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DSC INVESTIGATION OF INTERCHANGE REACTIONS IN THE MELT OF DIFFERENT POLYESTERS

J. BUDÍN AND J. VANÍČEK
Chemopetrol-Silon, Research Department, Planá nad Lužnicí, 391 02 Sezimovo Ústí (Czechoslovakia)
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ABSTRACT

The course of a randomization process in the melt of poly(ethylene terephthalate) and other polyesters during melt-blending was observed by determining changes in T_g, T_c and T_m measured by DSC. The melting point of isothermic annealed copolyesters is the most advantageous criterion for determining the degree of randomization process. On the other hand, T_g and T_c are influenced by further processes taking place during the melt-blending of two kinds of homopolyesters, e.g. the changes of molecular mass and molecular mass distribution etc.

INTRODUCTION

The ester links of poly(ethylene terephthalate) (PET) formed during polycondensation are still reactive and the molecules of different sizes can continue to react together in different ways. Ester interchange reactions also take place in the melt of PET and other polyesters[1, 2]

$$R_1CO\text{–}OR_2 + R_3OH \rightleftharpoons R_1CO\text{–}OR_3 + R_2OH$$
$$R_1CO\text{–}OR_2 + R_3COOH \rightleftharpoons R_3CO\text{–}OR_2 + R_1COOH$$
$$R_1CO\text{–}OR_2 + R_3CO\text{–}OR_4 \rightleftharpoons R_1CO\text{–}OR_4 + R_3CO\text{–}OR_2$$

Three types of interchange reactions are possible, but the concentration of the end-groups is 400 times lower than that of ester groups for the polyester, $\bar{P}_n = 100$. Owing to these interchange reactions, block copolyesters formed at the first stage of melt-blending undergo randomization. When the interchange reaction is allowed to proceed to completion, random copolymer is produced identical with that prepared from the corresponding monomers by melt polycondensation. The course of the randomization process was followed by measuring the melting point of copolyesters (by penetrometer[1], by using a Kofler block[2] or by NMR[3]). Most of these studies are concerned with a modification of PET to obtain improvements in certain textile PET fibre properties. Recommended concentrations of modifying component are from 5 to 10 mole%.

In the present work, we have made an attempt to determine the course of the randomization process in the melt of PET and poly(ethylene isophthalate) (PEI), poly(2,2-dimethylpropylene terephthalate) (PNT) or poly(tetramethylene terephthalate) (PBT), respectively, observing the changes in T_g, T_c and T_m measured by DSC (Perkin-Elmer 1B).

EXPERIMENTAL

The above polyesters were prepared by normal methods from the respective dimethylesters of dicarboxylic acids and diols using $Mn(CH_3COO)_2$ and $Sb(CH_3COO)_3$ as catalysts and H_3PO_4 as a stabilizer of the thermal degradation. A desired amount of dried polyester chips was added to a PET melt after a polycondensation so that the concentration of modifying component was 8 mole%. The contents of the reaction vessel were stirred under N_2 at 280°C and the samples taken in a form of a quenched amorphous foil. It was possible to carry out the melt-blending reaction under vacuum (113 Pa). The amount of the comonomer in the samples was checked by IR spectroscopy (isophthalic acid) and gas chromatography (2,2-dimethylpropylene glycol and tetramethylene glycol) and it was 8 mole% (related to the structural units) in all cases.

Specific viscosities of the samples taken during melt-blending were determined in the phenol–tetrachlorethane (1 : 3) mixture at 30°C, $c = 1$ g/ 100 ml. The amount of diethylene glycol (DEG) in PET ranged from 0.7 to 0.8 wt.%.

DSC measurements were carried out on a DSC-1B instrument (Perkin-Elmer). The weight of polymer sample was 10 mg and the sensitivity of the measurement on DSC was 33.4 mJ s^{-1} full scale. The characteristic temperatures of transitions were determined as follows.

Glass transition temperature, T_g (ref. 4)

A sample in the quenched amorphous state was heated to 80°C at a heating rate of 16 K/min, annealed for 1 min at this temperature to remove the effects of its previous thermal history and then cooled at a rate of 4 K/min. After cooling to room temperature, the sample was again heated to 80°C at a heating rate of 16 K/min. The temperature of the maximum of the endothermic peak was read from the chart. This value was extrapolated to zero heating rate and zero weight of sample. This procedure ensures good reproducibility of the measurement.

Cold crystallization temperature, T_c (ref. 5)

An amorphous sample was heated to 160°C at a heating rate of 4 K/min. The temperature of the maximum of an exothermic peak (T_c) was read from the chart.

Melting point, T_m

The melting point of the reaction product after melt-blending was determined after isothermal crystallization of a sample at 200°C for 8 h under dry nitrogen. A rate of heating of 16 K/min was used for the measurement of melting points. Under these conditions, two endothermic melting peaks T_{m1} and T_{m2} appear on the chart. To find the reason for the double melting peak, the sample was annealed for varying times and was then scanned at various heating rates. The value of T_m at different heating rates was corrected for thermal delay on the basis of the shifts in melting points of standard metals at different heating rates.

RESULTS AND DISCUSSION

The considerable fall in T_g (Fig. 1) after the mixing of polyester melts is characteristic of this system. As is evident, two separate T_g values are not observed but the addition of a polyester acts as a plasticizer. T_g again increases as randomization proceeds and it next reaches the value determined for the corresponding statistical copolyester.

The temperature of cold crystallization, T_c, is the temperature of the maximum of the exothermic peak of the crystallization of an amorphous sample. A value of T_c can be affected by many factors including the molecular mass of a polymer, the orientation of molecules, the presence of nuclei of crystallization, the chemical and structural type of the comonomer and its distribution along the polymer chain. Generally, T_c increases with increasing value of molecular mass (η_{spec}) for a given type of polymer[5].

At the initial part of the reaction, T_c decreases (Fig. 2), especially in the case of melt-blending PET and PBT, due to the decrease of specific viscosity (Fig. 3) and the higher rate of crystallization of PBT in comparison with PET. An increase of T_c at the further stage of the melt-blending can be ascribed to the formation of a random

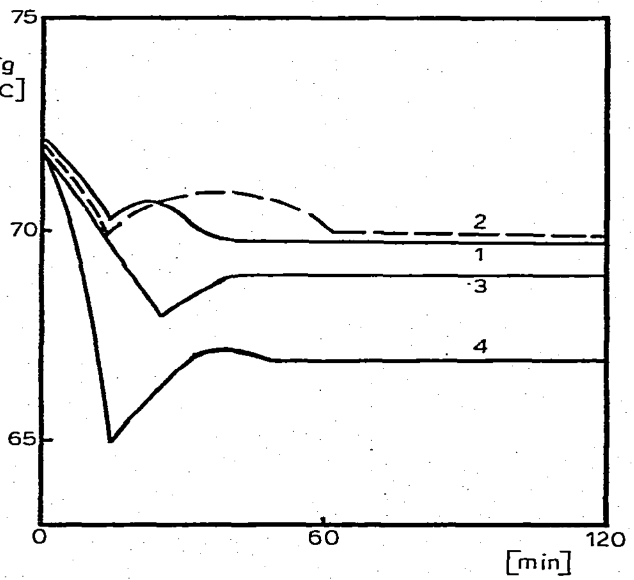

Fig. 1. Changes in T_g during the interchange reaction between PET and different polyesters 1, PEI under N_2; 2, PEI under vacuum; 3, PNT; 4, PBT.

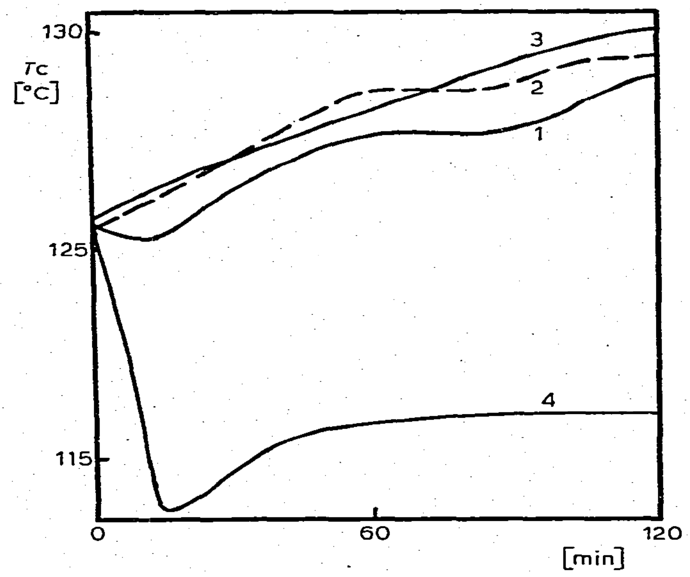

Fig. 2. Changes in T_c during the interchange reaction between PET and different polyesters. 1, PEI under N_2; 2, PEI under vacuum; 3, PNT; 4, PBT.

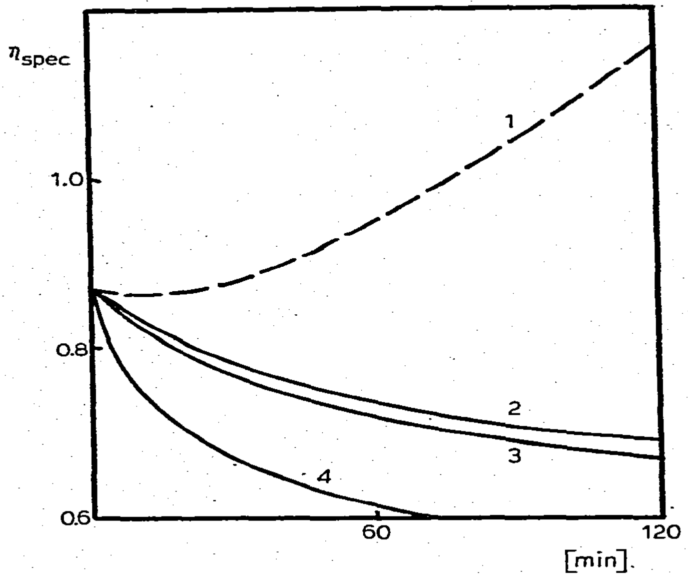

Fig. 3. Changes of η_{spec} during the interchange reaction between PET and different polyesters. 1, PEI under N_2; 2, PEI under vacuum; 3, PNT; 4, PBT.

copolyester. The value of T_c approaches that for the corresponding random copolyester with the same value of the molecular mass. The increase of T_c from the very beginning of the reaction in the case of melt-blending PET and PEI under vacuum can be attributed to the increase of η_{spec} due to a polycondensation reaction taking place under these conditions.

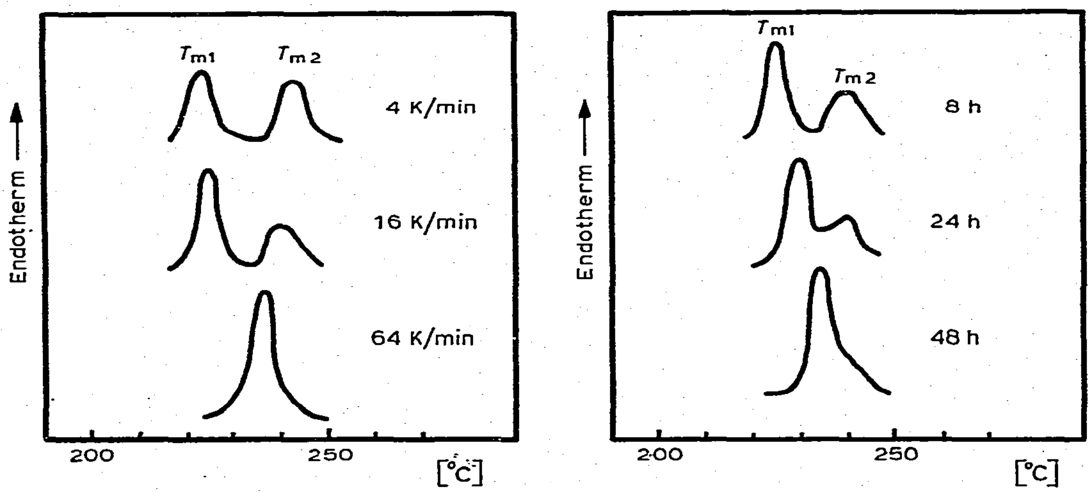

Fig. 4. The effect of the heating rate and time of isothermal annealing at 200 °C on the heating curve random copoly(ethylene terephthalate/isophthalate) (92/8). (a) Annealing time 8 h; (b) heating rate 8 K/min.

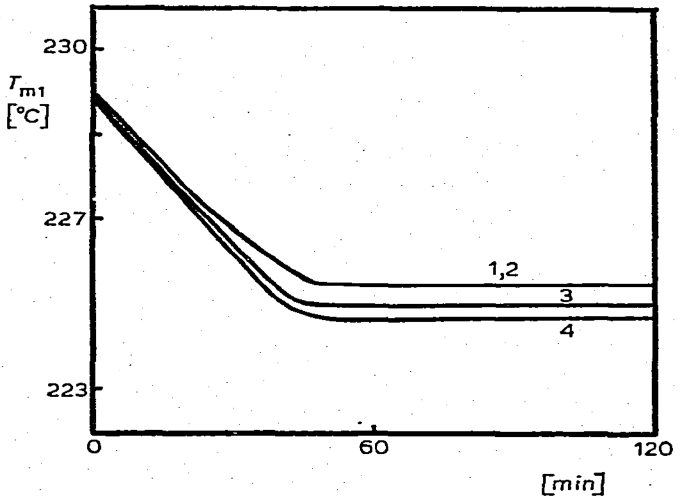

Fig. 5. Changes of T_{m1} during the interchange reaction between PET and different polyesters. 1, PEI under N_2; 2, PEI under vacuum; 3, PNT; 4, PBT.

In order to eliminate the influence of recrystallization[6] on melting point, T_m was determined after annealing at 200 °C for 8 h. Under these conditions, there are two endothermic melting peaks, T_{m1} and T_{m2}. We investigated the effect of the heating rate and the annealing time at 200 °C on the course of melting, in order to identify the origin of these endothermic peaks (Fig. 4). As the experiments indicate, the more pronounced and narrower peak T_{m1} evidently corresponds to the melting of crystals formed during annealing at 200 °C. This assumption seems to be quite reasonable with respect to the fact that T_{m1} becomes more pronounced with increasing annealing time at 200 °C [Fig. 4(b)] and that overheating becomes greater by using the higher heating rate on DSC [Fig. 4(a)]. The other peak, T_{m2}, can be ascribed to

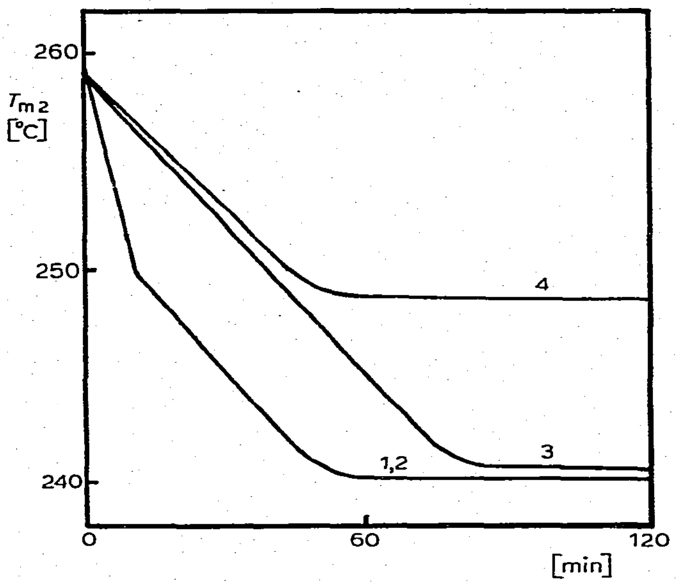

Fig. 6. Changes of T_{m2} under the same conditions used in Fig. 5.

the melting of crystals formed during heating a sample on DSC. The higher rate of heating of a sample on DSC, the less perfect polymer crystals are formed during heating. Owing to this phenomenon, the area of the T_{m2} peak and the value of T_{m2} decrease [Fig. 4(a)]. The area of the T_{m2} peak decreases with increasing time of previous annealing at 200 °C [Fig. 4(b)] because the possibility of recrystallization is reduced.

The changes in T_{m1} and T_{m2} were similar during melt-blending of PET and other polyesters (Figs. 5 and 6). The melting point decreases during the reaction in agreement with theoretic assumption until it reaches the value for a fully random copolyester with an identical thermal history. In the case of the melt-blending under nitrogen, the specific viscosity of the reaction product decreases during the reaction. In the other case (melt-blending under vacuum), the specific viscosity increases during reaction due to the polycondensation reaction which takes place under these conditions (Fig. 3). The changes of molecular mass (specific viscosity) during melt-blending did not influence the course of the randomization reaction characterized by the fall in T_{m1} and T_{m2}. This is in agreement with the theoretical expression for the melting point of polymers[7].

To summarize the results obtained, the melting point of isothermally annealed copolyesters is the most advantageous criterion for determining the degree of the randomization process. The melting point decreases during the reaction until it reaches the value of a random copolyester with the same thermal history. On the other hand, T_g and T_c are influenced by further processes taking place during the melt-blending of two kinds of homopolyesters, e.g. the changes of molecular mass, the molecular mass distribution, etc.

As was mentioned above, T_{m2} is influenced by recrystallization during measurement on DSC and is therefore less suitable for the determination of the course of the randomization process than T_{m1}. At the early stage of melt-blending, considerable changes in T_g and T_c take place, but their values for random copolyesters are not reached at the same time as in the case of T_{m1}. On the other hand, the changes in T_g and T_c help to characterize the reaction products and the particular phases of a melt-blending better, from the mixture of polymers through a block copolymer to a random one.

REFERENCES

1 P. Kresse, *Faserforsch. Textiltech.*, 11 (1960) 353.
2 K. Yoda, *Makromol. Chem.*, 136 (1970) 311.
3 M. Murano and R. Yamadera, *Polym. J.*, 2 (1971) 8.
4 J. Vaníček, in I. Buzas (Ed.), *Thermal Analysis: Proceedings of the 4th ICTA*, Vol. 3, Akademiai Kiado, Budapest, 1975.
5 J. Vaníček, J. Budín and M. Berka, *J. Therm. Anal.*, 12 (1977) 83.
6 P. J. Holdsworth and A. Turner-Jones, *Polymer*, 12 (1971) 195.
7 L. Mandelkern, *Crystallization of Polymers*, McGraw-Hill, New York, 1964.