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CALORIMETRIC STUDIES OF HIGH MOLECULAR POLYETHYLENE OXIDE FILMS ISOTHERMALLY UNIAXIALLY STRETCHED AT ROOM TEMPERATURE

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The melting behaviour of oriented polyethylene oxide (PEO) films when the film samples were heated in the free state and in the isometric state were investigated by use of DSC. It was shown that in the first case the endotherms of melting have multiple peaks, while in the other case they have one peak. Non-linear dependences of the melting temperature and enthalpy of oriented films on the pressing temperature of the initial PEO isotropic film samples were determined.

High molecular polyethylene oxide (PEO) has been successfully used in all spheres of application of water-soluble polymers [1]. The possibility of using ultra high molecular PEO in order to obtain water-soluble films [2, 3] and fibres [4] has been less examined. It is therefore of practical value to investigate this type of oriented polymer system. Such studies can also contribute to the further explanation of structural changes and orientation processes in crystalline polymers in general.

Investigations which formed the subject of another report [5] proved that the tensile strength of uniaxially stretched ultra high molecular films of different origins, but of practically the same average molecular weights, is an extreme function of the melt-pressing temperature, as is the tensile strength of isotropic films. Using differential scanning calorimetry (DSC) and light microscopy [6], we have also studied the effect of temperature history on the structure of isotropic (non-oriented) PEO films.

The present paper reports results of calorimetric investigations on PEO uniaxially oriented films, which have been stretched until breaking at room temperature.

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Experimental

Calorimetric investigations were performed with a DSC–111 differential scanning calorimeter, manufactured by Setaram, France, with non-isometric and isometric heating of PEO film samples obtained from the Union Carbide Chemicals Co., USA, under the trade name Polyox. The heating rate used was 5 deg/min at temperatures ranging from – 13° up to 130°. The sample weight was approximately 12 mg. The PEO film sample was denoted PEO–2 in [5] and [6] and had an average intrinsic viscosity (η) of 10.0 dl/g in benzene at 18°.

When heated non-isometrically, oriented films were placed free, spirally rolled in a calorimetric measurement cell. When heated isometrically, the films were rolled up along an aluminium sheet, and were then fixed at both ends by bending and pressing the sheet (Fig. 1) and placed in a measurement cell.

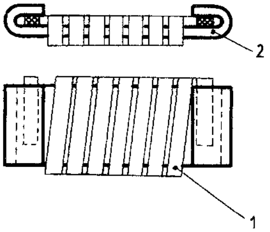

Fig. 1 Polymer film sample (1), isometrically fixed by an aluminium sheet (2)

It was found that the shapes of the melting and crystallization DSC curves do not change when such a sheet is placed in a calorimetric measurement cell and the samples are heated non-isometrically. We have used this method of fixing the samples when performing calorimetric measurements to examine other types of polymers as well. It makes possible variation of the sample weight in a wider range as compared to the method discussed in [7].

Results and discussion

The results obtained using DSC show that the heating of polymer films in a free or in a fixed isometric state has a measurable effect on the shapes of the DSC curves of melting, and on the melting enthalpy and temperature values as well. Several DSC curves of melting of oriented PEO–2 films are shown in Fig. 2. It is seen that isometric melting endotherms have one peak (curves 1 and 4), while non-isometric melting endotherms have three peaks (curves 2 and 3). At the same time, the intensity, the area of the two low-temperature maxima (from 62 to 66–68°) in the

DSC curves, increases considerably, while the high-temperature maximum (from 72 to 76°) intensity decreases when the pressing temperature is raised. This is seen in Fig. 2 by comparing curves 2 and 3. Similar alterations in the shapes of melting DSC curves reflect corresponding structural changes in oriented PEO films. In general, when the pressing temperature of the initial PEO film samples is raised, an increase in the content of low-melting structural elements of lower order than in the oriented films is observed.

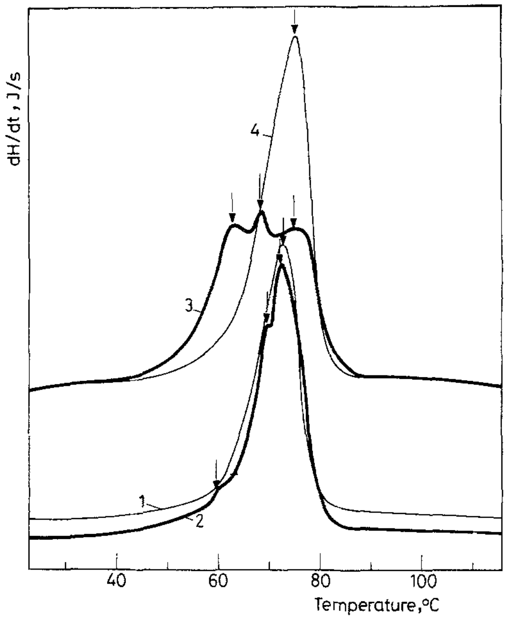

Fig. 2 DSC curves of isometric (1 and 4) and non-isometric (2 and 3) melting of uniaxially isothermally oriented PEO–2 films. Moulding at pressing temperature of 50° (curves 1 and 2) or 150° (curves 3 and 4). Temperature of uniaxial stretching = 18°; rate of stretching = 40 mm/min

Figure 3 shows the intrinsic temperature ranges of isometric and non-isometric melting of oriented PEO films as a function of pressing temperature. These are the lowest (initial) and highest (final, completion) temperatures, T_m^1 and T_m^2, respectively, and the peak temperature, T_m^{max}.

When these results are compared with those obtained in earlier investigations [6], a number of similarities and differences are found in the non-isometric melting temperatures of oriented and isotropic (non-oriented) PEO–2 films when the pressing temperature is raised. T_m^1 does not depend essentially on the pressing temperature. A weak minimum is observed at temperatures varying from 70 up to

120° (Fig. 3, curves 4 and 5) in the curves expressing the dependence of T_m^{max} and T_m^2 on the pressing temperature.

The melting temperatures T_m^{max} And T_m^2 of oriented PEO films in an isometrically fixed state are measurably higher as compared to the corresponding melting temperatures of films in a free state, when the pressing temperature is above 50 and below 150°. They do not change measurably when the pressing temperature is raised throughout the whole temperature range investigated. The temperatures of the highest temperature peak of the multiple endotherm of non-isometric melting of samples pressed at temperatures varying from 50 up to 150° coincide with the corresponding temperatures of samples which were not stretched, but pressed under the same conditions.

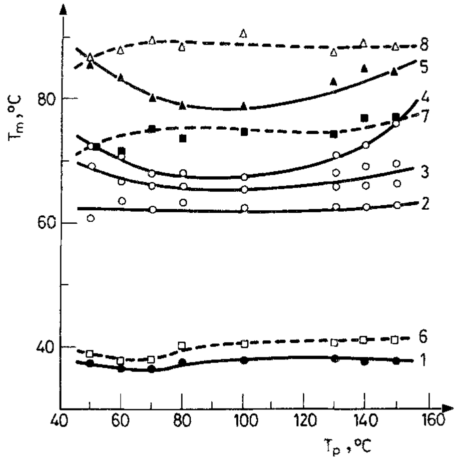

Fig. 3 Dependence of non-isometric (curves 1–5) and isometric (curves 6–8) melting temperatures (T_m^1 — curves 1 and 6; T_m^{max}—curves 2-4 and 7; T_m^2—curves 5 and 8) of uniaxially oriented PEO–2 films on pressing temperature. Stretching temperature = 18°, rate of stretching = 40 mm/min

In order to find a more adequate explanation of these interesting results, further investigations have to be carried out. Taking into consideration the respective differences in the mechanisms of isometric and non-isometric melting of oriented polymer films, we can assume that when oriented polymer films are being isometrically heated, inner (entropic) tensions that have arisen are registered in the process of uniaxial stretching; they relax almost simultaneously and show a narrow unbroken spectrum of relaxation times. They cause an increase of melting temperature and relax isometrically after a high degree of melting is reached. Under non-isometric conditions, inner tensions and their relaxation times are not uniform and that is why the endothermic effect of melting shows a multiple tendency. The relaxation shrinkage strength in amorphous polymers [8] is known to be directly proportional to the degree of orientation of macromolecular segments. We can therefore assume that the increase of melting temperature that has been observed when fixed oriented films are being heated, compared to the melting temperature of non-isometric heating, is due to inner entropic tensions that arise in non-crystalline areas [9]. The quantity of these entropic tensions probably depends on the concentration and degree of stretching strain of the molecules among the crystallites.

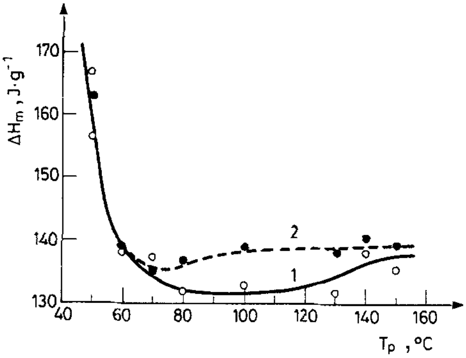

Fig. 4 Dependence of enthalpy of non-isometric (curve 1) and isometric (curve 2) melting of uniaxially oriented PEO–2 films on pressing temperature. Stretching temperature = 18°, rate of stretching = 40 mm/min

Similarly to the enthalpies of melting of the starting non-oriented PEO films of the same type [6], the enthalpies of restrained (isometric) and free (non-isometric) melting of oriented PEO–2 films (Fig. 4) are extreme functions of the pressing temperature. They decrease extremely and in a non-linear way when the pressing temperature is raised. At a pressing temperature higher than 70°, isometric melting enthalpies are measurably bigger than non-isometric melting enthalpies of oriented PEO–2 films. The difference, however, is not considerable.

We have to note as well that the values of melting enthalpies of oriented films and of the corresponding starting isotropic films are quite close. Consequently, we come to the conclusion that structural reorganization develops without a considerable change in the concentration of the crystal phase when film samples are being isothermally uniaxially stretched up to a high degree at room temperature.

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Zusammenfassung — Das Schmelzverhalten orientierter PEO-Filme beim Erhitzen der filmproben im freien und isometrischen Zustand wurde mittels DSC untersucht. Es wurde festgestellt, daß im ersten Falle der Schmelzvorgang durch mehrere endotherme Peaks gekennzeichnet ist, während im anderen Falle nur ein endothermer Peak auftritt. Nicht-lineare Abhängigkeiten der Schmelztemperatur und -enthalpie orientierter Filme von der Temperatur, bei der die Bestimmung der ursprünglich isotropen PEO-Filme erfolgte, wurden untersucht.

Резюме — Методом ДСК исследовано плавление ориентированных пленок окиси полиэтилена при нагревании их в свободном и изометрическом состояниях. Показано, что в первом случае эндотермы плавления имели мультиплетные пики, тогда как в изометрическом состоянии — они имели один пик. Определены нелинейные зависимости температуры плавления и энтальпии ориентированных пленок от температуры прессования начальных изотропных пленок окиси полиэтилена.