Blends of poly(ethylene oxide) samples of different molecular weights: thermal and mechanical properties

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(Received 27 February 1978; revised 17 April 1978)

Differential scanning calorimetry and mechanical measurements have been performed on binary poly(ethylene oxide) blends of different molecular weight samples. Some thermodynamic and mechanical properties, such as the melting point and the ultimate stress and strain are strongly affected by blend composition. The enthalpy of fusion and the Young's modulus, however, vary only slightly over the entire range of composition. Also the time for dissolution in water, at two different temperatures, has been measured on blends made from the lowest and the highest molecular weight components.

The results indicate that by blending two different molecular weight samples, even of the same polymer, it is possible to influence the physical properties of the relative blends, so obtaining improvements of technological importance.

INTRODUCTION

Poly(ethylene oxide) (PEO) is a water soluble polymer with relatively good mechanical properties and it is used as a drag reducing agent, in seed tape systems to mechanize sowing and harvesting, as a suppository support, and as capsules for medicinal powders or granules which can be orally ingested.

In a previous paper[1] the influence of molecular weight on the isothermal kinetics of crystallization of monodisperse fractions of PEO, has been reported. More recently, the effect of blend composition on the isothermal crystallization kinetics of PEO blends of components having different molecular weights has been studied[2]. Furthermore a comparison of melt viscosity behaviour with thermal melting features has been made on monodisperse fractions and their blends[3].

In the present work, we have studied the thermal and tensile properties, and the dissolution behaviour in water of the same blends examined in the first paper[2] of the present series.

EXPERIMENTAL

Materials

Two poly(ethylene oxide) (PEO) fractions, PEO 2 (M = 2000) and PEO 20 (M = 20 000) produced by Fluka AG and a commercial sample PEO 200 (M_w = 197 000) provided by Sorin, Italy and produced by Union Carbide, USA, were used to prepare three blends: PEO 2–PEO 20, PEO 2–PEO 200, and PEO 20–PEO 200.

Blend and sample preparation

Two different techniques were used to prepare samples for d.s.c. and for the mechanical measurements, respectively. In the first case, as described in detail elsewhere[2], the two components in the desired proportions were dissolved in chloroform. The solvent was then evaporated and a thin film was obtained on a glass plate. The film was detached, dried *in vacuo*, weighed and sealed in a d.s.c. aluminium pan. In the second case (mechanical measurements) the two components were dissolved in chloroform as before; then a non-solvent (petroleum ether) was added to the solution to precipitate the blend. The filtered solid was left for 24 h under vacuum to remove any residual solvent. The material so obtained was then compression moulded in a water-cooled press to form 3 mm thick slabs, according to the following procedure. The press plates were first heated to a temperature (120°C) higher than the PEO melting point (70°C) and the mould was introduced between them. After 2 min a pressure of about 100 kg/cm^2 was applied to the press to eliminate air bubbles from the melted material; 3 min later the press was water cooled down to room temperature within about 4 min. Dumb-bell-shaped samples were cut from the slabs by means of a hollow punch.

Methods

The melting point, T_m, and the apparent enthalpy of fusion/g, ΔH_F^*, were determined by differential scanning calorimetry (d.s.c.) using a Perkin–Elmer DSC-1B instrument. The melting point of the blends was determined from the position of the maximum of the peak along the temperature scan. The calibrations of the temperature scale and of melting area peak were made with standards of known melting point and enthalpy of fusion. The standards used in the present work were: azobenzene (T_m = 68°C), benzil (T_m = 95°C) and indium (T_m = 156.3°C).

All the measurements were made at a scanning rate of 16°C/min and at a range sensitivity of 16 mcal/sec. The

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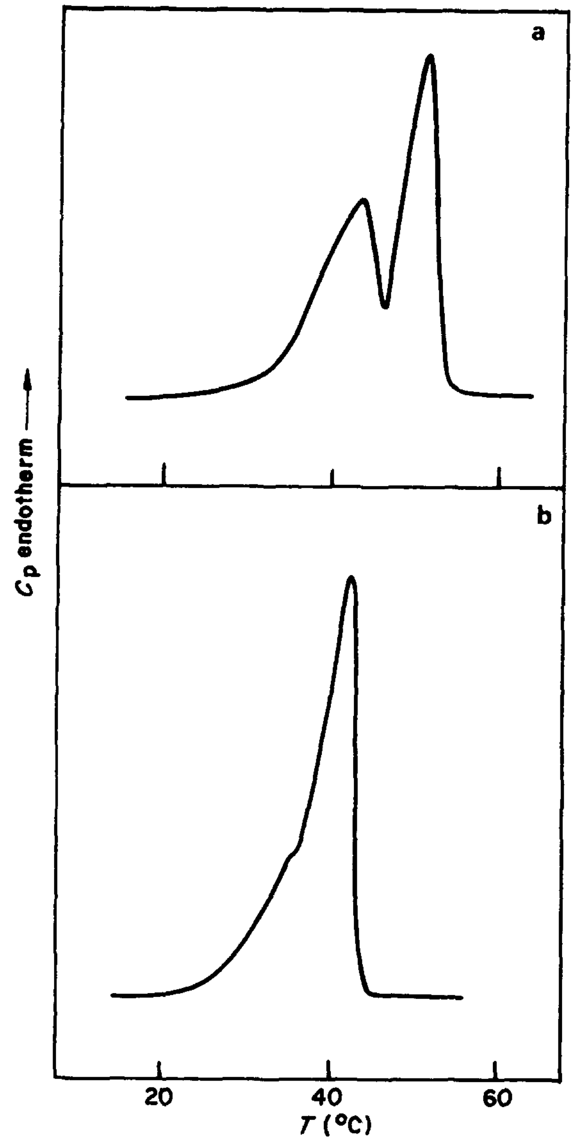

Figure 1 Typical scan thermogram for a PEO 2–PEO 200 blend: (a) first run; (b) second run

amount of material used in each run ranged from 5.0 to 9.0 mg.

The sample was heated in the first cycle up to a temperature of 87°C and kept at this temperature for 3 min to erase any previous thermal or mechanical history and then crystallized at room temperature for 10 min. At this point a second heating cycle was started to determine thermal parameters.

An Instron machine (Table model 1122) was used for tensile measurements at room temperature and at a crosshead speed of 2 cm/min for all the samples, except for PEO 2–PEO 20 blend samples which were too brittle to handle.

The Young's modulus, the yield point, the tensile strength and the elongation at break were determined for these samples. Measurements were also made of the time necessary to dissolve strip samples of PEO 2–PEO 200 blends in water.

The strips, all of the same dimensions, were cut from the compression moulded slabs described above. The comparative tests were made at two different temperatures, 30° and 85°C, by immersing 0.5 g sample in water, stirring gently and measuring the time taken for its complete disappearance.

RESULTS AND DISCUSSION

Differential scanning calorimetry (d.s.c.)

All the d.s.c. thermograms of PEO 2–PEO 20 and PEO 20–PEO 200 blends show a single peak in the first as well as in the second heating cycle, whereas those obtained for the PEO 2–PEO 200 blends show two peaks during the first run and one peak, with a small shoulder, in the second run (*Figure 1*).

The two peaks can be attributed to a segregation effect which occurs during the casting of the film. Such an effect is detectable only in the case of PEO 2–PEO 200 blends in which the molecular weight difference between the two components is much greater than in the other cases. The segregation behaviour is further enhanced by the fact that the PEO 2 fractions tend to crystallize in the form of extended chains differently from PEO 200 samples which crystallize as folded chains[4]. The ratio of the area of the first endothermic peak to the area of the entire fusion endotherm (*Figure 1a*) as a function of PEO 200 content, is reported in *Figure 2*. The full straight line with negative slope represents the behaviour expected when complete segregation occurs over the entire range of composition, since both the fractions have about the same heat of fusion (*Figure 3*). The apparent enthalpy of fusion ΔH_F^*, related directly to the crystallinity content of the blend, is nearly constant over the entire range of composition for the PEO 2–PEO 20 blends, as shown in *Figure 3*. For the two other blends, PEO 2–PEO 200 and PEO 20–PEO 200, it remains constant up to about 40% PE 200 content and then decreases slightly with increasing PEO 200 content. The consequent decrease in crystallinity is probably due to the reduction of chain mobility of bulk material with increasing amount of PEO 200. The melting points T_m as a function of the higher molecular weight component of the blend are reported in *Figure 4* for all the blends. The PEO 20–PEO 200 blends show a slight linear increase with

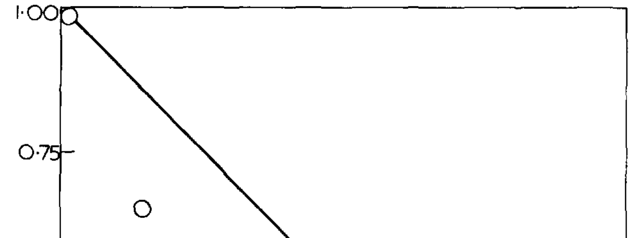

Figure 2 Ratio of the area of the lower temperature peak to the total area given in *Figure 1a* as a function of % PEO 200 content, for PEO 2–PEO 200 blends. ——, Represents complete segregation behaviour over the entire range of composition

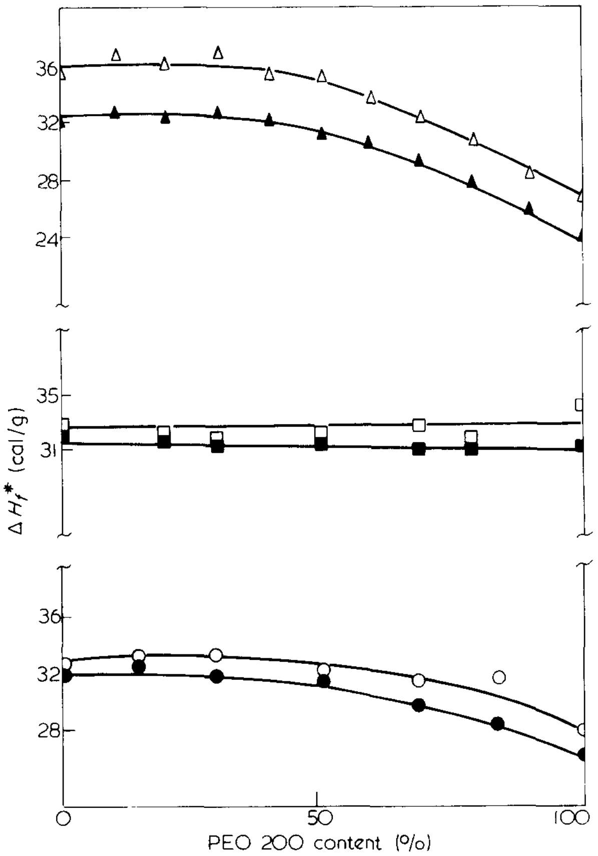

Figure 3 Apparent fusion enthalpy, ΔH_F^* as a function of the higher molecular weight component for the blends. PEO 20–PEO 200 (△, ▲); PEO 2–PEO 20 (□, ■); PEO 2–PEO 200 (○, ●), △, □, ○ and ▲, ■, ● refer to the first and to the second run respectively

increasing PEO 200 content. A monotonic increase is also observed for the PEO 2–PEO 20 blend with increasing PEO 20 content. The thermograms of the PEO 2–PEO 200 blends in the first run typically show two melting peaks, as shown in *Figure 1*. The lower melting temperature peak (ó) is almost independent of composition, whereas the higher melting temperature peak (ó) shows the same monotonic trend as the single peak observed in the second run (●) Such behaviour confirms the PEO 2 segregation during casting and the consequent formation of two distinct crystalline phases. Between the first and the second run the material is melted and the two components are mixed, forming a unique solid phase.

The second run melting point is almost coincident with the higher melting peak temperature obtained in the first run and decreases monotonically with increasing PEO 2 content. This is in agreement with the incomplete segregation observed at increasing concentration of PEO 2 as shown in *Figure 2*. Therefore an increasing fraction of PEO 2 molecules enters the PEO 200 crystals, lowering their thermodynamic stability.

Mechanical properties

Typical stress–strain curves of the PEO 2–PEO 200 blends for different PEO 200 concentrations are reported in *Figure 5*. Such curves show a strong dependence of mechanical response on the blend composition. The behaviour goes, indeed, from a polyolefin-like trend with necking formation for pure PEO 200 (curve A) to brittle behaviour for the 30% PEO 200 content blend. It was not possible to test at lower concentrations because of the excessive brittleness of the samples.

For a more quantitative analysis the Young's modulus, E, the yield stress σ_y, the yield strain, ϵ_y, the strength, σ_u, and the elongation at break, ϵ_u, are reported in *Table 1*. The Young's modulus is very slightly dependent on composition, whereas σ_y and ϵ_y show a maximum for a 70% PEO 200 content blend. Furthermore from the visual observation of the sample during the test it was noticed that PEO 200 blends with concentrations higher than 70% PEO 200 underwent necking formation. At a lower PEO 200 content, ranging from 50 to 70%, the necking stopped and the sample whitened uniformly. At a PEO 200 concentration lower than 50% the samples underwent brittle fracture (see *Figure 5*, curve D). Such behaviour can be explained as being due to a reinforcing effect of

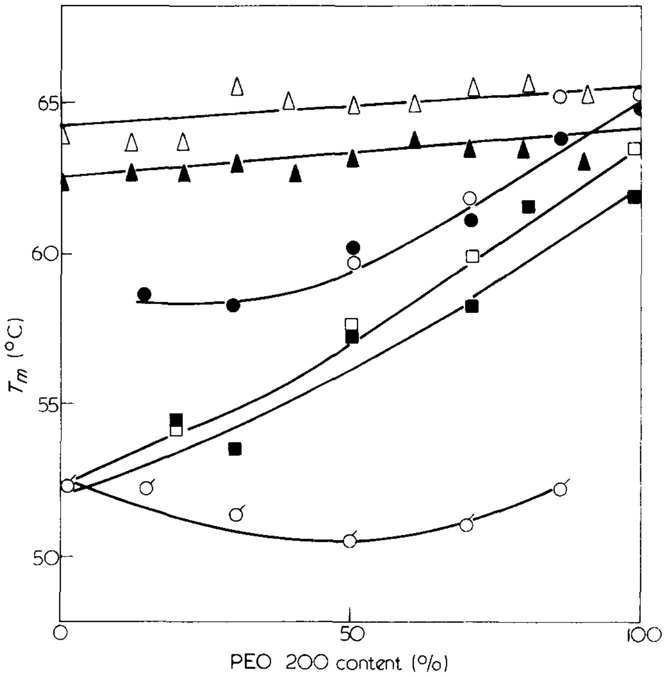

Figure 4 Melting point T_m as a function of the higher molecular weight component of the blends: PEO 20–PEO 200 (triangles); PEO 2–PEO 20 (squares); PEO 2–PEO 200 (circles). First run, △, □, ○ (higher temperature melting peak), ó (lower temperature melting peak); second run ▲, ■, ●

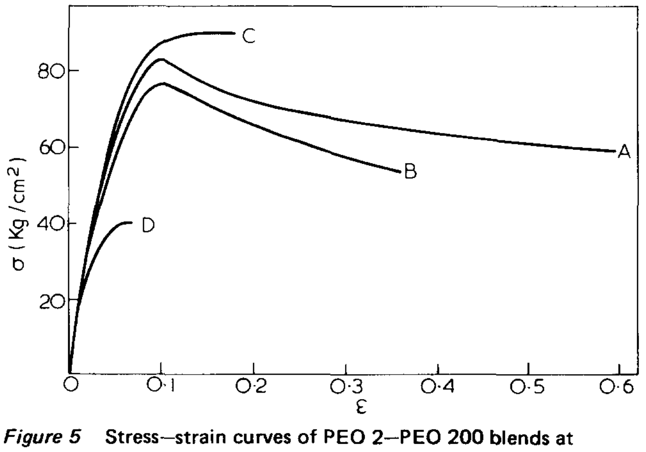

Figure 5 Stress–strain curves of PEO 2–PEO 200 blends at different PEO 200 content: A, 100%; B, 85%; C, 70%; D, 30%

Table 1 Mechanical properties of PEO 2–PEO 200 blends as a function of PEO 200 content

PEO 200 (%)	E (kg/cm^2)	σ_y (kg/cm^2)	$\epsilon_y \times 10^2$	σ_u (kg/cm^2)	$\epsilon_u \times 10^2$
30	1100	38.4	6.0	38.4	6.2
50	1400	54.7	8.0	50.6	8.0
70	1200	90.9	14.0	90.0	17.7
85	1400	77.0	10.0	55.0	35.5
100	1300	80.0	7.0	60.0	60.0

small PEO 2 crystallites as indicated by the shoulder in the fusion endotherm of *Figure 1b*. Their presence, beyond a certain concentration, inhibits the necking formation, allowing an increase in σ_y and ϵ_y. Below this critical value (70% PEO 200) the material becomes more and more brittle. In conclusion there is a transition from the plastic behaviour characteristic of pure PEO 200 to the brittle behaviour of a 30% PEO 200 content blend, passing through an inversion of matrix at a critical composition that in our case lies at about 70% PEO 200. Such an inversion has been already observed for other systems such as polyolefin–polystyrene blends[5]. One may infer that such features are characteristic of systems having plastic and brittle components, irrespective of the microstructure of the latter constituents which can be either crystalline (as in the case of PEO 2) or glassy (as in the case of polystyrene).

Solubilization

The time necessary to dissolve the PEO 2–PEO 200 strip samples in water, previously described, as a function PEO 200 content is shown in *Figure 6*. At each temperature the time increases monotonically with increasing PEO 200 concentration. The value for pure PEO 200 is higher by a factor of 3/2 than for the blend containing 70% PEO 200. As shown before, such a critical blend exhibits the best mechanical performance of all the PEO 2–PEO 200 blends. Therefore it can be utilized for producing films suited to medical applications and other uses in which good mechanical properties coupled with very prompt water solubility are required.

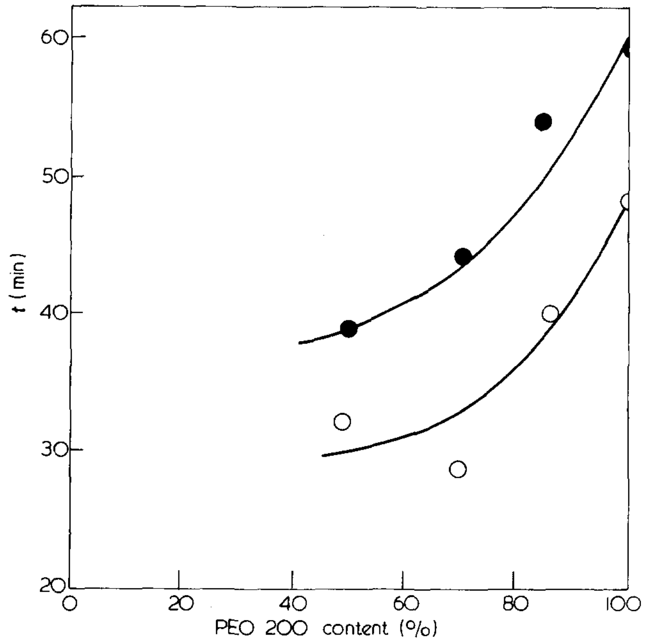

Figure 6 Solubilization time of PEO 2–PEO 200 strip samples as a function of PEO 200 content at two different temperatures: ○, 30°C; ●, 85°C

In conclusion, blending different molecular weight fractions or samples of the same polymer affects thermodynamic and physical properties, giving rise to new materials with improved end use characteristics.

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