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Influence of Phase Morphology on Molecular Mobility of Poly(propylene)-(ethylene-vinyl acetate) Copolymer Blends

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Summary: The dynamic mechanical and dielectric behaviours of Polypropylene (PP) and (Ethylene-Vinyl Acetate) Copolymer (EVA) blends are reported as a function of the morphology. For EVA contents lower than 20%, blends show the two-phase morphology characteristic of immiscible blends, with spherical EVA droplets finely dispersed in the PP matrix. After stretching in the molten state, the morphology of EVA fibers is observed. Mechanical Relaxation Spectroscopy display three relaxation processes: the EVA and PP α-relaxations associated to the glass transitions and a β-transition corresponding to a PP crystalline phase relaxation. The PP α-relaxation shifts to higher temperatures when EVA presents a fiber morphology, corresponding to a decrease of PP chain mobility since it is hindered by the reinforcement effect of EVA fibers. Quite different results are obtained by DRS analysis. In blends containing EVA fibers, only one main relaxation associated to the EVA α-transition is observed whereas one additional relaxation can be noticed in the blends containing EVA droplets. This new relaxation might be assigned to interfacial polarization effects, phenomena that are sometimes observed in heterogeneous polymer blends when a low content of one polar component is embedded in a non conductive matrix. In this case, the occurrence of a characteristic interfacial polarization relaxation appears to be correlated to the accessible experimental frequency.

Keywords: dielectric relaxation spectroscopy; (ethylene-vinyl acetate) copolymer; mechanical relaxation spectroscopy; polymer blend morphology; polypropylene

Introduction

Nowadays, polymer blends are considered as one of the most important developments in polymer engineering because of the possibility of obtaining new materials with specific properties. An example is the system polypropylene/ poly(ethylene vinyl acetate) (PP/EVA) which combines two important commercial polymers : a semi-crystalline thermoplastic and an elastomer. This system has been the subject of several studies considering more particularly miscibility and compatibilization aspects [1-4]. Nevertheless, few papers are devoted to the correlation between

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the relaxation phenomena and the blend morphology in such heterogeneous systems [5-6]. More specifically, the interfacial polarization or Maxwell-Wagner-Sillars effect is scarcely described [7-8], particularly in polymer blends [9-10]. This paper presents a study of PP/EVA blends with low EVA contents (non miscible domain), considering the influence of blend morphology on molecular mobility. Dynamic and dielectric mechanical relaxation spectroscopy is used to investigate phase relaxations in relation to the conductive EVA phase behaviour.

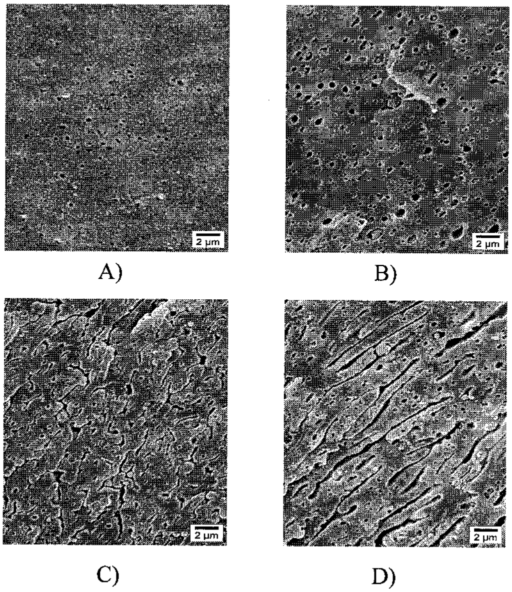
Experimental

The materials investigated in this study are blends of polypropylene (iPP), as the main component, with an ethylene-vinyl acetate copolymer (EVA) as the dispersed phase. The PP supplied by ExxonMobil Chemicals is an Escorene 4352 F2 having a melting temperature of 163 °C, a specific gravity of 0.908 and a melt-index of 3 g/10min (ISO 1133). The EVA copolymer (EVATANE 28-03 from ATOFINA) has a melt-index of 3 g/10min (ISO 1133) and contains 28% vinyl acetate by weight. Blends were prepared with a twin screw extruder (Leistritz LSM 34 mm model, L/D=33.5) at 200 °C and 200 rpm with a 4 kg/h flow rate. EVA contents were respectively 2.5, 5, 10, 20 and 30 weight percent. For each composition, blends were extruded through a 50 x 2 mm slot die either without any drawing (pressed samples) or drawn uniaxially (drawn samples). DSC measurements were performed using a 2920 TA Instruments apparatus in the temperature range of –50 to 210 °C with a heating rate of 10 K.min^{-1} under nitrogen atmosphere. The temperature calibration was achieved using indium. Blend morphologies were examined with a HITACHI S800 Scanning Electronic Microscope (SEM) with a field emission gun, working at an acceleration voltage of 15 kV, on Au-Pd coated cryogenically fractured samples, after extraction of EVA with toluene.

Mechanical Relaxation Spectroscopy experiments were carried out using a DMA 2980 analyzer from TA Instruments, in the tensile film mode. The experimental conditions were a heating rate of 3 K.min^{-1}, a frequency of 1 Hz in the temperature range from –50 to 160 °C, using 500 µm thick films. For the dielectric measurements, circular aluminium electrodes (30 and 10 mm diameter) were evaporated on the top and the bottom of the sample. The complex dielectric function $\varepsilon^*= f(T, \nu)$ was measured as a function of temperature T (from –50 to 150 °C) and frequency (between 10^{-1} and 10^5 Hz) by a lock-in amplifier (Stanford Research 810) interfaced to the sample by a broadband dielectric interface (BDC, Novocontrol). The temperature T dependence of the α and β relaxations can be described by an Arrhenius equation: $f = f_1 \exp[-\frac{E_a}{kT}]$ which has allowed us to estimate the activation energy E_a (k is Boltzmann constant and f_1 is the pre-exponential factor).

Results and Discussion

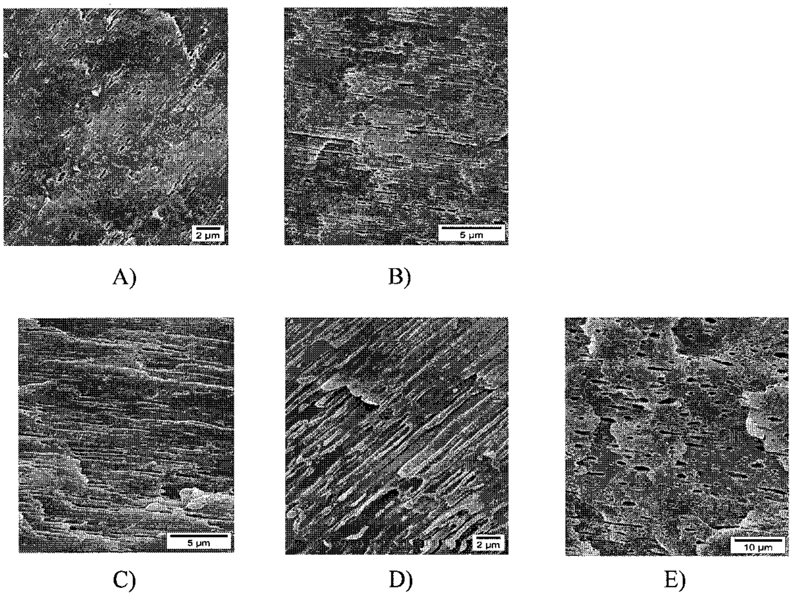
Morphologies of PP-EVA blends were examined using SEM. Typical images are presented in Fig.1 and Fig.2 for samples without drawing and with uniaxial drawing respectively.



A) B)

C) D)

Figure 1. PP/EVA blend morphologies, without any drawing A: 95/5, B: 90/10, C: 80/20, D: 70/30.



A) B)

C) D) E)

Figure 2. PP/EVA blend morphologies, with uniaxial drawing A: 95/5, B: 90/10, C: 80/20, D: 70/30, E: 70/30 perpendicular to extrusion direction.

Micrographs obtained from samples without drawing show a two phase morphology of EVA droplets finely dispersed in the PP matrix for EVA content lower than 20%. This morphology is characteristic of immiscible blends. For higher contents (20-30%), co-continuity is reached with two interpenetrated phases. For samples uniaxially drawn at the die exit, a morphology of EVA fibers is observed. Their length increases with EVA content, up to 20% EVA. The PP-EVA 70/30 blend shows a fairly irregular and mixed morphology with larger EVA fibers, corresponding to the beginning of co-continuity.

In the composition domain studied (low EVA contents), no significant evolution of glass transition, crystallization and melting temperatures was observed, corresponding evidently to immiscible blends. PP melting enthalpies remain identical as well, giving a crystallinity ratio almost constant over the composition range studied and equal to *ca.* 42 %.

Thermal characteristics were identical for drawn and non drawn samples. In particular, no influence of drawing on PP crystallinity ratio was observed.

Three relaxation processes, designated α_{EVA}, α_{PP} and β_{PP} in order of increasing temperature, can be observed on MRS spectra obtained from samples without drawing and uniaxially drawn. The temperatures associated to these relaxations for different EVA contents in the blends are given in Table 1. The transition noted β_{PP} is assigned to a PP crystalline phase relaxation. For drawn samples, this transition appears only as a shoulder on the tan δ *vs* T curve. The positions of α_{EVA} and α_{PP} relaxations, which are associated to the EVA and PP motions in the amorphous phases respectively, do not show any significant evolution with the EVA content in the blend. This is a confirmation of the immiscibility of these blends. It can be can noticed that the α_{EVA} relaxation is not influenced by the blend morphology whereas an increase in the temperature associated to the α_{PP} transition is observed in blends containing EVA fibers.

Table 1. MRS values for PP-EVA blends (pressed and drawn samples).

	pressed samples			drawn samples	
% EVA	Tα EVA (°C)	Tα PP (°C)	Tβ PP (°C)	Tα EVA (°C)	Tα PP (°C)
0		6.5	96.1		6.9
2.5	n.o.	6.2	98.3	n.o.	15
5	-27	5.6	98.8	n.o.	14.1
10	-32.7	5.1	91.4	-31.3	11.3
20	-26.5	6.7	96	-28.3	10.7
30	-27.4	5.8	91.7	-36.5	9.1
100	-18.7	3.3		-19.2	

n.o.: not observed
T taken at the maximun of Tan δ

These results can be explained by the reinforcement effect of EVA fibers which favours a decrease in molecular mobility and gives rise to a higher $T_{\alpha PP}$ for drawn samples than for pressed samples.

Results obtained with Dielectric Relaxation Spectroscopy (DRS) on the same blends are significantly different from those observed on MRS spectra. Fig.3 and 4 show the dielectric data (log ε” = f(T)) at frequencies between 0.6 and 39100 Hz for the PP-EVA 90/10 pressed and drawn blend respectively.

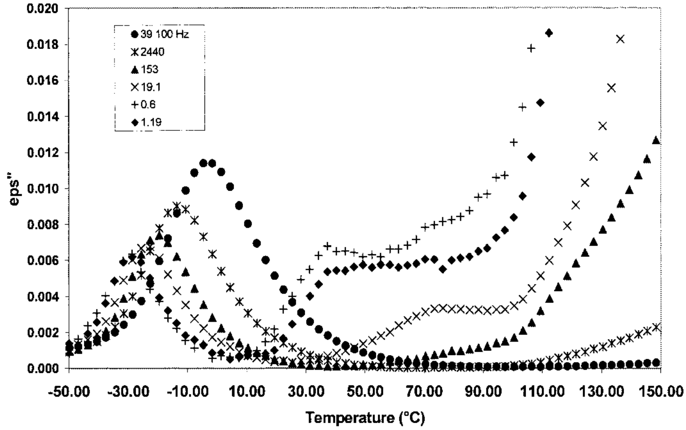


Figure 3. Dielectric loss as a function of temperature at several frequencies for PP-EVA 90/10 blend (pressed sample).

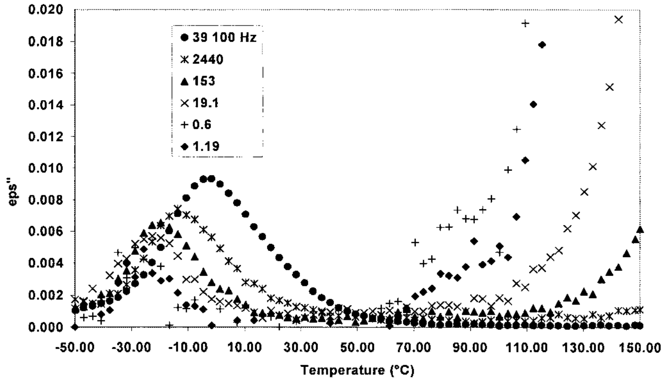


Figure 4. Dielectric loss as a function of temperature at several frequencies for PP-EVA 90/10 blend (drawn sample).

Two relaxation processes are detected for the pressed sample whereas only one relaxation process is observable for the drawn sample. The α_{EVA} relaxation, located at –28.7 °C at 1.19 Hz (pressed sample) and assigned to the EVA glass transition, shows only a slight dependence on the frequency and is observed at similar temperatures for both morphologies. The activation energy estimated for the α_{EVA} process is of the order of 275 kJ.mol^{-1} which is an expected value for such cooperative motions. The PP amorphous phase relaxation (α_{PP} transition) cannot be detected by DRS in these blends because of the low polarity of PP which does not give rise to sufficient fluctuations of dipolar moments to be measured efficiently.

An additional relaxation phenomenon can be noticed on the dielectric spectra of the pressed sample (observed at 52°C for 1.19 Hz) (Fig.3) which seems to be extremely frequency dependent. The activation energy associated to this relaxation can be estimated to 78.5 $kJ.mol^{-1}$ which is characteristic of a weakly activated phenomenon. It could be attributed to an interfacial polarization effect corresponding to the probable migration of the free charges in the applied electrical field which are then blocked at the interface between the EVA droplets and the PP matrix. The values of temperature and frequency observed for this relaxation are in good agreement with theoretical calculations (presented in detail in a further article). Such a process cannot be observed for drawn samples in the range of frequency accessible in the present work. In fact, the modification of the EVA morphology directly influences the shape factor A (length of the long a to b short axis ratio for spheroids), resulting in too long relaxation times (too low frequencies) which are not experimentally measurable.

Conclusion

The dynamic and dielectric mechanical behaviours of PP-EVA blends have been reported as a function of morphology. Both DRS and MRS give evidence of the α-relaxation associated to the EVA glass transition without significant influence of EVA morphology. In contrast, a reinforcement effect is obtained with EVA fibers that contributes to a decrease in the mobility of PP, and therefore shifts the mechanical α_{PP}-relaxation to higher temperatures. An interfacial polarization effect is evidenced in some blends. Further investigations are in progress to obtain a better understanding of this phenomenon occurring in such heterogeneous systems in relation to the morphology of the dispersed phase.

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