The Compatibility Study of Polycarbonate–Polyvinyl Pyrrolidone Blend Using High-Resolution Solid-State Nuclear Magnetic Resonance

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ABSTRACT: The combining nuclear magnetic resonance techniques in the solid state permit the evaluation of the polymeric systems homogeneity. In the polycarbonate–poly(vinyl pyrrolidone) (PVP) blends, the response of proton spin–lattice relaxation time in the rotating frame was the determinant to obtain information on the transition when the quantity of PVP is close to 40% by weight and a better organization of amorphous phase was detected. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67**: 449–453, 1998

Key words: compatibility; polycarbonate; PVP; solid state NMR

INTRODUCTION

It is well known that increasing the *n*-vinyl pyrrolidone content increases the hydrophilic character of a sample and also the adhesiveness in the blends. Surface-active properties usually increase with increasing vinyl pyrrolidone content. Poly(vinyl pyrrolidone) has been found to be compatible with many natural and synthetic resins as well as with many inorganic salts.[1] Several uses can be found for this class of polymers in pharmaceuticals,[2] adhesives, and stabilizers.[3] Because of the diversity of poly(vinyl pyrrolidone) uses and its compatibility with vinylpolymers, blends with polycarbonate have been studied in the present work by applying nuclear magnetic resonance (NMR) at solid state. NMR is a powerful spectroscopy to determine chemical interaction and mobility.[4–10] As for the study of PC–PVP blends, we have been using the most powerful NMR solid-state techniques for a better understanding of the behavior of these blends, such as magic angle spinning (MAS), in order to observe the flexible region; cross-polarization magic angle spinning (CPMAS), to characterize the chemical structure; variation contact time to evaluate the molecular mobility and proton spin–lattice relaxation time in the rotating frame, measured from carbon 13 CPMAS spectra used to obtain a NMR response of solid polymeric blend compatibility.

EXPERIMENTAL

Samples Preparation

Films of poly(vinyl pyrrolidone) (PVP), polycarbonate (PC), and their blends with different compositions (up to 70% by weight) were prepared by solution using $CHCl_3$ as a solvent. The temperature used was 60°C. The solutions were cast onto plates and kept in a dessicator at room temperature for one week. After that, the films were removed dried in a vaccum oven at 50°C for 48 hours and stored at room temperature in a dessicator.
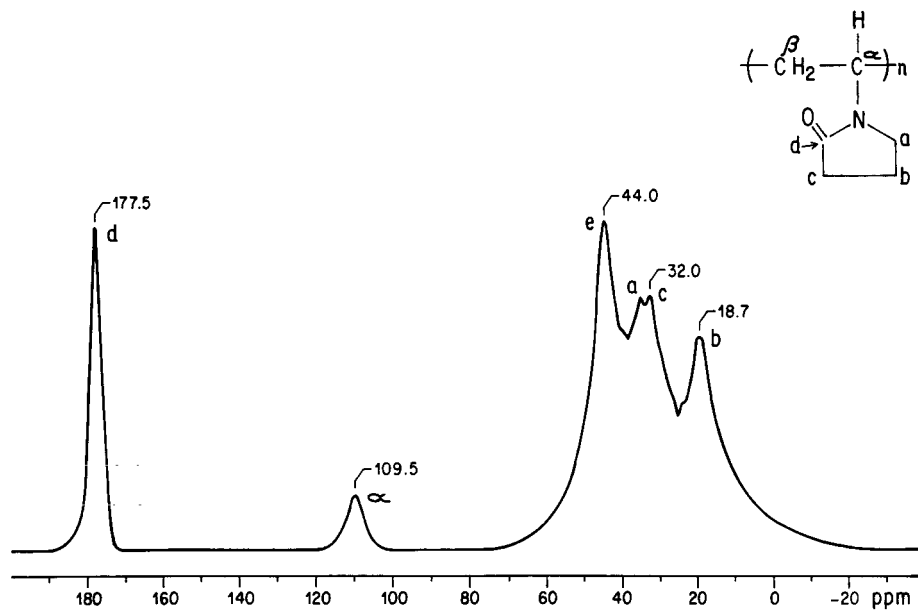
Figure 1 ^{13}C-NMR CP–MAS spectrum of PVP.

NMR Measurements

All NMR spectra were obtained on a Varian VXR 300 spectrometer operating at 299.9 MHz and 75.4 MHz for ^{1}H and ^{13}C, respectively. All experiments were done at ambient probe temperature and were performed using gated high-power decoupling. A zirconium oxide rotor of 7 mm diameter with Kel-F caps were used to acquire the NMR spectra at rates of 6.8 kHz. ^{13}Carbon spectra re-ferred to the chemical shift of the methyl group carbons of hexamethyl benzene (17.3 ppm). The ^{13}C were carried out in the cross-polarization mode with magic-angle spinning (CP–MAS), using a 90° spectral with 50 kHz; and CP–MAS with dipolar dephasing (CP–MAS–DD), where the dephasing time was 40 μs and variable contact time (VCT). A range of contact time was established as 50 to 8000 μs. Proton $T_1\rho$ were determined from the intensity attenuation of ^{13}C peaks with
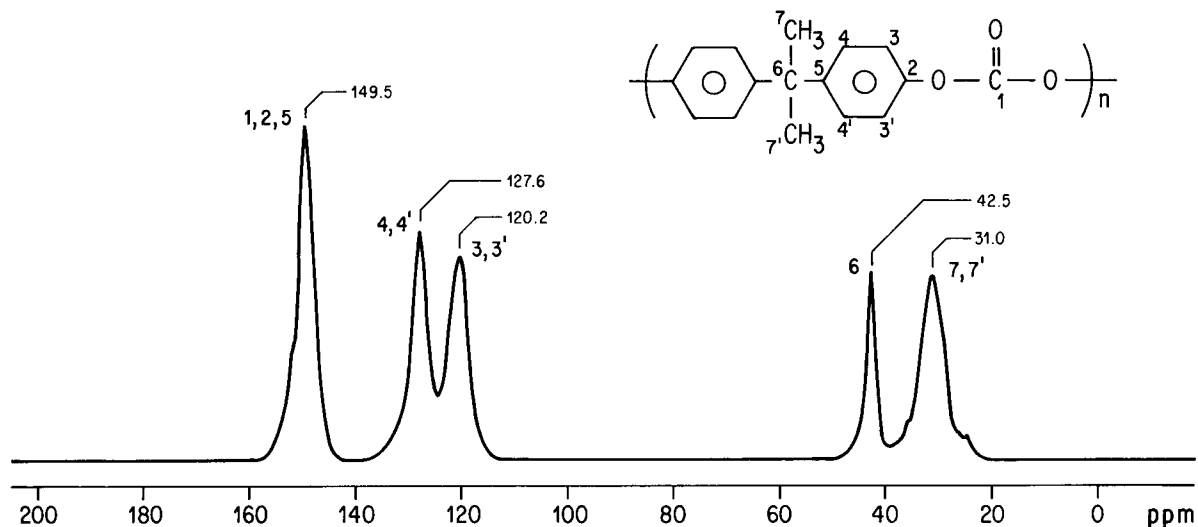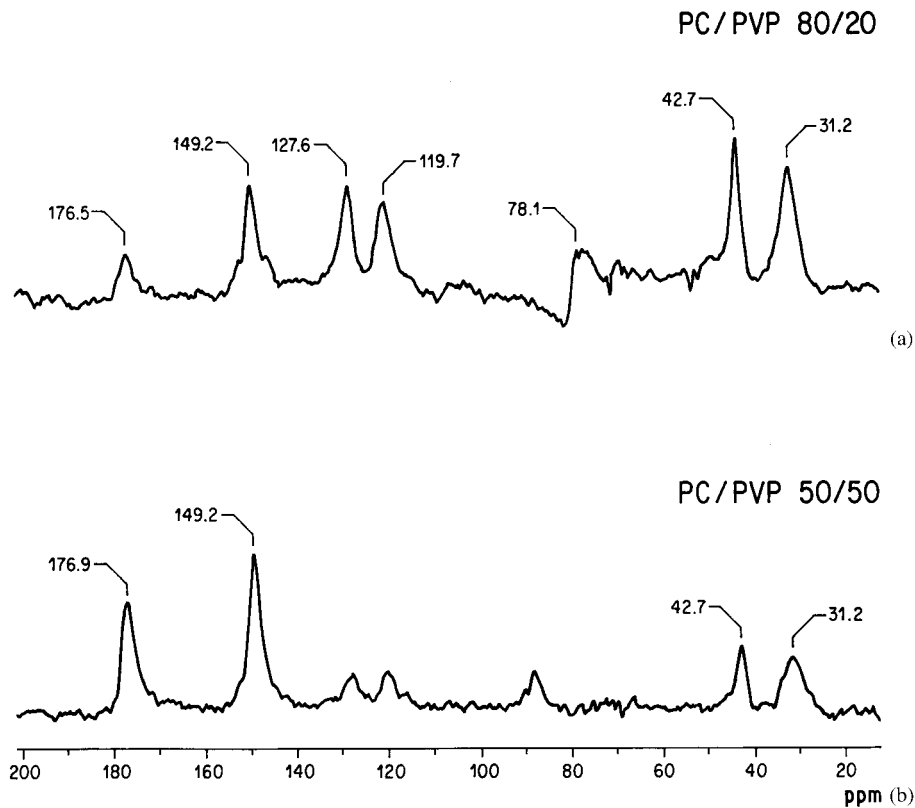

Figure 2 ^{13}C-NMR CP–MAS spectrum of PC.

PC / PVP 80/20

(a)

PC / PVP 50/50

(b)

Figure 3 ^{13}C-NMR CP–MAS–DD spectra of PC–PVP blends: (a) 80 : 20 composition and (b) 50 : 50 composition.

RESULTS AND DISCUSSION

Since the NMR is well established for studying the structure and dynamics of solid polymers, the MAS technique can be applied to verify the flexible region present in a polymer system. In studies using MAS technique, it was observed that the polycarbonate presents two domains with distinct mobilities. In blends of PC–PVP, for all compositions, only signals from PC were detected when the delay time was short enough to detect only the flexible phase. The interesting fact was that even with 50% of PVP, the NMR signals assigned still belonged to the polycarbonate.

The carbon 13 CP–MAS spectra of PVP, PC, and all compositions were also recorded. The assignments of the PVP resonance are shown in Figure 1. These assignments were our contribution, based on a variable contact time experiment. The resolved resonance assigned as a and c could also be distinct only in a specific contact time in the cross-polarization array. Figure 2 shows the assignments of PC lines based on the literature.[11]

Considering the dipolar dephasing experiment, the ^{1}H decoupler was turned off for 40 μs before data aquisition started; this is a treatment that
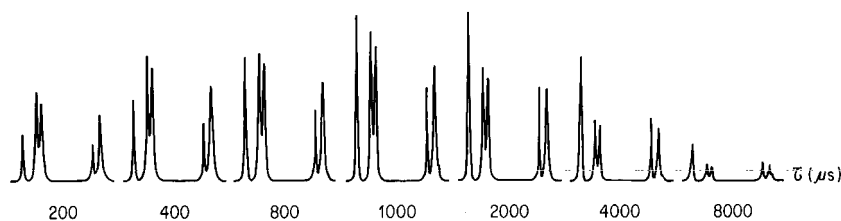
increasing contact time using a computer program.
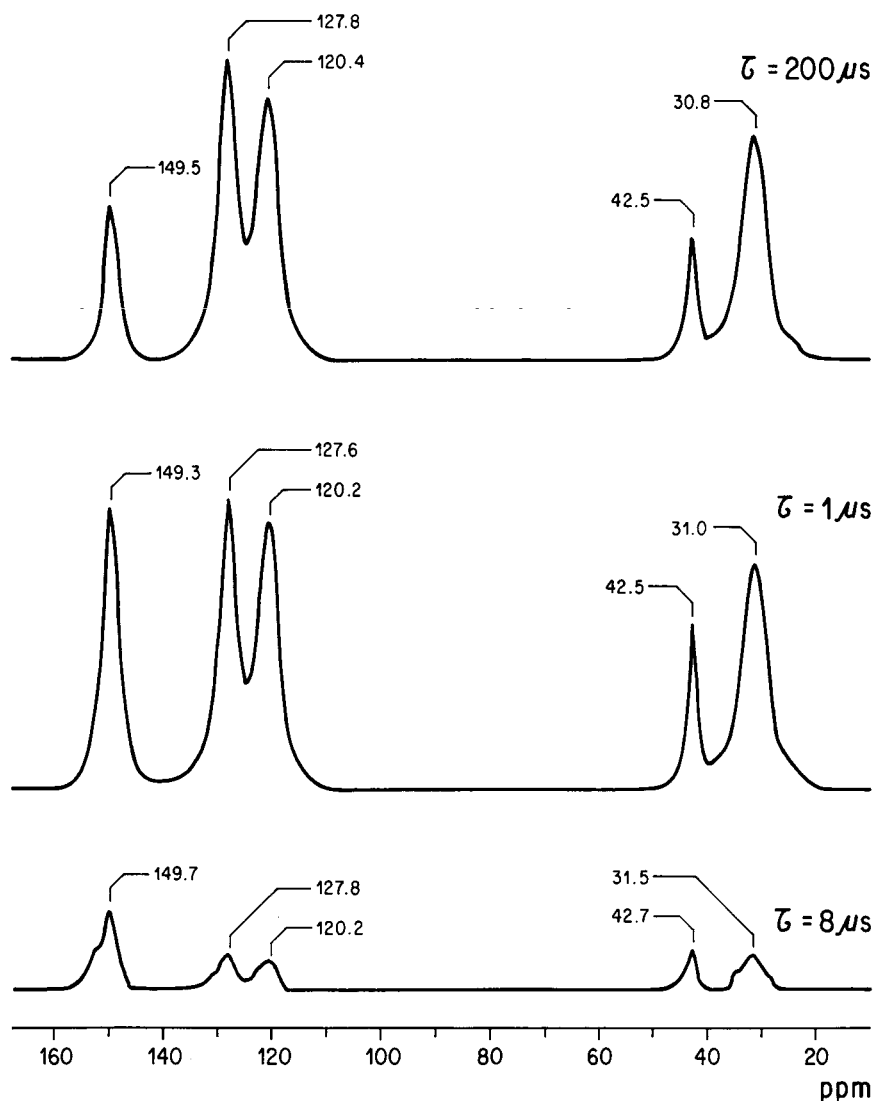

Figure 4 Variable contact time experiment of PC.

Figure 5 ^{13}C-NMR spectra of PC at three contact times (200 μs, 1 ms, and 8 ms).

typically quenches signals due to the solid phase because strong dipolar interactions with linked protons, and nonprotonated carbons were detected. However, carbons that have rapid rotation, even in solids, attenuate ^{13}C–^{1}H dipolar interactions, such as methyl carbons, can also be detected. Two different compositions [Fig. 3(a) and (b)] were analyzed by this technique; the resonance lines detected by CP–MAS–DD were from the mobile region, and the NMR lines detected come from either polycarbonate or PVP, which confirmed that the interaction between both polymers occurs in the amorphous phase.

The interpretation of the decay form of variable contact time experiment can be able to help us to understand the behavior of molecular dynamic in

a polymeric system.[4,10,12,13] Figure 4 shows the variable contact time experiment for the PC. In this experiment, the decay form is specifically well distributed along the contact times. Figure 5 exhibits the three distinct NMR carbon-13 spectra of PC at different contact times, and no difference in the chemical shift was detected.

NMR offers numerous ways to study dynamic aspects over a large range of characteristic rates. Various relaxations measurements have utility for elucidating polymer dynamics in the solid state. In this work, the compatibility and the interaction of the blends were studied by proton spin–lattice relaxation time in the rotating frame by using the variable contact time experiment. In this way, these transfers track the decay of the

protons after having been placed in the rotating frame so that, in NMR, the proximity of molecular units is probed by spin diffusion, which is most effective among protons. Table I shows the values of proton spin–lattice relaxation time in the rotating frame for the carbonyl group of PC and the blends compositions.

The $T_1\rho$ of these protons are sensitive to spatially dependent proton–proton spin diffusion. Thus, in a blend of two protonated compounds, they are sensitive to the proximity of protonated chains to one another. The result is that the cross-polarization transfers between protons in the two components can be used to characterize the homogeneity of the mixture. From Table I, it can be verified that the systems seem to be compatible. The increase in the proton $T_1\rho$, when PVP is added to a polycarbonate, indicates that the PVP acts as a plasticizer. Another interesting observation is related to the 60 : 40 blend. In this composition, a change in the value of proton $T_1\rho$ parameter is an indication that the two following situations can be happening: one is related to the separation phase; the other one is attributed to a change in the configurational arrangement.

The values of the proton $T_1\rho$ for the carbonyl group belonging to the PVP polymer present in it and in their blends are shown in Table II.

From Table II, it is clear that changes in the amorphous phase occur in the system when the quantity of PVP is close to 40% by weight. These changes can be interpreted in terms of better organization of amorphous phase through the increase of momentary freedom in relation to the molecular motion of chains.

CONCLUSION

In accordance with the main purpose of this work, the NMR technique gave detailed information on

Table I   Proton Spin–Lattice Relaxation Time in the Rotating Frame of the Carbonyl of PC, PVP, and Their Blends

PC to PVP Proportions	$T_1^H\rho$ (ms)
100 : 0	3.3
90 : 10	5.9
80 : 20	5.8
70 : 30	5.8
60 : 40	3.9
55 : 45	9.3
50 : 50	5.8
60 : 40	4.8

Table II   Proton Spin–Lattice Relaxation Time in the Rotating Frame of the Carbonyl of PVP and Their Blends

PC to PVP Proportions	$T_1^H\rho$ (ms)
0 : 100	2.3
70 : 30	3.7
60 : 40	3.2
55 : 45	4.9
50 : 50	6.3
60 : 40	4.8

the compatibility of blends. Therefore, combining results from more than one NMR solid techniques enables one to better understand the interaction process of polymer blends in the amorphous phase. In the system investigated, based on the strong interaction, a wide range of compatibility was found.

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