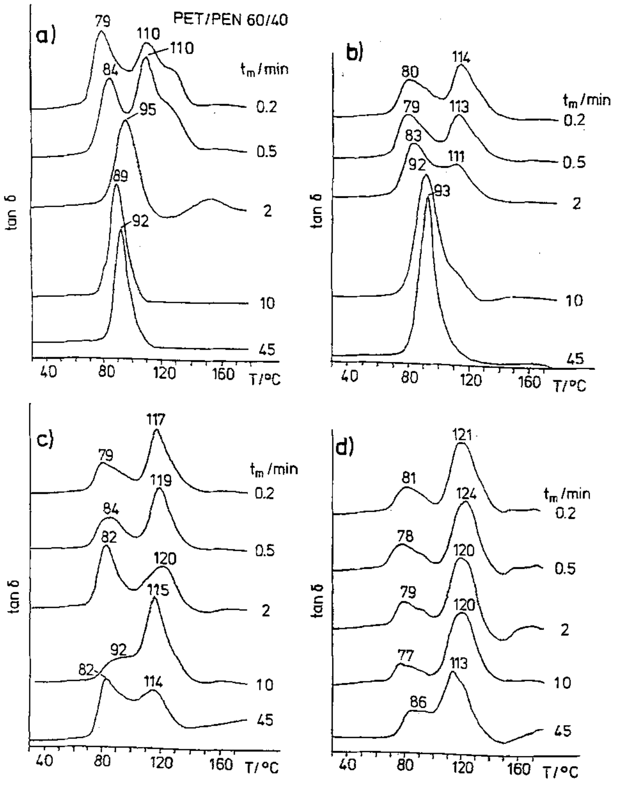

Fig. 7 Tanδ as a function of temperature during heating of blends PET/PEN containing 60 wt.-% PET blended a) in solution b) as powder (0.5 mm) c) as powder (2 mm) d) in the form of 2 films. Parameter: time of melt-pressing t_m at 280 °C

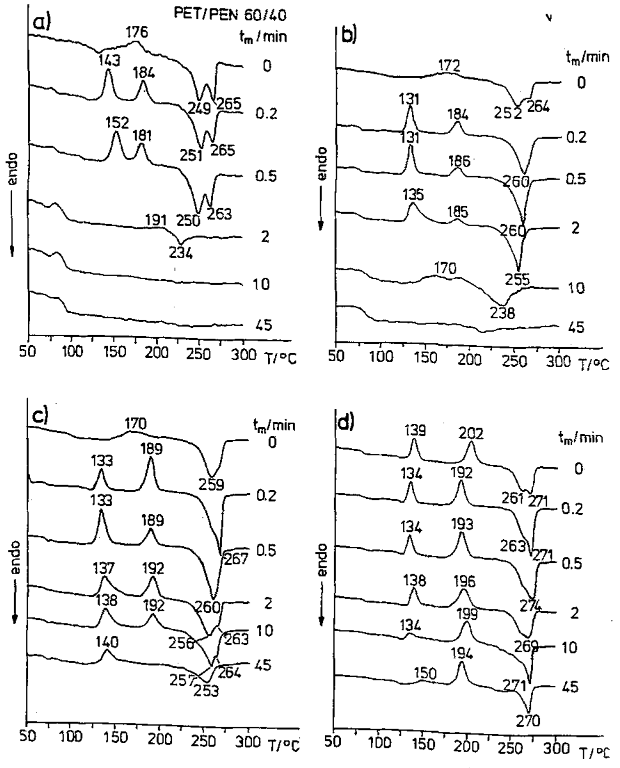

Fig. 8 DSC curves of blends PET/PEN containing 60 wt.-% PET blended a) in solution b) as power (0.5 mm) c) as powder (2 mm) d) in the form of 2 films. Parameter: time of melt-pressing t_m at 280 °C

Another question is that of how far the kinetics of transesterification are influenced by the catalysts. Table 1 shows the catalysts used. All samples showed essentially the same changes of the DMA and DSC curves with increasing melting time t_m. The only exception was the sample without Sb_2O_3 in which transesterification seemed to proceed slightly more slowly.

2. *WAXS*

Further information on the crystallization behavior is obtained by means of WAXS measurements. Unfortunately, the crystal reflections of the two components PET and PEN lie quite close together. Figure 9 shows the diffraction diagram of PET, of PEN, and of a superposition of a PET and a PEN film. The samples have been crystallized for 12 h at 240 °C. Looking for reflections

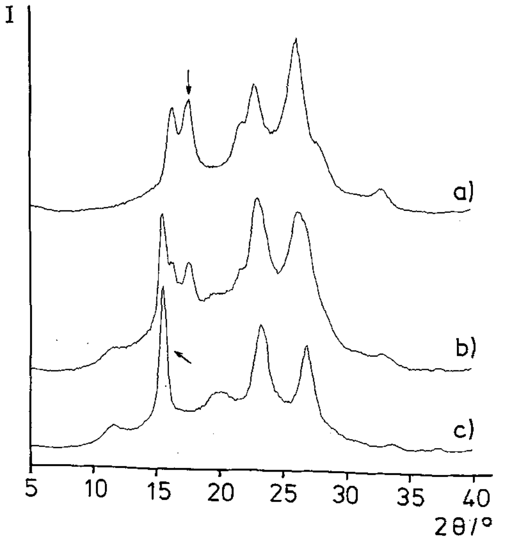

Fig. 9 WAXS of a) PET b) films of PET and PEN c) PEN after crystallization for 2 h at 240 °C

which are different for the two components, PEN is best characterized by the strong reflection at $2\Theta = 15.5°$. Close to this (at $2\Theta = 16.3°$) a PET reflection is observed which, however, is not so intensive as the one of PEN. PET is best characterized by the reflection at $2\ \Theta = 17.6°$ where no reflection of PEN appears. However, one must consider that the doublet at 16.3° and 17.6° is not well separated if the crystallization temperature is less than 200 °C and even becomes a single broad reflection at approximately 17.3° if the sample is crystallized below 160 °C.

Figure 10 shows the diffraction diagrams for blends of different compositions obtained from the powder (Fig. 10a), from a film melt-pressed for 0.5 min (Fig. 10b), and from a film melt-pressed for 45 min (Fig. 10c). In each case the samples were crystallized for 14 h at 180 °C before the measurements were performed. In the diagrams obtained from the precipitated powder the broad PET reflection at $2\Theta = 17.3°$ only appeares if the PET content is 30 wt.-% and above. Similarly, the PEN crystal reflection at 15.5° is only visible at PEN contents of at least 30 wt.-%. Thus, in a broad range of compositions both crystals are present. If the sample has been melt-pressed for 0.5 min (Fig. 10b) the results are almost the same. If however, melt pressing has occurred for 45 min (Fig. 10c) the material containing 40 wt.-% PEN does not crystallize at all. In the other samples, only one component is crystallizing, namely, PEN in the samples containing 56 wt.-% and more PEN, and PET in the samples containing 70 wt.-% or more PET. This is exactly the same crystallization behavior as observed with corresponding copolyesters of PET and PEN. This is further evidence for transesterification.

Interesting results have been also obtained by means of studies of the kinetics of crystallization. Figure 11 shows the change of WAXS during isothermal crystallization at 161.5 °C of a blend containing 60 wt.-% PET melt-pressed for 0.5 min. One can clearly recognize that the PET reflection grows within the first 3 min while the PEN reflection starts to grow after 8 min. Thus, PET crystallizes faster than PEN. Figure 12 shows the corresponding results obtained from a blend containing 44 wt.-% PET and crystallized at 204.5 °C. Here, PEN crystallizes faster than PET.

In this way the rate of crystallization of blends with different compositions at various temperatures was studied. The half times of crystallization of PEN were determined from the increase of the intensity of the reflection at 15.5° with time; for PET, the reflection at 17.3° was used. Figure 13 shows the results. The upper part represents the half time of crystallization of PET while the lower part shows that of PEN as a function of crystallization temperature. The study of the crystallization at lower temperatures was performed by heating amorphous samples from room tem-

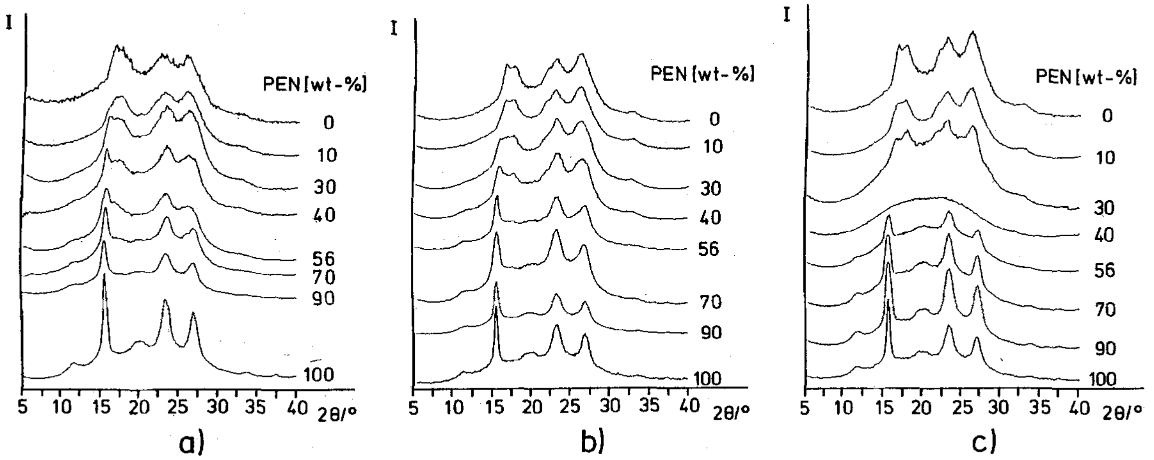

Fig. 10 WAXS of PET/PEN blends containing different amounts of PEN a) precipitated powder annealed for 14 h at 180 °C. b) precipitated powder melt-pressed for 0.5 min at 280 °C, quenched in iced water and annealed for 14 h at 180 °C. c) as b) but melt-pressed for 45 min

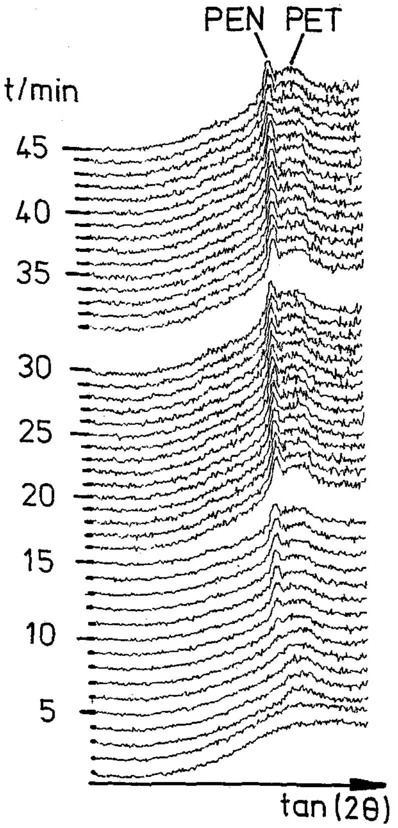

Fig. 11 Change of WAXS during isothermal crystallization of a PET/PEN blend containing 60 wt.-% PET at 161.5 °C after rapid heating from the glassy state

perature; for the studies at the higher temperatures the samples were cooled down directly from the melt of the crystallization temperature. It is most interesting to compare the rate of crystallization in the blend with that in the pure material. In the temperature range close to the glass transition, PEN in the blend crystallizes at a lower temperature than in the pure state. For example, in the blend, the half time of crystallization of PEN is 5 min at 160 °C, while one must heat a pure PEN sample to 190 °C to have $\tau = 5$ min. On the other hand, PET in the blend starts to crystallize at a higher temperature than in the pure state. In the temperature range close to the melting point, in the blend both PEN and PET only crystallize if the supercooling is larger than for the pure material. For example, in a blend containing 40 wt.-% PEN one has to cool the melt down to 218 °C in order that the half time τ

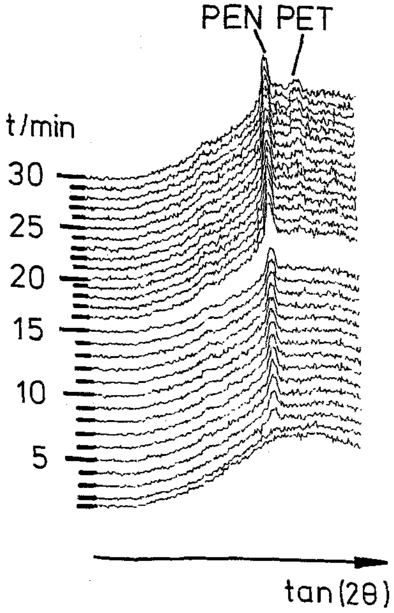

Fig. 12 Change of WAXS during isothermal crystallization of a PET/PEN blend containing 44 wt.-% PET at 204.5 °C after rapid cooling from the melt

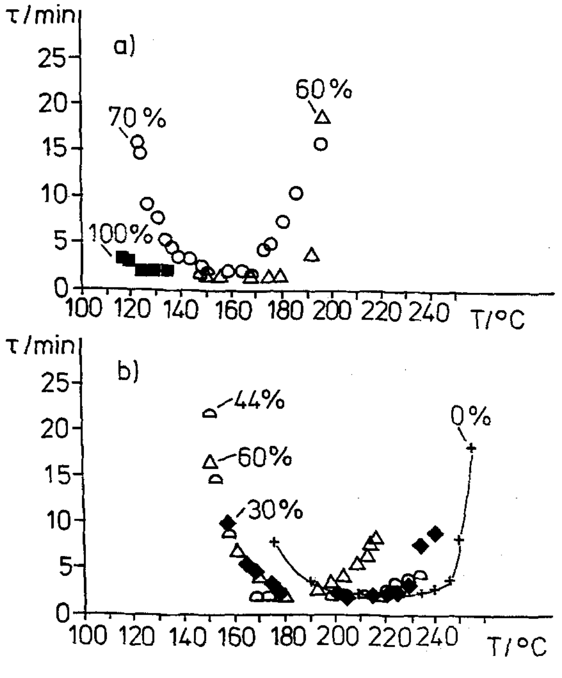

Fig. 13 Half-time τ of crystallization of PET (a) and of PEN (b) in PET/PEN blends after melt-pressing at 280 °C for 0.5 min. The PET content in wt.-% is indicated for each kind of symbol

of crystallization of PEN in 5 min, while in pure PEN, $\tau = 5$ min is already obtained at 250 °C. All these effects can be explained if one assumes partial miscibility of the two components (see discussion).

Discussion

1. Rate of isothermal crystallization

As described in the section "Results", in the high temperature range of crystallization ($T_c > 150$ °C in the case of PET and $T_c > 190$ °C in the case of PEN) the half-time of crystallization of PET and PEN in the blend is smaller than in the pure material. How can this be explained? In the case of phase separation the half-time of PEN will either not be affected by the presence of PET or it will be decreased as a consequence of a nucleation effect. Therefore, we conclude that there exists miscibility. In this case two possible effects may be considered:

i) A melting point depression. However, no melting point depression of 30 °C is observed in the DSC diagrams after melt-pressing for 0.5 min.
ii) Dilution of PEN by PET. Due to that dilution, the rate of formation of crystal nuclei is decreased. We believe that this is the explanation for the effect we have observed.

In the low temperature range, in the blend PEN crystallizes at lower temperatures and PET at higher temperatures than in the pure state. This can again be explained by assuming partial miscibility. As the glass transition temperature of PET (70 °C) is lower than that of PEN (120 °C) the presence of PET increases the mobility of the PEN molecules and the presence of PEN decreases the mobility of the PET molecules.

2. Transesterification

The following experimental results clearly demonstrate that transesterification between PET and PEN takes place at 280 °C in the blend of these components obtained by coprecipitation from the solution:

i) The decrease of the melting point with increasing melting time t_m (Figs. 5 and 6).
ii) The disappearance of the crystallization and melting peak in the DSC curves during heating with 10 °C/min after melt-pressing for 45 min.
iii) After 45 min of melt-pressing-even if annealed for a long time at high temperature - no crystallization occurs when the PET content is 60 wt.-%, and only one component, namely the one which predominates, crystallizes at the other compositions (Fig. 10). The WAXS, DSC, and DMA curves of the material obtained by melt-pressing for 45 min are the same as those of a copolyester obtained by usual synthesis [19]. From this we conclude that transesterification is completed after 45 min of melt-pressing. On the other hand, in a mixture of the two components composed of grains with a diameter of 0.5 mm or larger, the rate of transesterification is drastically reduced. Thus, transesterification alone cannot result in a one-phase system when the system is initially phase separated on a scale of 0.5 mm.

Another point to consider is whether transesterification within short times is possible if the separated phases are smaller than 0.5 mm. It is shown [22] in another two-component system consisting of the isotropic ternary copolyester of PEN, PET, and Poly(*p*-hydroxybenzoic acid) (PHBA) (35:35:30) and the liquid crystalline binary copolyester PET-co-PHBA (30:70) that no transesterification occurs within 45 min, even if blending has been performed by coprecipitation from solution. This may indicate that single phase formation is necessary for transesterification to take place.

3. Miscibility

The appearance of a single peak in tan δ and G'' after 2 min of melting indicates that a single phase is formed. It is clear that some miscibility already exists in the films melt-pressed for 0.2 and 0.5 min. This is supported by the following results:

i) The rate of crystallization of PET and PEN in the blend is different from that of the pure phases
ii) The glass transition peak of PEN in the blend appears at a temperature 15 °C below that of pure PEN

iii) In the blend containing only 30% PEN the glass transition peak of PEN in both the G'' and $\tan\delta$ curve has completely disappeared. This indicates that the PEN is dissolved in PET though the glass transition temperature of PET is not changed.

Thus, we conclude that coprecipitation is accompanied by phase separation, the two phases being highly dispersed. During the following melt-pressing a single phase is formed within 2 min by diffusion.

We want to stress that, as is well known, a single T_g does not necessarily mean that there exists miscibility on a molecular scale. A single maximum also appears if the components are separated, forming phases which are smaller than about 10 Å [23].

The question of how far transesterification has occurred within the first 2 min of melt-pressing is difficult to answer. By dissolving the sample after melt-pressing and coprecipitating it again, one sees small changes in the DSC diagram indicating that some transesterification has taken place.

The question arises if the miscibility is enforced against thermodynamics by the transesterification process. In other words: Can a single phase be formed within such a short time just as a consequence of transesterification, even if there is no thermodynamic tendency to form a single phase? The results obtained on a blend of the liquid crystalline copolyester PET-co-PHBA (30:70) and the isotropic copolyester PEN-co-PET-co-PHBA (35:35:30), which are mentioned above, seem to be an indication that this is not possible. Transesterification and therewith a single phase is not achieved if thermodynamics do not favor at least partial miscibility. If, however, partial miscibility exists for the homopolymeric components of the blend, the formation of copolymers by transesterification may increase the miscibility, thus leading to a copolyester showing total miscibility of the components.

E. Conclusions

We can conclude from our results that

i) after coprecipitation from solution, PET and PEN are more or less phase separated;
ii) after melt pressing for 0.5 min, two mixed phases are obtained, indicating that PEN and PET are at least partially miscible;
iii) this miscibility is of great influence on the rate of crystallization;
iv) the miscibility also makes it possible that transesterification occurs between PEN and PET;
v) after 2 min of melting a one-phase system is formed. From the present experiment it cannot be concluded whether this is solely induced by thermodynamics or is a consequence of transesterification. Investigations of other systems, however, indicate [22] that transesterification becomes extremely slow if not at least partial miscibility exists.

Acknowledgements

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