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Transport properties of dichloromethane in polymeric blends

Part I *Low density polyethylene-isotactic polypropylene*

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Low density polyethylene (LDPE) and either isotactic polypropilene (IPP) or a copolymer of isotactic polypropilene with 3% of ethylene (CPP) were blended, and analyzed with X-rays, differential thermal calorimetry, dynamic mechanical analysis, and transport properties of dichloromethane vapour at different activities. The results show that polyethylene and polypropylene crystallize in different domains in the usual crystalline forms (orthorhombic and monoclinic respectively). Also the amorphous phases are not miscible; moreover in the blend LDPE-IPP, in which PE crystallize less, the transport of the vapours occurs mainly through polyethylene, whereas the opposite is true in the blend LDPE-CPP, in which polypropylene crystallizes less. The sorption properties are in agreement with the additivity of sorption of the two amorphous phases.

1. Introduction

For a number of years there has been a great interest in blending polymers, for many reasons, both theoretical and technological [1, 2].

In fact this process offers many possibilities of obtaining tailored or unique behaviour. Also, synergistic behaviour can be shown with respect to particular properties, for example strength, modulus, or drawability. Furthermore, blending can be a useful process for reuse of waste plastics.

Many authors have studied blends of low density polyethylene (LDPE), high density polyethylene (HDPE) and isotactic polypropylene (IPP) [3–10]. Generally the low cost materials, such as polyolefins, comprise the major volume of waste, and a reprocessed blend may contain significant portions of each type of polyolefin.

A number of fundamental studies have been reported, regarding mechanical properties and crystallization rate. HDPE-LDPE-IPP are described as incompatible and composed of segregated crystalline phases of both polyethylene (PE) and polypropylene (PP).

In the investigation of the blends, it is less clear what happens in the amorphous phase. On the other hand the thermodynamic state and the morphology of the amorphous phase are principally determinant for the mechanical properties of the materials. It is, therefore, important to have the soundest description of this phase. Transport properties of vapours in polymers are very sensitive to the state and the fraction of the amorphous phase. They have been often used for studying the amorphous component in polymers, both oriented and after drawing, showing the big potentialities of this technique in evidencing even small differences in the amorphous phase [11–15].

In the case of the blends, when the amorphous phases are incompatible, the interpretation of the data is complicated by the fact that we must take into account the distribution of the penetrant into two different amorphous phases [16].

This paper is a part of a wider project, in which we will analyse the transport properties of blends of polyolefins in order to find any possible correlation of the transport parameters with the morphology and the thermodynamic state of the amorphous components. Here we present results on the blend LDPE-IPP and LDPE with a random copolymer of polypropylene and 3% of polyethylene (CPP). This second sample of polypropylene was used in order to verify if a small presence of polyethylene can produce a better miscibility of the two components in the amorphous part of the blend.

2. Experimental

Low-density polyethylene (LDPE) of $M_n = 24{,}000$ and $M_w = 215{,}000$ and isotactic polypropylene (IPP) of $M_n = 15{,}600$ and $M_w = 307{,}000$ were kindly supplied by RAPRA (UK). Isotactic polypropylene, randomly copolymerized with 3% polyethylene (CPP) was kindly supplied by Montell (Italy).

Blends of LDPE-IPP and LDPE-CPP (50/50 in weight of the two polymers), were prepared by co-dissolving the proper weight of the polymers in p-xylene at high temperature, and, then, evaporating the solvent. The precipitate was vacuum dried at 70 °C for 2 days, to ensure complete removal of solvent. Films

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of the blends were obtained by heating the powders at a temperature higher than the melting points of the two polymers, pressing them into a film shape of thickness 0.15–0.20 mm, and cooling them in the air.

Wide angle X-ray diffractograms (WAXD) were obtained by using a PW 1050 Philips powder diffractometer ($\mathrm{Cu}K_\alpha + \mathrm{Ni}$ filtered radiation). The scan rate was $2^\circ \vartheta\,\mathrm{min}^{-1}$.

The thermal analysis was carried out over the temperature range 0–200 °C, using a Mettler TA3000 DSC instruments. Runs were conducted on samples of about 15 mg at heating rate of 20 K/min.

Dynamic-mechanical properties were performed using a Polymer Laboratories Dynamic Mechanical Thermal Analyser, interfaced with a Polymer Laboratories controller. Dynamic mechanical spectra were recorded in the tensile mode, at a frequency of 1 Hz and a heating rate of 3 °C/min in the range −75–100 °C.

The elastic modulus of the blends and pure polymers was detected at 25 °C within the linear trend (deformation less than 1%). The detected values were averaged over ten measurements.

The transport properties, sorption and diffusion, were measured by a microgravimetric method, using a quartz spring balance, having an extension of 15 mm/mg. The penetrant used was dichloromethane and the experiments were conducted at a temperature of 25 °C. Sorption was measured as a function of vapour activity, $a = p/p_0$, where p is the actual pressure to which the sample was exposed, and p_0 the saturation pressure at the temperature of the experiment. The samples were tested 1 week after the preparation.

3. Results and discussion

3.1. Structural organisation of the blends

In Fig. 1 the wide-angle X-ray diffractograms of the two blends LDPE-IPP and LDPE-CPP, are reported.

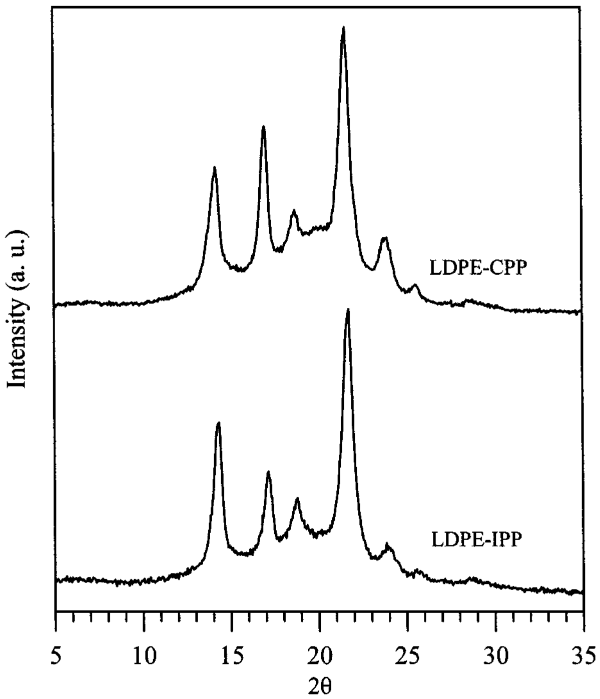


Figure 1 Wide angle X-ray diffractograms of the blends LDPE-IPP and LDPE-CPP.

TABLE I The crystallinity (derived from DSC), the thermodynamic diffusion parameter, D_0 (cm^2/s), and the elastic modulus, E (MPa), for the blends and the pure LDPE, IPP and CPP

Sample	X_C (LDPE)	X_C (PP)	D_0 (cm^2/s)	E (MPa)
LDPE-IPP blend	0.38	0.45	4.7×10^{-8}	241
LDPE-CPP blend	0.48	0.33	4.1×10^{-9}	370
LDPE	0.45		4.0×10^{-8}	141
IPP		0.60	2.2×10^{-9}	777
CPP		0.45	4.73×10^{-9}	661

Both the crystalline diffractograms of orthorhombic polyethylene, showing the main peaks at 21.4 and 23.8° of 2ϑ, and of the monoclinic α form of isotactic polypropylene, showing the peaks at 14.1, 16.8, 18.4° of 2ϑ are present in the blends, confirming that LDPE and PP crystallise independently in the common crystalline form shown by the homopolymers. However, in the case of the blend LDPE-CPP, the intensity of the PP peaks at 14.1 and 16.8° of 2ϑ is inverted, and this is indicative of a more disordered and less crystalline form of polypropylene; on the contrary the peak at 23.8° of 2ϑ of LDPE is more intense and better resolved, suggesting that polyethylene crystallises more when it is mixed with CPP than with IPP.

In Fig. 2 the differential scanning calorimetry (DSC) curves are reported for both the blends. Also this technique gives the information that the two polymers crystallise independently in their usual crystalline form. Two melting peaks are, in fact, well observable, whose temperatures correspond to the melting temperatures of the starting polymers, that is about 110 °C for LDPE, 163 °C for IPP, and 150 °C for CPP. The lower melting temperature of CPP respect to IPP is due to the fact that it is a copolymer, containing 3% of polyethylene. For this reason, the two melting peaks are better resolved in the LDPE-IPP blend, allowing the determination of the ΔH of melting, for both the components. We obtained the crystallinity, normalizing with the ΔH_0 of the two crystalline phases (ΔH_0 taken as 241 and 168 J/g for LDPE and IPP respectively) [17]. The values of crystallinity are reported in Table I. In the case of the LDPE-CPP blend, an approximated evaluation of the melting enthalpy for the two crystalline phases, as shown in the Fig. 2, gave the values of crystallinity for LDPE and CPP, also reported in Table I. For CPP the same value of IPP, as ΔH_0, was assumed. In spite of the uncertainty in the resolution of the peaks for the LDPE-CPP blend, the calorimetric analysis gives the same indication as the X-ray diffractograms, that is a substantially higher crystallinity of LDPE when it is mixed with CPP, than in the blend with IPP. The opposite is true for polypropylene, that is much more crystalline in the blend with the homopolymer than in the blend with the copolymer, in spite of the very small fraction of copolymerization (3%).

It is also worth noting that the melting curve of polyethylene starts very soon, just after 50 °C, indicating a broad distribution of crystal dimensions and very small and defective crystals.

As for the crystalline phases, we can conclude that PE and PP crystallise in separated domains, in the usual

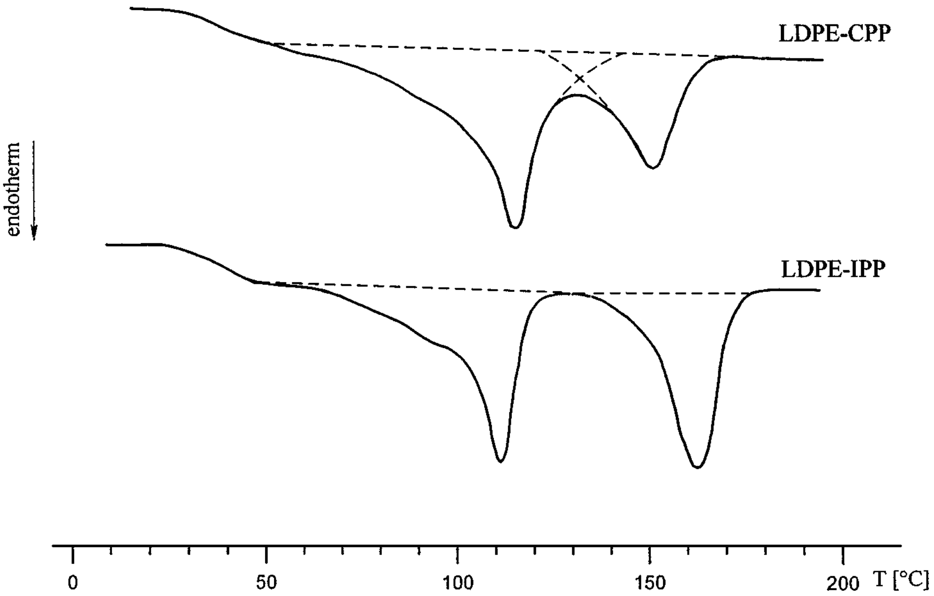


Figure 2 Differential Scanning Calorimetry (DSC) curves for both the blends.

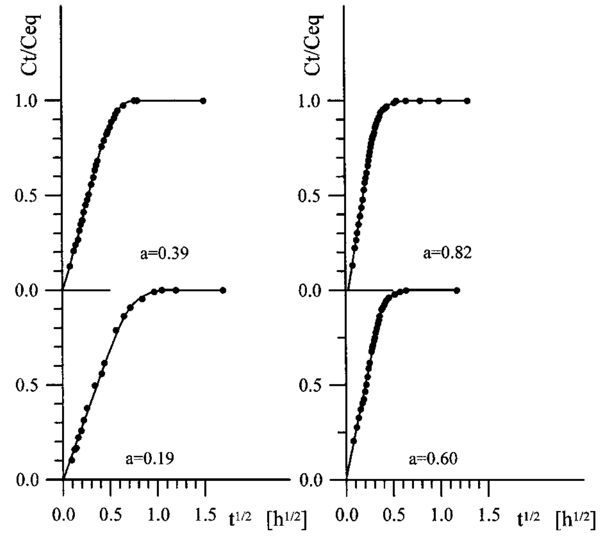


Figure 3 The reduced sorption, that is C_t/C_{eq} (g/100 g) is reported as a function of square root of time, at different vapour activities, $a = p/p_0$, for the LDPE-IPP blend.

crystalline forms, that is the orthorhombic form for PE and the monoclinic α form for PP. The presence in the polypropylene of a small copolymerized fraction of polyethylene, either reduces the crystallinity of PP or increases that of PE in the blends. In fact polyethylene crystallizes more in the blend LDPE-CPP with respect to the pure polymer, and less in the blend LDPE-IPP. The crystallinity of polypropylene is reduced in either blend.

3.2. Transport properties

In Fig. 3, the reduced sorption, that is C_t/C_{eq} (g/100 g), is reported as a function of the square root of time, at different vapour activities, $a = p/p_0$, for the LDPE-IPP blend. All the curves follow a Fickian behaviour, with a single diffusion coefficient. This parameter can be derived, from the slope of the linear part of the sorption curve, from the relation:

$$C_t/C_{eq} = \frac{4}{d}\sqrt{\frac{\bar{D}t}{\pi}} \qquad (1)$$

where $\bar{D}$ is the mean diffusion coefficient, and d the thickness (cm) of the sample.

The diffusion parameter is not constant at each vapour activity, but increases increasing vapour concentration; it is, therefore important to determine the dependence of diffusion on concentration, in order to extrapolate to zero penetrant concentration, and obtain the thermodynamic parameter, D_0, which is related to the fractional free volume present in the system. Generally the dependence is of the exponential form

$$\bar{D} = D_0 \exp(\gamma C_{eq}) \qquad (2)$$

where γ is the concentration coefficient, which is related to the fractional free volume, and to the effectiveness with which the penetrant plasticizes the polymer.

Fig. 4 shows the logarithm of the diffusion coefficient as a function of the equilibrium concentration for the blend LDPE-IPP and for the pure LDPE and pure IPP.

We can observe the interesting result that the diffusion of the blend follows very nearly that of LDPE, and the experimental points extrapolate to the same thermodynamic parameter, $D_0 = 4.7 \times 10^{-8}$ cm^2/s. Only the concentration coefficient is slightly different. The coincidence of the D_0 parameters of the blend and pure LDPE, allows us to suggest that the matrix through which the passage of the vapour occurs is mainly a polyethylenic matrix, whereas the amorphous polypropylene does not participate the net passage of the penetrant.

Fig. 5 shows the equilibrium concentration of sorbed dichloromethane, as a function of the vapour activity, for the blend and the pure components. At low activity

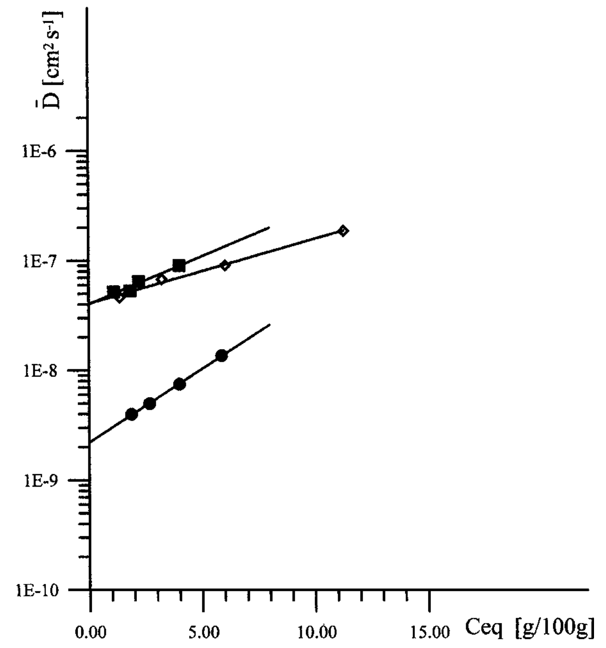


Figure 4 The logarithm of the diffusion coefficient as a function of equilibrium concentration, for the pure LDPE (■), pure IPP (●), and their blend (◇).

($a = 0.2$) the sorption of the blend is slightly higher than that of the pure components. For the pure polyethylene, as well as for the pure polypropylene, it has been always found that the sorption is proportional to the fraction of the amorphous phase. If we indicate with C_{sp} the sorption of a completely amorphous sample, at each activity, the sorption of a crystalline sample will be expressed as:

$$C_{sp} = C_{eq}/X_a \tag{3}$$

where X_a is the amorphous fraction. In Table I the crystallinities of the pure polymers are reported. It is evident that LDPE and IPP are less crystalline in the blend, therefore the higher sorption at low activity is an expected result.

Furthermore, considering the values of C_{sp} relative to LDPE pure (2.1 g/100 g) and IPP pure (2.9 g/100 g), at activity $a = 0.2$, we can evaluate the theoretical value of C_{eq} of the 50/50 blend, from the relationship:

$$C_{eq_{(blend)}} = \frac{1}{2} C_{sp_{(LDPE)}} X_{1a} + \frac{1}{2} C_{sp_{(IPP)}} X_{2a} \tag{4}$$

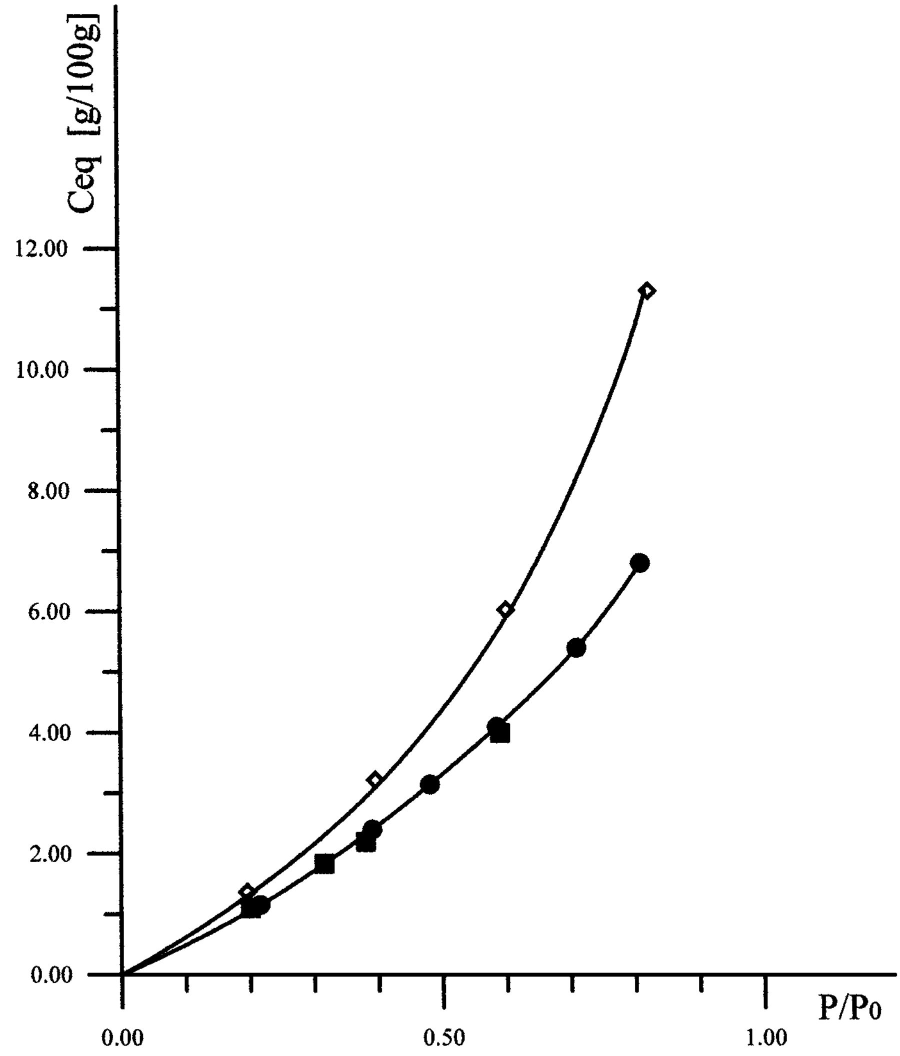


Figure 5 The equilibrium concentration of vapour as a function of vapour activity, $a = p/p_0$, for the pure LDPE (■), pure IPP (●), and their blend (◇).

where X_{1a} and X_{2a} are the amorphous fractions of LDPE and IPP in the blend. Substituting the proper values, taken from Table I, we obtain, at activity $a = 0.2$, $C_{eq} = 1.42$ g/100 g, which is very near to the experimental value 1.38 g/100 g, confirming the proportionality between sorption and amorphous fraction, at low activities, and the additivity of the sorption of the two amorphous phases.

Not trivial, instead, the result of the much higher sorption of the blend, at high activities. This result can be explained either assuming that a part of the crystalline phase is very defective and formed by very small crystals, and therefore becomes permeable at high activities, or that the system is much more open, allowing the clustering of the solvent molecules at high activities.

Also, in the case of the LDPE-CPP blend, the reduced sorption curves (not reported here) show a Fickian behaviour, giving the possibility to derive, for each activity, a mean diffusion coefficient, $\bar{D}$, cm^2/s. The derived values are reported in Fig. 6 as a function of the equilibrium concentration. Also in Fig. 6, the values for the pure LDPE and CPP are reported, for comparison. Interestingly, the experimental points of the blend, at lower concentrations extrapolate to the same D_0 as pure CPP. This result allows us to suggest that, at variance with the previous case, in the blend of polyethylene and polypropylene containing a small fraction of ethylene, the matrix through which the passage of the penetrant molecules occurs is mainly polypropylenic. It is worth remembering that in the previous blend, that is LDPE-IPP, the polyethylene was less crystalline than polypropylene, consisting in an amorphous fraction of 64% vs. 55% of IPP. On the contrary, in the blend LDPE-CPP the opposite is true: the amorphous fraction of LDPE is 52% vs. 67% of CPP. We can conclude that, in this case, the polymer having the higher amorphous fraction determines the matrix through which the net transport of penetrant occurs.

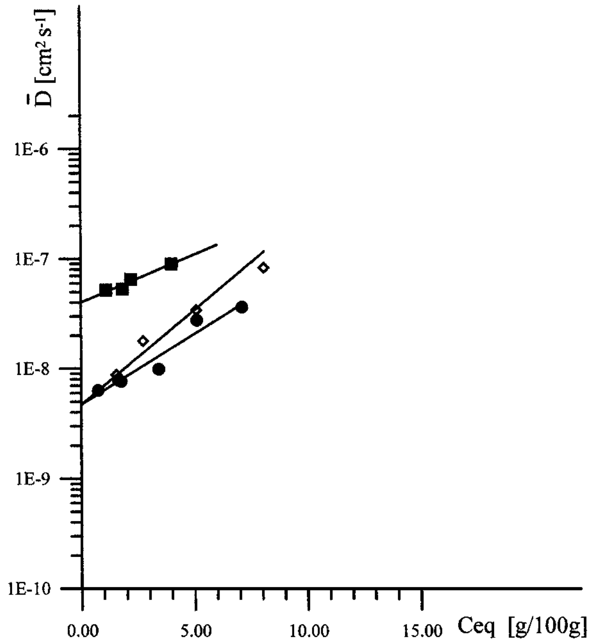
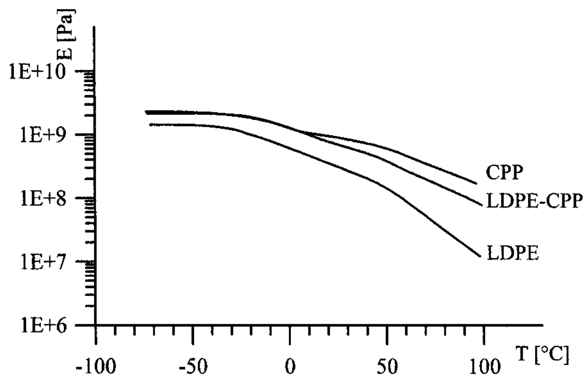


Figure 6 The logarithm of the diffusion coefficient as a function of equilibrium concentration for the pure LDPE (■), pure CPP (●), and their blend (◇).



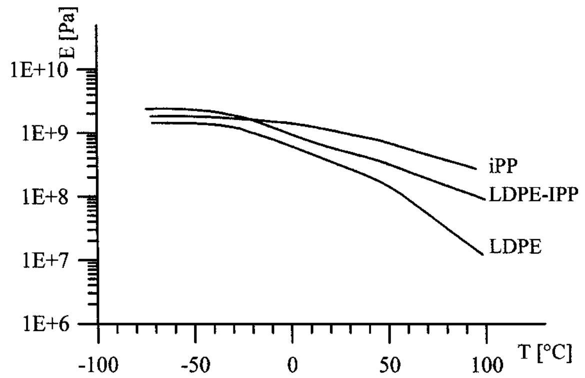


Figure 7 The dynamic-mechanical modulus as a function of temperature for pure LDPE, IPP, CPP, and their blends.

3.3. Mechanical properties

The dynamic-mechanical behaviour and the elastic moduli, measured at room temperature, confirm the results of the transport properties. In particular we report in Fig. 7 the elastic modulus as a function of temperature for the pure LDPE, IPP, CPP, and their 50/50 blends. In Table I we report the elastic moduli, E (MPa) measured at 25 °C, of all the samples.

In the case of the LDPE-IPP blend, the modulus starts decreasing at −20 °C, in analogy with the behaviour of pure LDPE. The behaviour of the blend is similar to that of LDPE, although after 40 °C, where for LDPE a steep drop is observed, the blend maintains the same dependence as IPP.

The elastic modulus of the blend, measured at 25 °C, shows a value of 240 MPa, which is closer to that of LDPE (141 MPa) compared to IPP (776 MPa).

At variance, the blend LDPE-CPP shows a dependence of the modulus on the temperature which is much more similar to CPP that to LDPE, in all the temperature interval. Moreover the modulus of the blend at 25 °C (370 MPa) is higher than that of the blend LDPE-IPP, and nearer to that of CPP (660 MPa).

4. Conclusions

The methods used to investigate the crystalline component of the blends, that is X-rays and DSC, confirm that, as already found, the two polymers crystallise in different crystalline phases, as well as when polypropylene is copolymerized with 3% of ethylene. In the latter case, low density polyethylene in the blend is more crystalline, reaching 48% of crystallinity, whereas polypropylene crystallizes only for 33%. The opposite is true in the other blend, in which LDPE is 38% crystalline and IPP 45%. The different crystallization behaviour of the two polymers in the different blends, is reflected in the transport properties of dichloromethane. In fact, in the blend LDPE-IPP in which polyethylene has a higher amorphous fraction (62%), the thermodynamic diffusion parameter, D_0 shows the same value as the pure polymer, indicating that the matrix through which the passage of the penetrant occurs is prevalently PE. The opposite is true in the other blend, in which polypropylene is more amorphous. In this case, the diffusion parameter coincides with that of the CPP copolymer.

The elastic moduli follow the same trend: the modulus of the LDPE-IPP blend, in which the amorphous matrix for the diffusion is polyethylenic, is lower than that of the LDPE-CPP blend, in which the amorphous matrix for the diffusion is polypropylenic, confirming the likelihood of what we suggested. In the first case, the stress on the amorphous phase is supported, prevalently, by polyethylene, in the other by polypropylene.

This can be an example of the potentialities of mixing polymers, in which the properties can be varied with a small structural variation. In our case, the copolymerization of a small quantity of ethylene (3%) with propylene changes the diffusion behaviour and therefore the permeability of the whole blend.

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