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Transport Properties of an Hydrophobic-Hydrophilic Copolymer

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SUMMARY: Sorption and diffusion properties of a copolymer composed by hydrophilic and hydrophobic blocks have been analyzed. The material, obtained as a film by moulding the powders under pressure, was submitted to thermal treatments, and the structural organization of the samples was investigated using water vapour and dichloromethane as permeants. The polar solvent (water) has been useful to investigate the hydrophilic amorphous regions, while the apolar one (methylene chloride) gave information about the organization of the hydrophobic amorphous phases.

Introduction

The study and application of the mass transfer properties in polymeric materials has been the focus of considerable research effort [1]. The characterization and understanding of the effect of one sorbate on the mass transfer properties of a penetrant in polymers is important due to the extensive use of these materials in the design of protective clothing, packaging, separation membranes, and many other industrial applications. The study of transport phenomena is very useful in investigating the amorphous component of the polymeric systems, to obtain structural and morphological information [2-4]. In the case of hydrophilic polymers, such as polyamides, it is well known that the presence of water has a significant effect on their barrier and physical properties [5]. The amount of water sorbed, the type of sorption isotherm and the mechanism of diffusion are strictly related to the morphology of the entire system and to the thermodynamic state of the hydrophilic regions [6-7]. On the other hand, in the presence of a hydrophobic phase, it is interesting to investigate its structural organization too, and how it influences the barrier and physical properties of the system. An easy way to investigate directly the hydrophobic amorphous regions, is to use an apolar solvent that is strongly interactive with the non-polar regions, giving information related only to the hydrophobic phase. The aim of this work is to study the structural organization of a copolymer composed by hydrophilic and hydrophobic blocks, through the analysis of the transport parameters using water vapour as permeant in the hydrophilic phase, and dichloromethane into the hydrophobic one.

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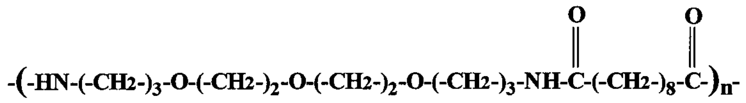
EXPERIMENTAL

The polymer used in this work has the following chemical structure:



$$-\!\left(\text{-HN-(-CH}_2\text{-)}_3\text{-O-(-CH}_2\text{-)}_2\text{-O-(-CH}_2\text{-)}_2\text{-O-(-CH}_2\text{-)}_3\text{-NH-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-(-CH}_2\text{-)}_8\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}\right)_n\text{-}$$

Wide-angle X-ray diffractograms (WAXD) were obtained by using a PW 1050 Philips powder diffractometer (CuKα-Ni filtered radiation). The scan rate was 2 degrees of 2θ/min.

Differential scanning calorimetry (DSC) was carried out over the temperature range −50 to 200 °C, using a Mettler TA3000 DSC instrument purged with nitrogen and chilled with liquid nitrogen. Runs were conducted on samples of about 10 mg at a heating rate of 20°C/min.

Transport properties, sorption and diffusion, were measured by a microgravimetric method, using a quartz spring balance, having an extension of 16 mm/mg. The penetrants used were methylene chloride and water vapour, and the experiments were conducted at 25°C. Sorption was measured as a function of vapour activity, a=P/Po, where P is the actual pressure to which the sample was exposed, and Po the saturation pressure at the temperature of the experiment. The penetrant concentration at the time t, Ct, divided by the equilibrium concentration Ceq was plotted as a function of the square root of time to calculate the average diffusion coefficient using the following relationship [8]:

$$Ct/Ceq=4/d\,(Dt/\pi)^{1/2}$$

where d is the thickness of the sample.

Our samples were obtained by moulding the powders of the polymer in a hot press at 150°C, into a film shape 0.05 mm thick, and quenching them in air (sample A). The film were: annealed 1 hour at 105°C (sample B), and 1 hour at 120°C (sample C).

Results and discussion

Calorimetric analysis

In fig.1 the DSC curves relative to all the samples are shown. A first change in the slope of the curves, at about −10°C, is probably due to the glass transition temperature of the material. A second thermal phenomenon, displayed as a very broad endotherm, appears for all the samples, between 50°C and 100°C. It could represent a prefusion of an imperfect crystalline phase or loss of water inside the structure, followed by a reorganization, as represented by the exotherm. A big endothermic phenomenon, centered at about 140°C, is related to the fusion of the polymer.

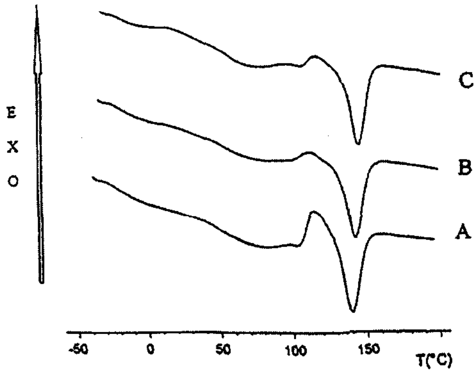


Fig. 1. DSC curves

X- ray analysis

In fig. 2 the diffractograms relative to all the samples are reported. The original film (A) appears as a semicrystalline sample. The thermal treatment at 105°C (B) has a disordering effect, in fact it is not possible to recognize the crystalline peaks centered at about 21[°2θ] and 23 [°2θ], but only a broad peak is present between 20 [°2θ] and 25 [°2θ]. After annealing at 120°C (C) the sample results semicrystalline like the original one (A).

Transport properties

Water vapour

Generally, for polymer-solvents systems, the dependence of the diffusion coefficient on the vapour concentration follows the empirical law:

$$D = Do \exp (\gamma C) \qquad (1)$$

where Do is the diffusion coefficient extrapolated to Ceq=0, related to the fractional free volume (FFV) of the permeable phase, and γ is the concentration coefficient, related to the plasticizing power of the solvent on the polymer.

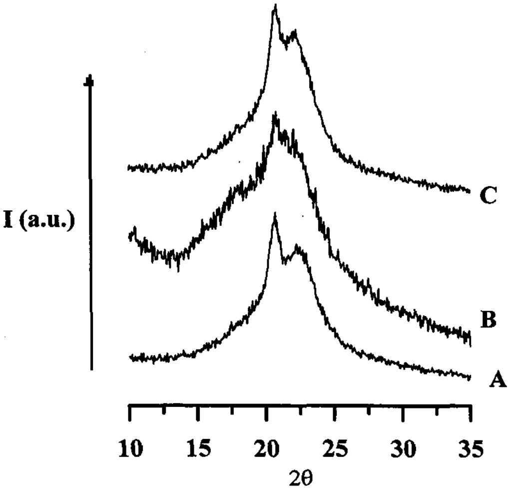


Fig. 2. WAXD patterns

In fig. 3 the diffusion coefficients evaluated at each concentration, D[cm^2/sec], as a function of the equilibrium concentration of water sorbed by the samples, Ceq[g/100g] are reported.

It is evident that the diffusion of water vapour results independent of the concentration, in the investigated range; in fact the values of D(C) fit the same straight line for all the samples. The Do coefficient is the same for all the analysed films (2.7×10^{-8} cm^2/sec), indicating that the amount of free volume of the hydrophilic phase and its thermodynamic state do not change after the thermal treatments.

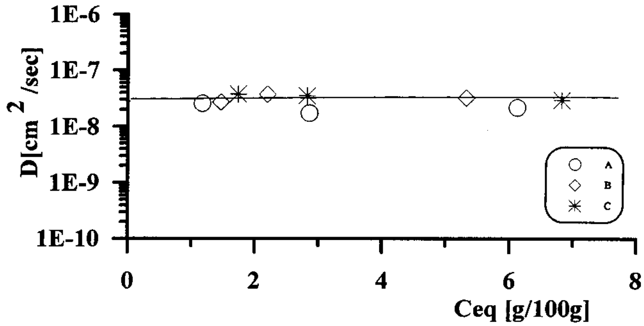


Fig. 3. Diffusion of water vapour

Fig. 4 displays the sorption curves of all the samples. The two thermal treatments have different effects on the structural organization of the amorphous hydrophilic phase of the material. The isotherm relative to the sample C, annealed 1h at 120°C, is similar to that of the untreated one (A), with values of sorbed penetrant a little bit higher in the range of low vapour activities. The sample B shows a sorption mode in which the solvent concentration increases following the Flory-Huggins law [8].

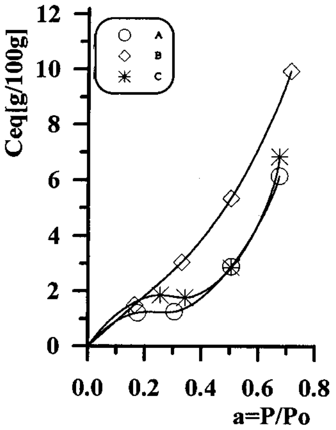


Fig. 4. Sorption of water vapour

This indicates that the thermal threatment at 105°C causes a rearrangement into the structure so that the amorphous hydrophilic phase becomes more permeable, but with no preferential sites of accomodation for the water molecules at low vapour pressure.

Methylene chloride

In order to obtain information about the hydrophobic part present in our samples, transport parameters were evaluated using methylene chloride as permeant.

In fig. 5 the diffusion coefficients, as a function of Ceq [g/100g], are reported for all the samples. The data relative to the sample treated 1h at 120°C (C) fit the same straight line of sample A, meaning that for these two materials the diffusing phase and its thermodynamic state are the same, independently of the thermal treatment. For the sample B we can recognize two different zones of diffusion. The first one, lower than that relative to the other two samples, up to Ceq about equal to

13.5 [g/100g]. The second one, from Ceq about 15 [g/100g], in which the experimental data are interpolated by the same line of A and C.

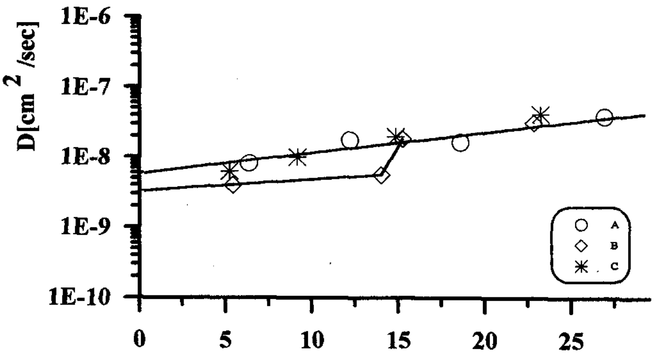


Fig. 5. Diffusion of ethylene chloride

Fig. 6 displays the isotherms relative to all the samples. The original sample shows a sorption nearly . linear with the solvent activity in all the investigated pressure range

The sorption mode of the sample C resembles that of A, with lower values of sorbed solvent, due to a small amount of hydrophobic phase permeable to dichloromethane vapour,. For the sample B, a transition is evident in the sorption curve between activity 0.3 and 0.5. The sorption increases after activity 0.2 and then abruptly decreases, following the curve of sample C.

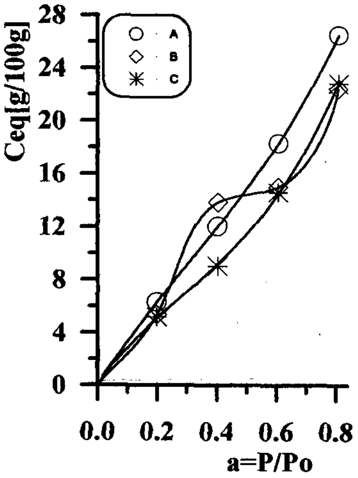


Fig. 6. Sorption of methylene chloride

The occurrence of a solvent induced crystallization can be hypotesized; in fact the sample exposed at activity 0.8 shows the same diffractograms of sample C, as shown in figure 7.

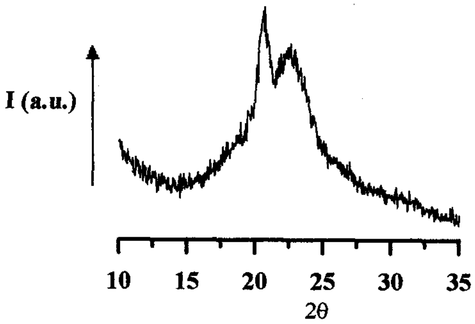


Fig. 7. WAXD of sample B after exposure to CH_2Cl_2 (a = 0.8)

CONCLUSIONS

The analysis of the structural organization of a copolymer obtained by sebacic acid and dimethyl-diethyl trioxi amine has been analyzed. The sample was also annealed for 1h at 105°C and 1h at 120°C, because in this range of temperature the original material shows an exothermic phenomenon, whose nature appeared interesting to be studied. The original material, for the thermal treatment at 105°C, passes through a form, which reorganizes returning to the usual crystalline one at 120°C. Transport properties of methylene chloride, showing two diffusion and two sorption zones, induced us to hypotesize that this "mesomorphic form" is transformed into the typical crystalline form, by the effect of dichloromethane at high activity.

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