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Miscibility of poly(ethylene terephthalate-co-diethylene glycol terephthalate)/poly(ethylene oxide) blends

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The miscibility behaviour of melt-mixed poly(ethylene terephthalate-co-diethylene glycol terephthalate) [PET-co-DEGT] with poly(ethylene oxide) was investigated in all composition ranges. The crystallization of the semicrystalline blend component at different compositions was evaluated by optical microscopy with crossed polarizers. Thermal analysis (d.s.c., t.g.a. and DMA) indicate that the system is miscible in the composition of some components, and partially miscible in other ranges of composition. For PET-co-DEGT/PEO mixtures there was a reduction in the fusion enthalpy of the semicrystalline component, showing favourable interactions between these polymers, with some influence on the PEO crystallization. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: miscibility; blends; poly (ethylene oxide))

INTRODUCTION

Polymer blends containing engineering polymers represent an important route for the development of new polymeric materials with good efficacy. Different blends of commercial polymer pairs have been reported in the literature in the last decades and may exhibit a miscible or partially miscible phase within a concentration range[1]. Physical homogeneous mixtures can occur due to different kinds of intermolecular forces that can provide a favourable energetic contribution to the mixing process. Some examples of miscible blends are poly(ethylene oxide) and amorphous novolak or poly(vinyl phenol) mixture (indicating hydrogen bonding between the hydroxyl groups of novolak or poly(vinyl phenol) and the ether oxygens of poly(ethylene oxide))[2], poly(4-vinyl pyridine) with zinc acetate[3], 1,2-polybutadiene with 3,4-polyisoprene in presence of inorganic salt[4], poly(ethyl acrylate-co-vinylpyridine) with zinc-neutralized sulfonated poly(ethylene terephthalate)[5].

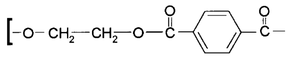
The poly(ethylene terephthalate) (PET) is a very important thermoplastic that has been studied as a component of various polymers and forms an important class of recyclable plastics[6–9], which, when manufactured by the esterification of terephthalic acid with ethylene glycol, and depending upon the exact conditions, can lead to the formation of a significant quantity of diethylene glycol units in the monomeric unit.

PEO has been shown to have protein-repelling activity. Lee *et al.*[10] have attempted to produce a biocompatible or a cell-non-adhesive surface using polyethylene glycol (PEG) or poly(ethylene oxide) (PEO) as a surface modifier. PEO appears to be an effective polymer for protein-resistant surface, probably due to its low interfacial free energy with water, unique solution properties and molecular conformation in aqueous solution, hydrophilicity, high surface mobility and steric stabilization effects. There has been much effort in minimizing or eliminating protein adsorption, because surfaces which show minimal protein adsorption are important in many applications, including blood-contact devices, membranes for separation processes, sensors, chromatographic supports, contact lenses, immunoassays, blood and protein storage applications, etc. Desai and Hubbell studied PET substrates modified by a surface physical interpenetrating network (SPIN) technique with PEO[11,12], where the biocompatibility of these materials was evaluated.

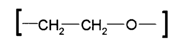
In the present work, the miscibility of PET-co-DEGT and PEO blends is examined in the complete composition range through physical mixtures of the melted polymers. These blends can result in material with different micro- and macroscopic properties which are different from the pure components. A further study in animal response to implant *in vivo* in the mouse peritoneal cavity will later be reported on.

EXPERIMENTAL

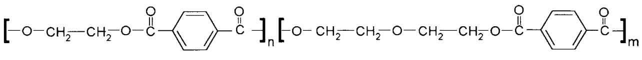
Poly(ethylene oxide) (PEO) and semicrystalline poly(ethylene terephthalate) (PET), were supplied by the Aldrich Chemical Company, with number-average molecular weights of 200 000 and 11 130 g/mol, respectively. Poly(ethylene terephthalate) with diethylene glycol units in polymer chain (PET-co-DEGT) was supplied by the Kodak Co. The polymer units are shown as follows, and these samples were used as received without any additional purification.



PET



PEO



PET-co-DEGT

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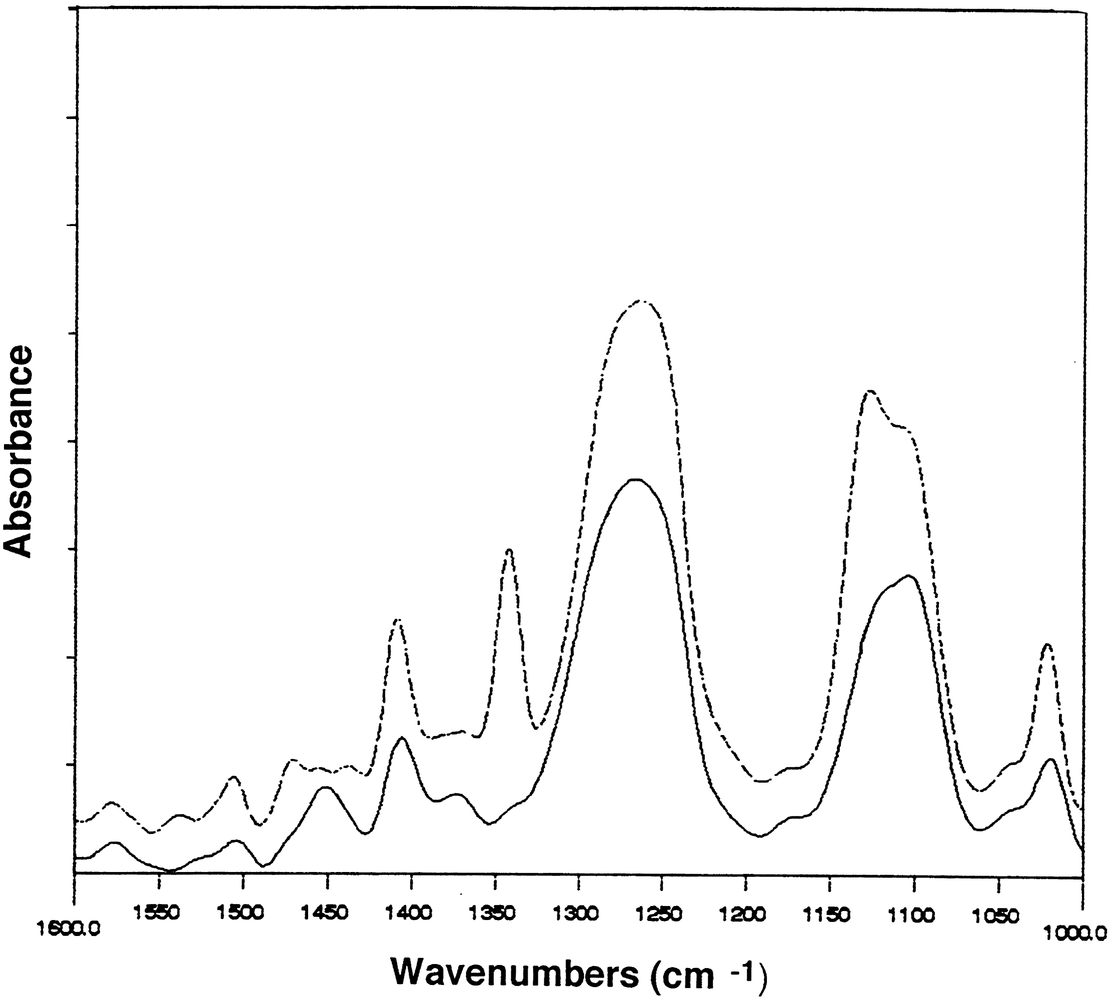

Figure 1 FT-i.r. spectra of undiluted semicrystalline PET (——) and amorphous PET-co-DEGT (– – –)

PET-co-DEGT average molecular weight of 56 640 g/mol was determined by viscosimetric measurement in *o*-chlorophenol at 25°C, with *K* and *a* Mark–Houwink's parameters equal to 6.56×10^4 dl/g and 0.73, respectively[13]. The percentage of diethylene glycol units in the copolymer was determined by n.m.r. The PET and PET-co-DEGT were dissolved in chloroform-d/hexafluorisopropanol at 95:5 wt.%, and the integration peaks at 8.09 ppm (4H phenyl), 4.69 ppm ($-OCH_2$), 4.04 ppm ($-OOCH_2$) of the n.m.r. spectrum show 37% of diethylene glycol.

The *FT*i.r. spectra were recorded on a Perkin-Elmer, Model 16 PC *FT*i.r. spectrometer with a minimum of six scans, and was signal-averaged at a resolution of 4 cm^{-1}.

To obtain the PET-co-DEGT/PEO blends: (i) pure PET-co-DEG was heated at 240°C; (ii) PEO was added slowly with thorough mixing; and (iii) finally, the mixture was pressed at 240°C and allowed to cool to room temperature.

Thermal analysis was carried out on a Shimadzu 50 differential scanning calorimeter (d.s.c.) and thermal gravimetric analyser (t.g.a.). Firstly, the samples were heated under nitrogen purges from room temperature to 300°C at 10°C/min. The samples were then quenched to room temperature and the heating process was repeated (second run) at the same rate from approximately 50°C under the glass transition temperature of rich-component in the mixture. The glass transition temperature was calculated at the midpoint of the heat capacity change between the rubbery and glassy states, without complicating effects due to enthalpy relaxation. The indium standard was used as a reference. Pure polymers and their blends are thermically stable under the temperature range used in d.s.c. analysis, considering that the degradation temperatures of pure PET-co-DEGT and PEO were 450 and 420°C, respectively.

Dynamic mechanical analysis, using a Perkin-Elmer DMA 7 with a parallel plate fixture, under isothermal conditions at 30°C, was used for all DMA measurements.

The morphology was studied by crossed polarizer microscopy using a Carl Zeiss-Jena Optical Microscope.

RESULTS AND DISCUSSION

Turi *et al.*[14] studied the influence of diethylene glycol (DEG) units in the PET polymer chain, with increased chain flexibility as a result of a higher aliphatic content and/or ether linkages that inhibit crystallizability arising from the structural irregularities. They related the intrinsic viscosity value of 0.83 to 1.00 dl/g with DEG levels ranging from 1.6 to 8.4%. The intrinsic viscosity of PET-co-DEGT used in this work is equal to 1.92 dl/g. This value is due to the high quantity of DEG in the copolymer chain. *Figure 1* shows the *FT*i.r. spectrum of PET-co-DEGT and the semicrystalline PET. The *FT*i.r. spectrum of semicrystalline PET shows a band at 1340 cm^{-1}, indicating a *trans* configuration of the ethylene glycol fragment. This configuration is also consistent with X-ray data which indicated a planar structure for PET[15]. This band is not observed in the

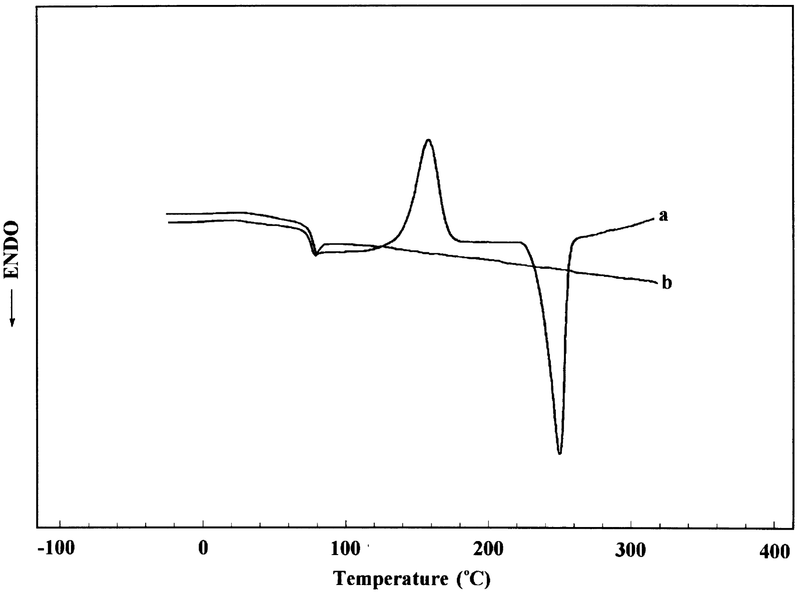

Figure 2 Representative d.s.c. thermograms of (*a*) undiluted semicrystalline PET and (*b*) amorphous PET-co-DEGT

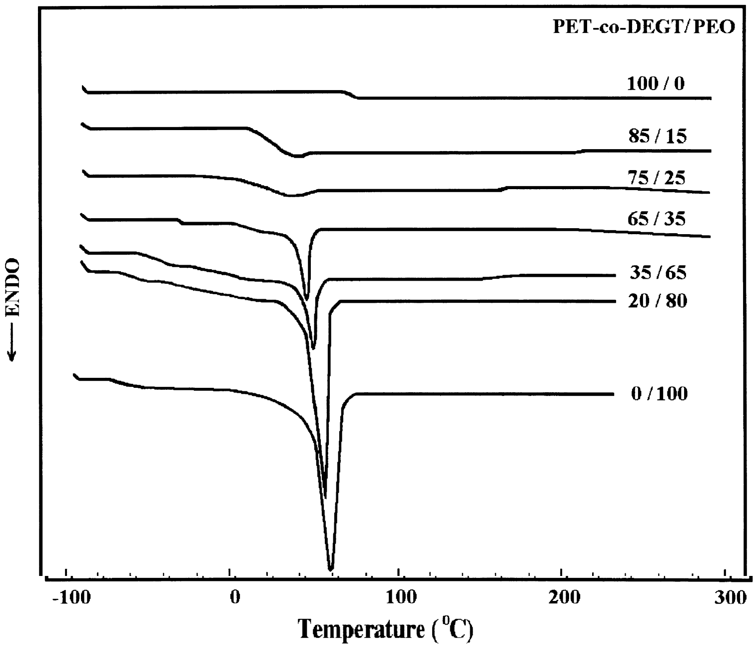

Figure 3 D.s.c. thermograms at a heating rate of 10°C min^{-1}, illustrating melting peak for PEO and glass transition temperature in the PET-co-DEGT/PEO blends of different compositions as indicated by the ratio

Table 1 Enthalpic heat of semicrystalline component and melting temperature (T_m) and glass transition temperatue (T_g) of binary mixture

PET-co-DEGT (%)	T_g (°C)	T_m (°C)	$\Delta H_{\mathrm{blend}}$ (J g^{-1})	$\Delta H_{\mathrm{blend}}/\Delta H_{\mathrm{PEO}}$
100	78			
95	66			
90	56			
85	46			
80	37			
75	27			
65	10 and -9	55	40	0.38
50	-3 and -45	55	66	0.62
35	-7 and -27	56	81	0.77
20	-50	57	90	0.85
10	-60	59	93	0.88
0	-70	60	106	1.00

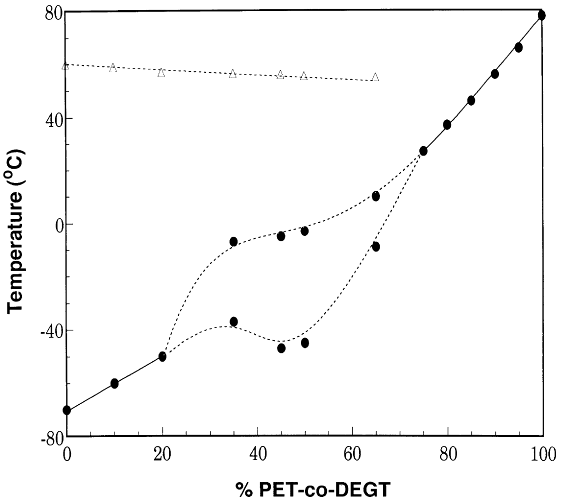

Figure 4 Concentration dependences of the melting (△) and single glass (●) transition temperatures during the d.s.c. heating trace

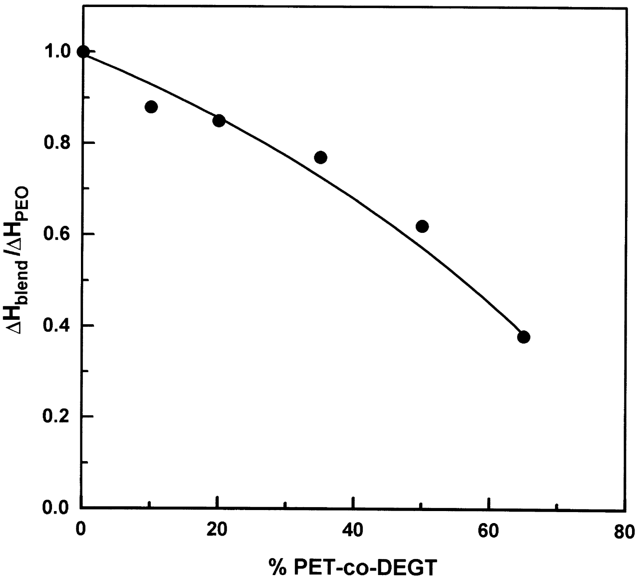

Figure 5 Ratio of enthalpic heat variation of pure PEO and the calculated value corresponding to PEO in the blend *versus* PET-co-DEGT percentage in the blend

PET-co-DEGT, which, due to its amorphous state, has a *gauche* configuration and a loss of planarity[16,17]. The FT-i.r. spectrum of PET-co-DEGT shows amorphous phase predominance and it is in agreement with d.s.c. thermograms of PET and PET-co-DEGT, shown in *Figure 2*. The glass transition temperature value is the same to semi-crystalline PET and amorphous PET-co-DEGT.

D.s.c. curves (second run) of undiluted components and PET-co-DEGT/PEO mixtures at different compositions are shown in *Figure 3*. From each thermogram we can determine the melting temperature (T_m) and glass transition temperature (T_g), as shown in *Table 1*, and they are represented graphically as temperature *versus* PET-co-DEGT weight percentage in the binary mixture with PEO (*Figure 4*). Semicrystalline PEO samples exhibit both transition temperatures, but amorphous PET-co-DEGT shows only T_g, which agrees with our discussion above. The melting temperature of PEO decreases around 10°C in the range of the component's composition studied. To evaluate the amorphous component's influence on the mixture, the enthalpic heat of the semicrystalline component was calculated from the d.s.c. thermogram through the corresponding PEO value in the mixture. The ratio of enthalpic heat of the undiluted semicrystalline component and this component in the mixture as a function of percentage of PET-co-DEGT is shown in *Figure 5*. This ratio, which is different from unity, might indicate the influence of the amorphous component, showing the formation of a miscible mixture. Likewise, the influence of the shift in glass transition temperature of the blending components at different component compositions agrees with what has already been discussed. Blends with PET-co-DEGT weight percentages less than 20% and more than 75% show only one T_g, indicating miscibility which is probably due to interaction or dispersion of one component in the other. In the range between 20 and 75% of weight percentage of PET-co-DEGT we observe two glass transition temperatures, different to the pure components. This behaviour must be due to a rich phase of PEO or PET-co-DEGT in the blend. Similar behaviour was observed in the syndiotactic poly(methylmethacrylate)/(vinyl chloride) system, which shows a single T_g when the PVC content is 40 wt.% or more, and two T_g values for blends containing less than 40 wt% PVC[18].

The PEO semicrystalline structure can be evaluated by polarizing microscopy between two cover-slips at low magnification. *Figure 6* shows a photomicrograph of pure PEO and blends with 10, 20 and 100% (w/w) of PET-co-DEGT, melted at 250°C and crystallized at room temperature. The photomicrograph reveals a characteristic feature of spherulitic structure with a formation of fibrous sub-units that extend radially outward from the central nucleus. In blends with PET-co-DEGT/PEO above 35% we did not observe spherulitic form. It appears that the small favourable interactions between these polymers frustrates the crystallization of PEO.

Richards and co-workers[19] have discussed the influence of a second polymer on the crystalline component in a mixture of the two polymers. There is no general rule by which one can predict the influence of miscibility on crystallinity, and the extent of crystallinity may be either increased or decreased. These modifications in the crystallization behaviour of PEO and the nucleation may be attributed to changes in the interfacial area between the polymer's components. It is postulated that the PET phase enhances the nucleation process of PEO. When PET is the dispersed phase, the interfacial area is greater than the continuous phase morphology for a blend composition of 50:50 wt.%. Thus, it could be concluded that when the second component is present as a dispersed phase, its size and shape affect the crystallization of the polymer matrix. Although morphological effects also may influence the decrease in melting point, this indicates PET-co-DEG/PEO miscibility. Such a fact is generally attributed to the thermodynamic interactions between the components[20,21].

Mechanical properties of blends with PET-co-DEGT contents equal to or higher than 75%, where the previous results indicated miscibility, were analysed by DMA. This technique has been widely used to measure the structural and intrinsic property changes in different materials[22]. The Young's (E) and compression moduli (G) are obtained from the stress–strain curve, indicating the upper limit of usefulness for different blend compositions. *Figure 7* shows Young's modulus for PET-co-DEGT/PEO composition between 100/0 and 75/25 wt.%. With the addition of a

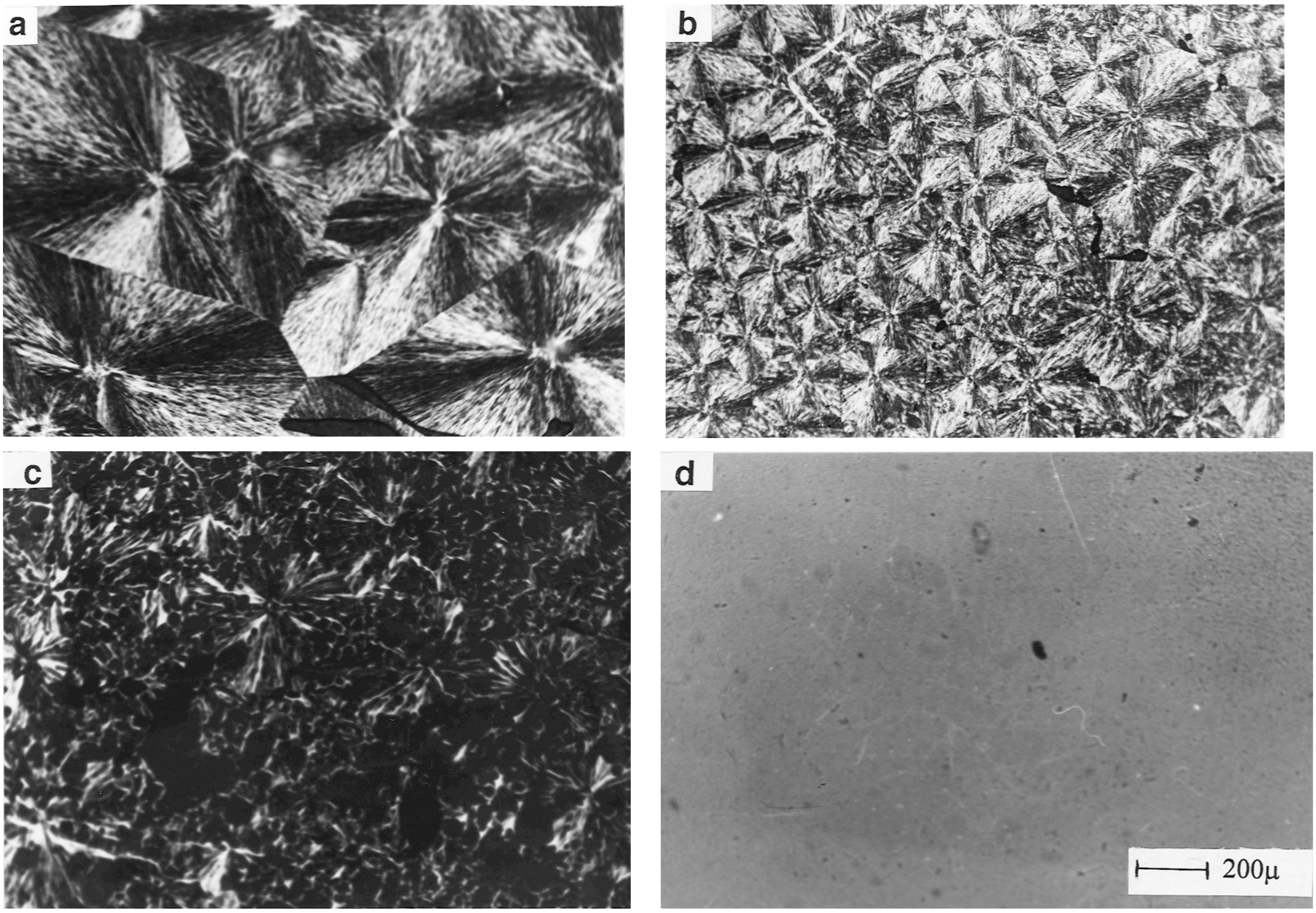

Figure 6 Optical polarized photomicrographs of PEO/PET-co-DEGT at (a) 100/0; (b) 90/10; (c) 80/20 and (d) 0/100 (w/w)

semi-crystalline component into the PET-co-DEGT matrix, Young's modulus increases up to 2.2 MPa when the PEO content is elevated by 25%. Pure PET-co-DEGT (amorphous) and PET (semi-crystalline) have E values equal to 0.54 and 7.16 MPa, respectively. Perhaps the semi-crystalline component is the load-carrying region, and the main role of the matrix is to transmit the load to that region, to protect its surface and to raise the energy for crack propagation. The strength of the PET-co-DEGT/PEO blend depends on the nature and strength of the bond between the semi-crystalline and amorphous polymer. The compression modulus (G) also decreases with the increase of the PET-co-DEGT percentage in the blend, as shown in *Figure 8*. In the region above 60%, the G values are lower than 1.2 MPa, which is in agreement with the corresponding value of amorphous phase reported in the literature[23]. These results also indicate that the material rigidity of the PEO/PET-co-DEGT mixture is decreased.

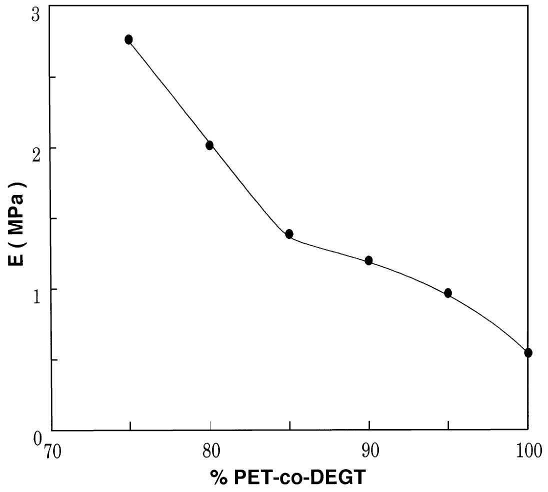

Figure 7 Young's modulus (E) at different PEO/PET-co-DEGT blend compositions

CONCLUSIONS

The results reported in this work indicate that the PET-co-DEGT (amorphous) and PEO (semicrystalline) system is miscible in some component compositions and partially miscible in other ranges of composition blends. The presence of the amorphous component hinders the nucleation and growth of crystal, suggesting interactions between the two blend components. The practical application of these blends in the biomedical area has been studied in our laboratory by implant in vivo, for different periods of time, into the mouse peritoneal cavity, in an attempt to evaluate the rejection by the living tissue.

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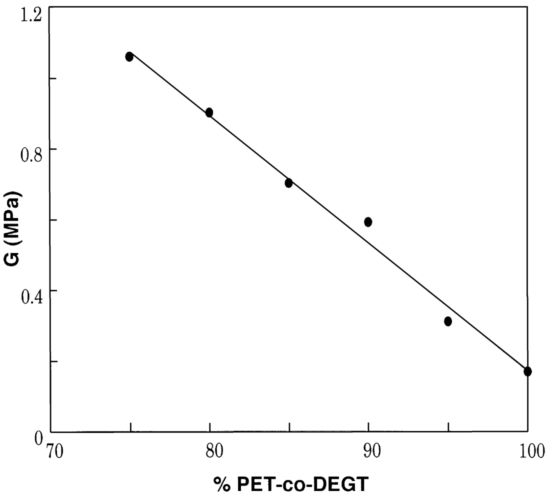

Figure 8 Compression modulus (*G*) at different PEO/PET-co-DEGT blend compositions

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