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Poly(ethylene oxide) blends with crosslinking polyester resin

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Abstract: The miscibility of polyethylene oxide (PEO) with oligoester and polyester resin, the morphology of the blends and the kinetics of PEO crystallization in the blends were studied by optical microscopy and differential scanning calorimetry. The blends were found to be miscible with uncured resin at 60 °C. After isothermal crystallization of PEO from liquid oligoester or UV cured polyester about 20% of the PEO material is still dissolved in the resin and it is incorporated between lamellae or in the interspherulitic regions. It was observed that the growth rate of PEO spherulites and the degree of crystallinity of PEO in the blends decreases very fast together with a decrease of the PEO content and the progress of the resin crosslinking.

Key words: Poly(ethylene oxide) blends – crosslinking polyester resin morphology – calorimetry – crystallization

Introduction

In the blends in which one of the components is crystallizable, the presence of another component strongly disturbs the crystallization process. Both the crystallization kinetics and the final crystal morphology of crystallizing component as well are different in blends of immiscible or partially miscible polymers [1–3]. The polymer blend miscibility where one component is crystallizable and another one is crosslinked has received relatively little attention [4–6]. The occurrence of partial miscibility in such polymer blends containing a highly crosslinked component is unexpected and requires further investigation.

The interrelations between morphology, crystallization kinetics, and composition or progressing crosslinking of the second component are a subject of this study. This work is concerned with an investigation of the effects of undercooling, composition, and crosslinking on the melting behavior, crystallinity, morphology, and spherulite growth rate of PEO/polyester resin blends using optical microscopy studies and differential scanning calorimetry.

Experimental

Materials and blend preparation

The poly(ethylene oxide) (Mn = 20000) was supplied by Polysciences Inc. USA. The unsaturated oligoester resin (OER) (Polimal 102) (Mn = 2000) containing styrene as a crosslinking monomer and UV curing agent was prepared in Polish laboratories. The polyester resin was used previously [7, 8] with good results as an amorphous and transparent matrix for preparing polymer dispersed liquid crystals (PDLC).

The liquid OER and crystalline solid PEO were mixed in appropriate quantities at 60 °C for a sufficiently long time to form a homogeneous clear liquid blend. The PEO is well soluble in oligoester resin at 60 °C up to 60% wt. fraction of PEO (the content under study). A small amount of the blended liquid was placed between two warm (60 °C) microscopic support glasses. A distance thickness was kept between the glasses by a thin teflon film of 20 μm.

To prepare PEO/PER blends of various crosslinking degree the liquid blends of PEO/OER were UV irradiated at 60 °C, allowing the sample to start solidifying from the homogeneous mixture during the time from 20 s up to 15 min. Such prepared samples of PEO/OER and PEO/PER of various compositions were directly transformed on the Bettius microscopic hot stage and crystallized isothermally at given temperature. The samples for DSC measurements were prepared in the same way.

Measurements and techniques

The radial growth rates of spherulites were determined from the radii of spherulites measured as a function of time during the crystallization, which was carried out on the microscopic hot stage and recorded by a video camera and video recorder.

The morphology of the PEO, PEO/OER, and PEO/PER blends was studied by means of an optical polarizing microscope.

The calorimetric measurements of the original (unprocessed) PEO/PER blends crystallized at 25° and 33 °C were performed using a Perkin-Elmer DSC-2 differential scanning calorimeter. All samples were scanned from − 50 °C to 70 °C at a heating rate of 10°/min. The melting point temperature (T_m) was taken as the maximum of the endothermic transition, the heat of fusion (ΔH) was taken as the standardized surface area under the melting transition.

Results and discussion

Morphology and crystallization

All the PEO/OER blends were transparent liquids at 60 °C. The optical micrographs of the PEO/OER and PEO/PER blends of various composition (50% and 25% wt. fractions of PEO) after undercooling and isothermal crystallization are shown in Figs. 1–3. The PEO spherulites growing in the PEO/OER blends engulf the oligoester

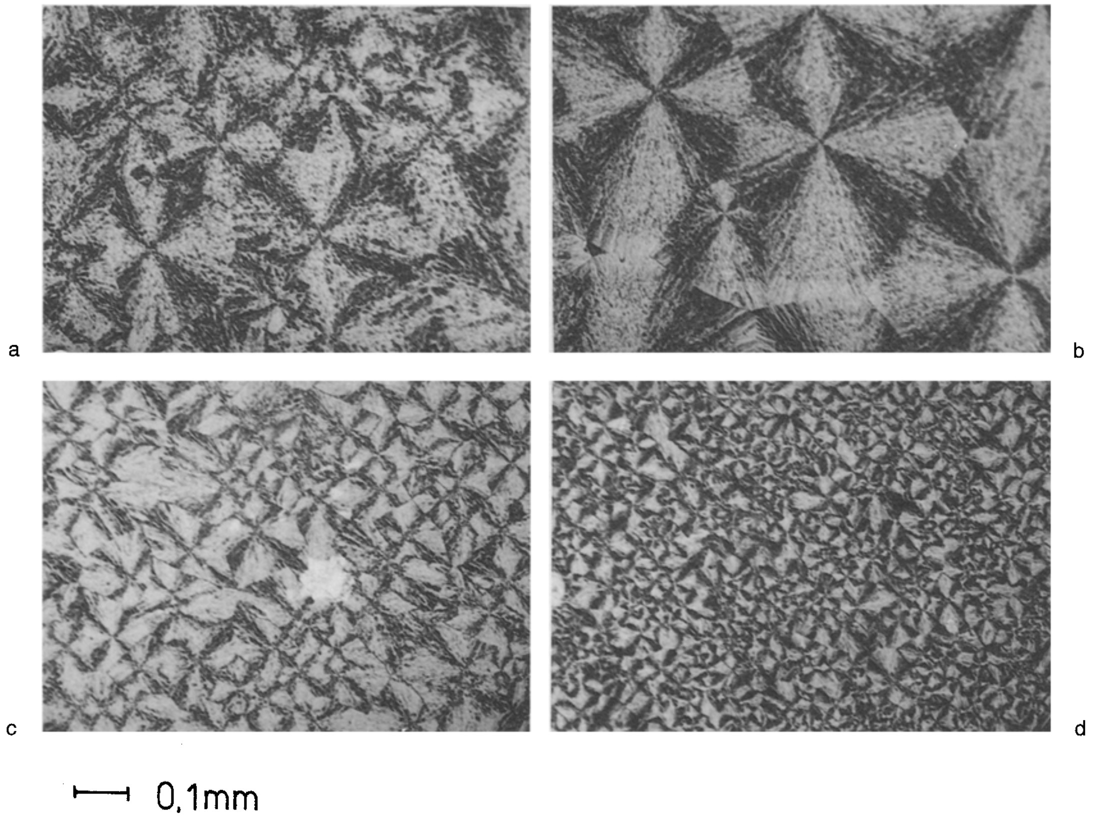

Fig. 1. Micrographs of morphological structure of PEO/OER blends containing 50% wt. fraction of PEO, crystallized at the temperatures: a) 48 °C, b) 43 °C, c) 34 °C, and d) 25 °C

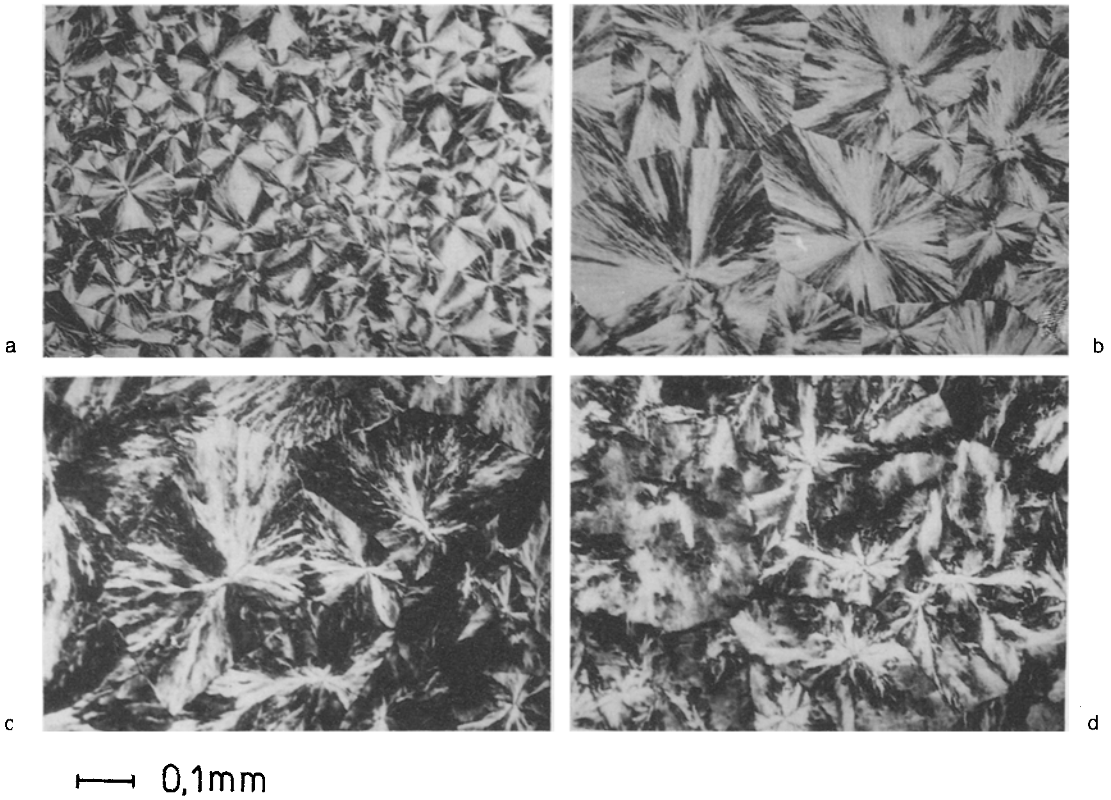

Fig. 2. Micrographs of morphological structure of PEO/PER blends containing 50% wt. fraction of PEO, crystallized at the temperatures: a) 43 °C, b) 37 °C, c) 31 °C, and d) 24 °C

inclusions. Thus, the radial orientation of lamellae within spherulites is disturbed by the presence of the oligoester inclusions (Fig. 1) which constitute some spatial obstacles for spherulite growth [9]. The crystalline lamellae of PEO are separated by amorphous regions which consist of the oligoester resin material containing insoluble uncrystallized PEO. In progressive crosslinking of polyester the initial, partial separation of the components occurs.

Thus, after the crystallization process a more regular shape of PEO spherulites is observed (Fig. 2). In that case, the PEO crystallization takes place outside the crosslinked polyester resin. The morphological structure of shape replica of molten spherulites in the polyester resin is still visible in Fig. 4. For oligoester blends with a low concentration of PEO (25% wt. fraction) the rate of crystallization is low but measurable. The crystallization of PEO in the polyester blend of low PEO concentration is observed only at a very slow cooling to room temperature and leads to various crystalline structures of PEO (Fig. 3). This is due to the fact that about 20% wt. fraction of PEO remains still dissolved and well dispersed in the crosslinked polyester. This fact is confirmed by DSC results.

The growth rate of spherulites versus temperature of pure PEO (curve 1) and of blended PEO (curve 2–50% wt. fraction of PEO in the oligoester and polyester, curve 3–25% wt. fraction of PEO in the oligoester) is presented in Fig. 5. The growth rates of PEO spherulites in the oligoester and polyester matrices are similar if PEO content is equal or higher than 50% wt. The crystallization of PEO in the solid polyester resin containing less than 40% wt. of PEO was not observed in the simple undercooling regime. Figure 6 shows the dependence of the spherulite growth rate of PEO on the oligoester blend composition. The result shows that the growth rate of spherulites decreases quickly reaching zero when the weight

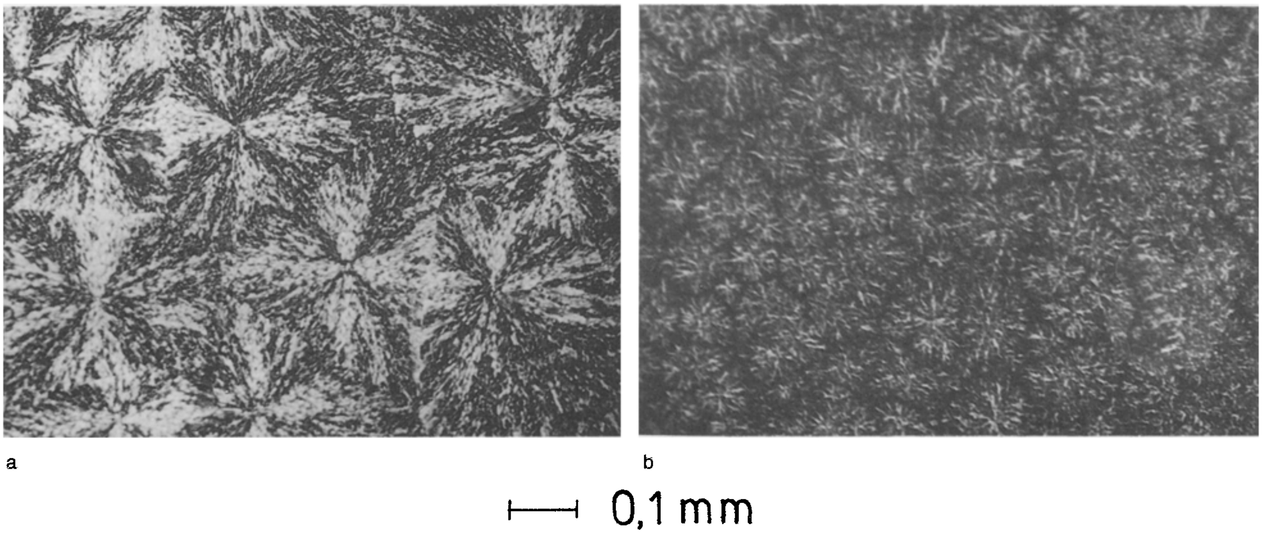

Fig. 3. Micrographs of morphological structure of PEO/OER (a) crystallized at 33 °C) and PEO/PER (b) crystallized by slow cooling to room temperature) blends containing 25% wt. fraction of PEO

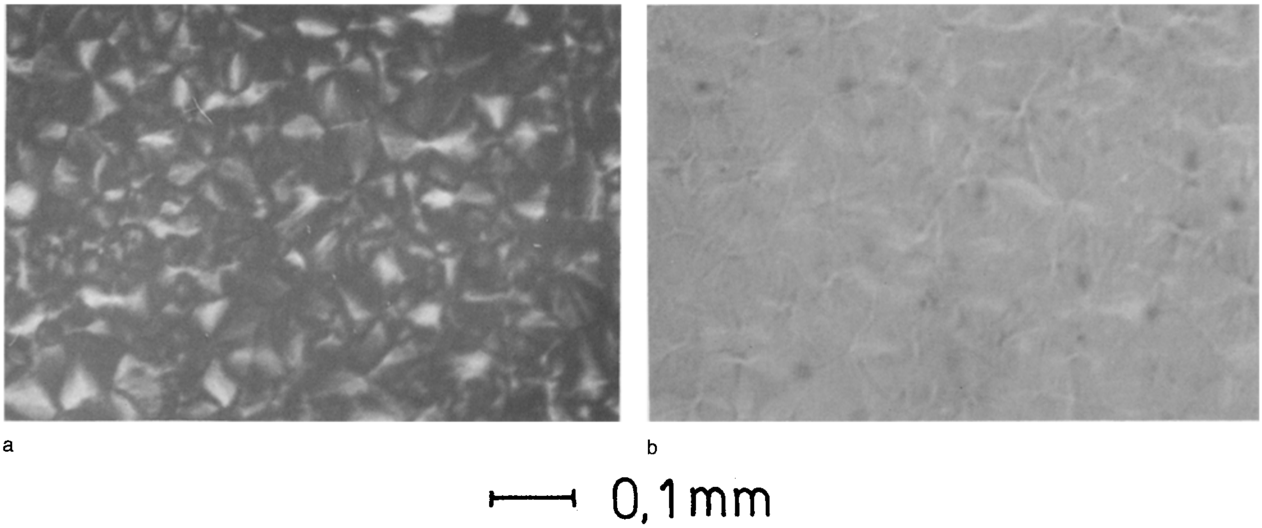

Fig. 4. Micrographs of morphological structure of PEO spherulites in the polyester resin (40% of PEO) a) in crystalline state, b) in molten state. Shape replica of the spherulites in the polyester matrix is visible

fraction of PEO in the oligoester is equal to 20% wt. It is due to some geometrical consideration for nucleation and crystallization of the well miscible components.

In order to find the effect of progressive crosslinking of polyester on the crystallization process of PEO the liquid blends were UV irradiated for various time. The resulting dependence of PEO spherulite radii on the crystallization time for the sample containing 40% wt. fraction of PEO is illustrated in Fig. 7. The PEO spherulite growth rate G (calculated from Fig. 7) drawn versus time of the matrix photopolymerization is presented in Fig. 8 which shows a fast decrease of the G value to zero. The matrix becomes almost completely solidified after 5 min of UV radiation.

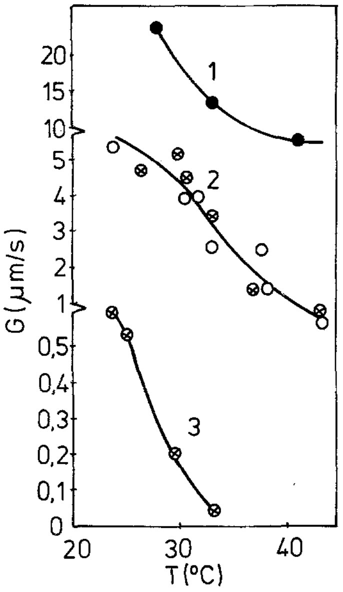

Fig. 5. Growth rate of PEO spherulites G as a function of temperature and weight fraction of PEO in blends: a) curve 1 – pure PEO, b) curve 2 – 50% wt fraction of PEO in polyester –○– and in oligoester –⊗–, c) curve 3 – 25% wt fraction of PEO in oligoester

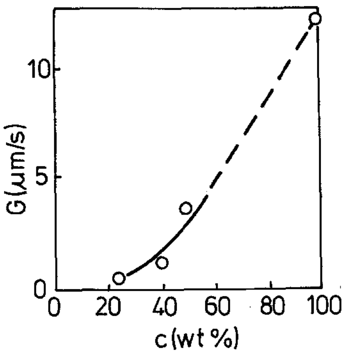

Fig. 6. Growth rate of PEO spherulites G at 33 °C as a function of weight fraction of PEO in blend with oligoester

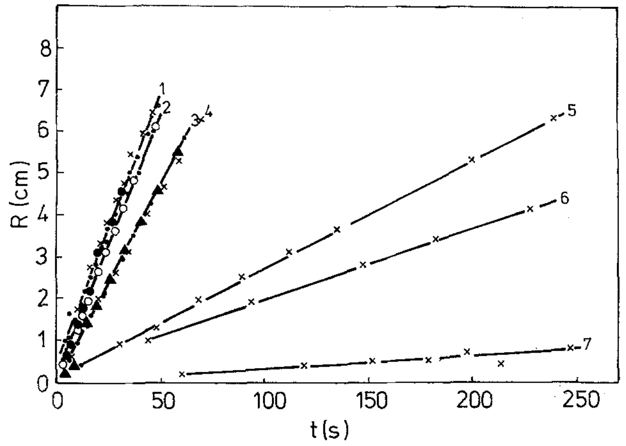

Fig. 7. Spherulite radius R (1 cm is equal to 15.6 μm) versus crystallization time at 33 °C (40% wt. fraction of PEO). Curves 1–7 are obtained for the following times of the matrix polymerization: 0, 1, 2.5, 3, and 5 min, respectively (Curves 2 and 4 are repeated measurements for 0 and 1 min)

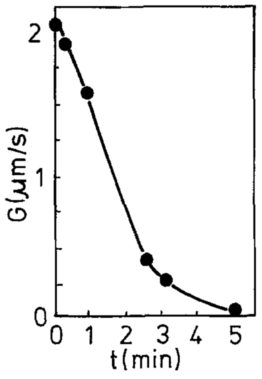

Fig. 8. Growth rate of PEO spherulites at 33 °C (40% wt. fraction of PEO) versus time of the matrix polymerization

Transition temperatures and degree of crystallinity

The blends were examined by DSC in order to obtain the melting temperature T_m, the heating of melting ΔH, and the glass transition temperature T_g of blended PEO. Some DSC thermograms obtained for two solid samples prepared in the above described way are shown in Fig. 9. The T_m and ΔH depression with an increasing polyester content shown in Fig. 10 is substantial. Both enthalpic and entropic effects contribute to the melting temperature drop in the blends due to the small molecular weight of the initial oligoester. Part of the oligoester material containing soluble PEO is probably still uncrosslinked and it is incorporated in the interlamellar regions of the PEO spherulites [2]. The observed melting temperature decrease is known as diluent effect of amorphous resin molecules on PEO crystals, and can be treated using a thermodynamic approach based on polymer–polymer mixing accompanied by an exothermic interaction between the two components. The range of the blend compositions under study was too narrow to allow for a quantitative calculation of the effect.

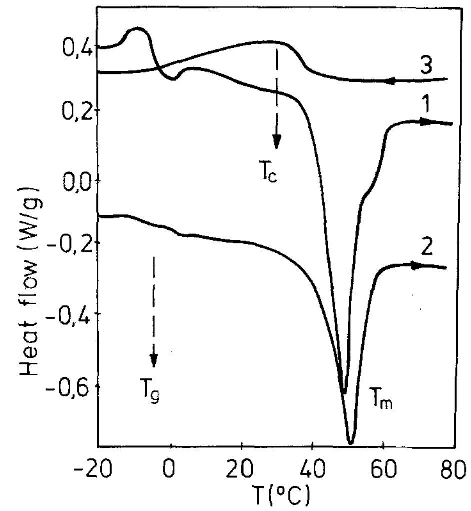

Fig. 9. DSC thermograms of the original (unprocessed) solid blends crystallized at 25 °C containing a) curve 1 – 60% wt. fraction of PEO, b) curve 2 – 40% wt. fraction of PEO, c) curve 3 – cooling curve of the second sample

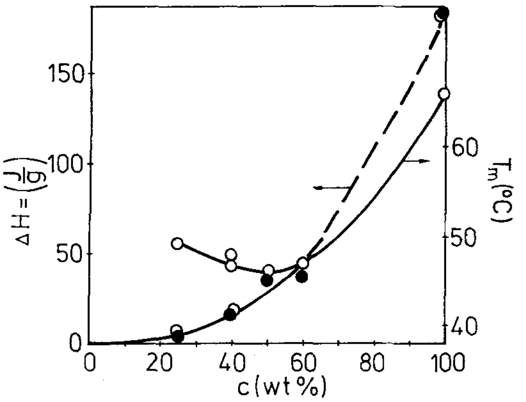

Fig. 10. Melting temperature T_m and heat of fusion ΔH of the original solid blends versus weight fraction of PEO in the polyester resin. $T_c = 25\,^\circ\mathrm{C}$

Heat of fusion ΔH of PEO (ΔH is proportional to overall blend crystallinity: $X_c(b) = \Delta H/\Delta H^0$, ΔH^0 – heat of fusion of 100% crystalline PEO) and T_m versus time of the polyester solidification taken for various blend compositions are drawn in Fig. 11.

Both ΔH and T_m decrease with the progressive crosslinking of the polyester which results from some geometrical aspects due to crystal nucleation and growth activity in the crosslinking matrix, leading to smaller and less perfect lamellar crystal of PEO of lower T_m.

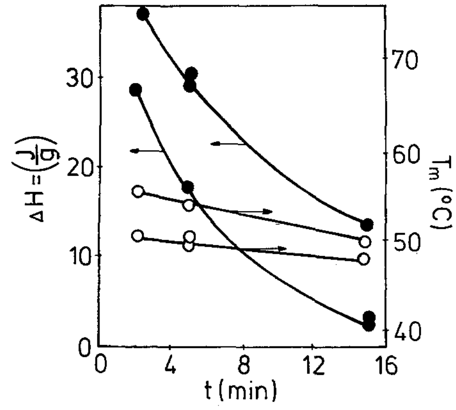

Fig. 11. Melting temperature T_m and heat of fusion ΔH versus time of matrix photopolymerization. Lower curves-original samples were crystallized at $T_c = 25\,^\circ\mathrm{C}$, upper curves-original samples were crystallized at $T_c = 33\,^\circ\mathrm{C}$

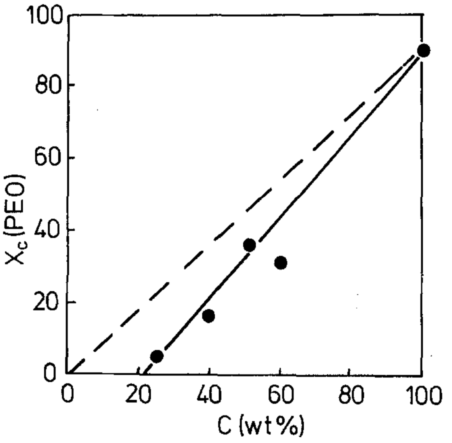

Fig. 12. Crystallinity degree of PEO X_c(PEO) versus weight fraction of PEO in the original blend with polyester. $T_c = 25\,^\circ\mathrm{C}$

The crystallinity degree X_c(PEO) of the PEO phase in the blends, as shown in Figs. 12 and 13, decreases with lowering of PEO content and with progressing of the blend solidification. The X_c(PEO) was calculated from Eq. (1):

$$X_c(\mathrm{PEO}) = \Delta H^*(\mathrm{PEO})/\Delta H^0(\mathrm{PEO})\,, \qquad (1)$$

where $\Delta H^0(\mathrm{PEO}) = 207$ J/g is the heat of fusion 100% of crystalline PEO [10], and $\Delta H^*(\mathrm{PEO})$ is the heat of fusion per gram of PEO in the blend. The smaller the content of PEO in the blend the lower the observed crystallinity degree of PEO.

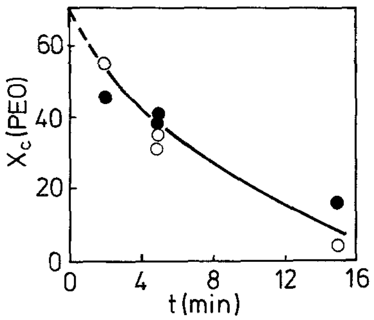

Fig. 13. Crystallinity degree of PEO X_c(PEO) versus time of the polyester matrix polymerization for the blends containing: -○- 25% and -●- 40% wt fraction of PEO

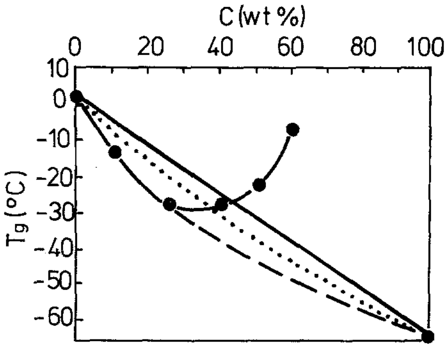

Fig. 14. Glass transition temperature T_g or original blends versus weight fraction of PEO: -●- experimental curve, --- linear dependence, ···· Fox equation

This is due to the fact that about 20% wt. fraction of PEO is dissolved in the resin and it does not crystallize in the experimental conditions. With the progress of the resin crosslinking, the crystallinity degree of PEO drops, reaching the value of about 10% at the end of the curing process. This means that almost all PEO stays dispersed in the crosslinked matrix. Thus, the nucleation activity, the efficiency of molecular migration, and the progress of crystallization vanish.

Figure 14 presents the glass transition temperature which varies with the overall blend composition as indicated by points. The single glass transition up to 25% wt. of PEO suggests that the blend presents a homogeneous amorphous phase, i.e., the two components are miscible in the amorphous phase. Some increase of the T_g values for higher PEO content results from decreasing of PEO content in the amorphous phase due to an initial separation of the components by crosslinking of resin and PEO crystallization. The T_g of pure PEO was taken from the literature [6]. The Fox equation (2) was used for the T_g composition dependence of miscible blends:

$$1/T_g = (1 - C)/T_{g1} + C/T_{g2} \tag{2}$$

where: T_g = glass transition temperature of the miscible blends,
T_{g1} = glass transition temperature of the polyester resin (2 °C),
T_{g2} = glass transition temperature of PEO (− 62 °C), and
C = weight fraction of PEO

The Fox equation, as shown in Fig. 14, does not fit the experimental data well in the miscible range up to 25% wt. fraction of PEO. The experimental T_g dependence on the composition is more pronounced due to the presence of the abovementioned exothermic interactions of both components coexisting in the amorphous phase of the PEO/PER blends.

Concluding remarks

The PEO is partially miscible with oligoester and crosslinked polyester resin. By undercooling to the crystallization temperature the PEO crystallizes in the blends forming spherulites of various morphological structures. The PEO spherulites growing in the blends with oligoester engulf the resin inclusions. In solid polyester the PEO spherulites grow outside the solid matrix as a result of the initial partial separation of PEO from crosslinked resin during photopolymerization. Some of the PEO material (~ 20%) is still soluble and well dispersed in polyester and it is incorporated between the crystalline lamellae of PEO. This leads to a decrease of the T_m and X_c(PEO) of PEO in the blends.

The spherulite growth rate and X_c(PEO) in the blends depend both on the blend composition and on the degree of crosslinking of the polyester resin. The melting temperature drop of PEO and strong change of T_g observed in the study may be described by the diluent effect of the amorphous resin molecules accompanied by exothermic interactions between the two components coexisting in the amorphous phase of the blends.

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