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Solid state NMR study of poly(methyl methacrylate)/polyvinylpyrrolidone blends

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Abstract

The behaviour of poly(methyl methacrylate)/polyvinylpyrrolidone (PNMA/PVP) blends was investigated by solid state nuclear magnetic resonance (NMR) using proton spin-lattice relaxation time in the rotating frame ($T_1^H\rho$), which was measured from the variable contact time experiment. From $T_1^H\rho$ relaxation measurements scale, it was possible to obtain a response of the degree of intimacy mixture of polymer blend components. Good compatibility was observed for all proportions studied, as a consequence of the interaction process of blends components.

Introduction

The main purpose of this work is to study the PMMA/PVP blends and improve the behaviour of these materials. Since PVP has a hydrophilic characteristic and the PMMA is transparent, their mixtures are expected to present good properties, like membranes. We have chosen solid state NMR spectroscopy to obtain information on molecular dynamics, and know about the behaviour of these materials.

Nuclear magnetic resonance permits the development of studies on chemical structure and molecular dynamics of solid polymers. Various relaxation measurements are used to elucidate polymer dynamics in the solid state. The principal advantage of cross-polarisation magic angle spinning (CPMAS) experiments, is that resolution allows relaxation data to be obtained on each resolved carbon[1-12]. In this work has been analysed proton spin-lattice relaxation time in the rotating frame for each resolved carbon[12,13].

Experimental

Sample preparation: films of PVP, PMMA and their blends with different compositions (up to 60% by weight of PVP) were prepared in solution using $CHCl_3$ as solvent, at 60°C. The solutions were cast onto plates and kept in a dissector at room temperature for one week. After that, the films were removed, dried in a vacuum oven at 50°C for 48 hours and stored at room temperature in a dissector.

NMR measurements: all NMR spectra were obtained on a VARIAN VXR 300 spectrometer operating at 299.9MHz and 75.4MHz for ^1H and ^{13}C, respectively. All experiments were done at ambient probe temperature and were performed using gated high decoupling. A zirconium oxide rotor of 7mm diameter with Kel-F caps were used to acquire the NMR spectra at rates of 5.5 kHz. ^{13}C spectra are referenced to the chemical

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shift of the methyl group carbons of hexamethylbenzene (17.3ppm). The ^{13}C NMR spectra were carried out in the cross-polarisation mode with magic angle spinning , using 90° pulse. For the variable contact-time (VCT), a range of contact time was established from 200 to 8,000 μsec. Proton $T_1\rho$ values were determined from the intensity decay of ^{13}C peaks with increasing contact-times, using a computer program.

Results and Discussion

The proton $T_1\rho$ evaluates the changes in the microstructure and the molecular mobility in polymer blends. It also permits to verify the homogeneity in the polymer systems as it is sensitive to the spatial proximity of chains. Generally speaking, for a compatible blend, just one value of this parameter is found. More than one value is an indication that at least two domains with distinct mobilities can be found. However, when proton $T_1\rho$ is measured by the variable contact-time experiment (VCT), this parameter is obtained from the intensity decay for all resolved carbons. So, one obtain the value of proton $T_1\rho$ for all types of hydrogen, which permits to evaluate the behaviour of the sample. Actually, not even all the values of proton $T_1\rho$ change with the variations in the samples, like an addition of other polymer or a plasticizer. There are some types of carbons nuclei that do not take part of the interaction process between different polymer components. For example the rigid phase or crystalline phase relaxation time and chemical shifts do not change with the addition of other polymer, because the CP rates of these carbons do not vary with the environment. However, a significant change in this parameter and the chemical shift values can be detected where the interaction process occurs. The values of proton $T_1\rho$ measured from the VCT are intimately linked with the process of polarisation transfer and to the chemical shift values for the type of carbon that they are linked. As the proton $T_1\rho$ are also sensitive to the proximity of protonated chains to one another, the distance between two protonated chains are directly related to the proton-proton spin diffusion. If the polymer blends chains components are very much close to each other, the spin-spin communication is good; but, if the spatial proximity of chains is not close enough the spin-spin communication can not be detected.

To interpret the results obtained, we have chosen the NMR signal of the carbonyl group to understand the behaviour of the blends, considering that this group makes part of the interaction process. Although, there is no proton directly linked to the carbonyl group, the nearest protons are responsible for the relaxation of this group in the rotating frame, during the cross-polarisation process. And it can inform on the behaviour of blend compositions when different proportions of PVP is added to PMMA. In this sense the spin-spin communication, among the chains can show the effect caused by PVP incorporation in the cross-polarisation mode of PMMA.

Table I shows the values of proton $T_1\rho$ and the chemical shifts found for the carbonyl group of the PMMA/PVP blends as the PVP content increases. Proton $T_1\rho$ data showed that just one value of this parameter for the carbonyl group was found. This fact shows that there is a communication between both blends components.

Table 1 - Proton $T_1\rho$ values of the carbonyl group of PMMA/PVP blends and the pure homopolymers

PMMA/PVP proportion	$T_1^H\rho$ (mesc)	δ (ppm)
0/100	2.3	177.2
90/10	4.3	178.2
80/20	4.2	178.2
70/30	3.9	178.2
60/40	4.5	177.2
55/45	3.8	177.1
50/50	4.1	177.1
40/60	5.3	177.5
100/0	5.1	178.4

According to the Table 1, PVP showed a low proton $T_1\rho$ value, as a consequence of being constituted for rigid domain, due to the packing of chains. Up to 30% of PVP no change in the chemical shift value of the carbonyl of PMMA was observed. However, an influence of PMMA on PVP domain was extracted by an increase of proton $T_1\rho$ value in relation to the pure PVP and a slight decrease concerned to the pure PMMA. PMMA affects PVP relaxation up to 30% of PVP, probably due to a smaller extent of PVP phases. From 40% to 50% of PVP it was registered a decrease in the chemical shift value of pure PVP and the proton $T_1\rho$ are higher than pure PVP and a little smaller than PMMA. We also observed that the distribution form of the variable contact-time decay showed two optimum contact-times (200 μsec and 800 μsec) for these proportions, which is related to a phase separation. Analysing the 40/60 proportion, the chemical shift of the carbonyl group is between the two homopolymers and the value of relaxation parameter is higher than the other one. As a result two situations can be happening: one can be related to the plasticization effect caused by PVP action as its domains are now better dispersed, and the other one is attributed to the phase separation.

Conclusion

From the NMR carbon-13 CPMAS variable contact time study of PMMA/PVP blends it was observed some spin-spin communication at molecular level. The proton spin-lattice relaxation time in the rotating frame was able to show an interaction between both components in the blends compositions.

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