NMR Study of Poly(vinylpyrrolidone)/Poly(ethylene oxide) Blends

TERESINHA M. F. F. DINIZ, MARIA I. B. TAVARES

Centro de Tecnologia, Cidade Universitária, Ilha do Fundão, Inst. de Macromoleculas Professora Eloisa Mano, Univ. Federal do Rio de Janeiro, Rio de Janeiro, CP 68525, Brazil

ABSTRACT: Development of polymeric blends has become very important for polymer industries because they have been shown to be successful and versatile alternatives to obtain new polymers. In this work binary blends formed by poly(vinylpyrrolidone) (PVP) and poly(ethylene oxide) (PEO) were studied by solution and solid-state NMR to determine their physical interaction, homogeneity, and compatibility for use as membranes to separate water/alcohol. The NMR results allowed us to acquire information on the microstructure and molecular dynamic behavior of polymer blends. From the NMR solution it was possible to evaluate the microstructure: PVP presented a preferential syndiotactic distribution sequence and PEO presented two regions, one crystalline and the other amorphous. Considering the solid-state NMR results it was possible to evaluate the molecular dynamics and all binary blends, showing that PEO behaves as a plasticizer; some intermolecular interaction was also observed. An important point was to evaluate the microstructure of the carbonyl PVP using cross polarization/magic-angle spinning (CP/MAS) and CP/MAS/dipolar decoupling that was not observed before. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2820–2823, 2002

Key words: poly(vinyl pyrrolidone); poly(ethylene oxide); syndiotacticity; microstructure

INTRODUCTION

Because polymers and polymer blends can be studied in depth by nuclear magnetic resonance (NMR), both in solution and in the solid state, we chose this method of spectroscopy to obtain response of the chemical and dynamic behavior of the blends formed by poly(vinylpyrrolidone) (PVP)/poly(ethylene oxide) (PEO) in different proportions.[1–8] The main purpose of this work was to evaluate the behavior of PVP/PEO blends in relation to their microstructure and molecular mobility. Solution and solid-state NMR were employed because of the particular contributions of both techniques. Changes in the line shapes and/or frequency of the resonance signals of the pure polymers compared to those of blend components were used as evidence of the interactions between the blend components.[5] Besides, the proton spin–lattice relaxation times in the rotating frame $(T_1^H \rho)$ allowed us to estimate the scale of miscibility of a polymer pair.[6–8]

EXPERIMENTAL

Blends

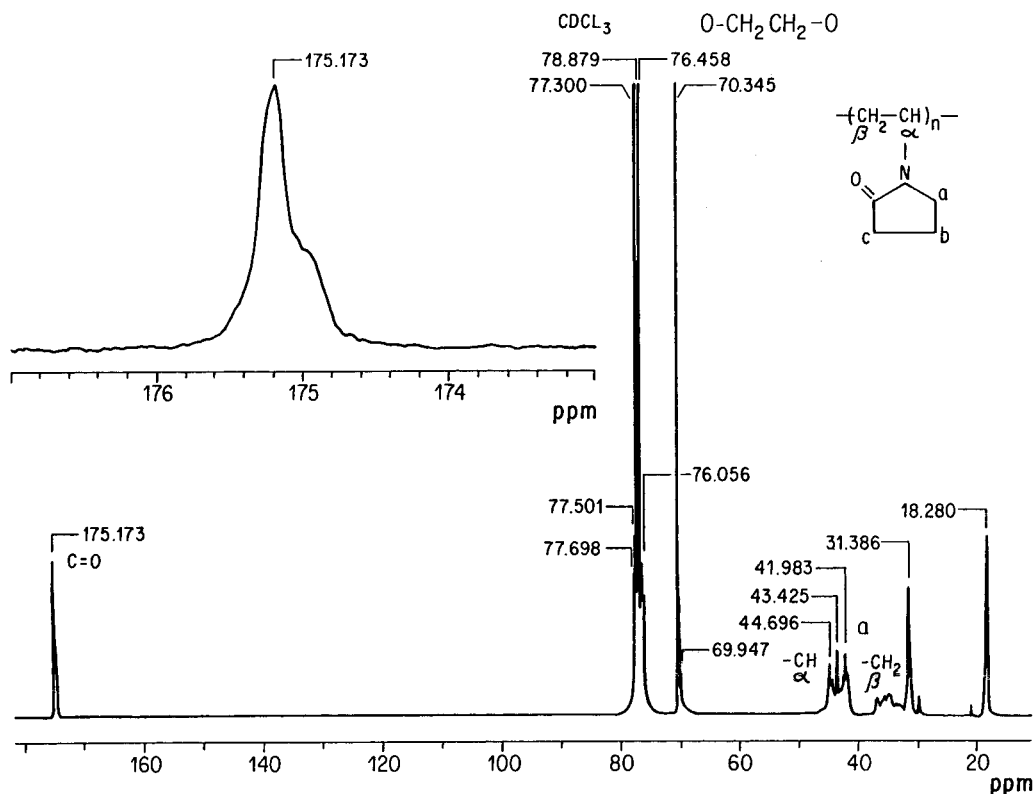The binary blends formed by PVP/PEO were prepared by solution of chloroform at different pro-

Figure 1 ^{13}C-NMR solution spectrum of PVP/PEO 90/10 blend.

portions, 90/10, 70/30, and 50/50. They were cast onto plates and kept in a dissector for 1 week, after which they were put in a vacuum oven at 50°C for 2 weeks to completely eliminate the residual solvent. This procedure was evaluated by infrared spectroscopy using the chloroform band.

NMR

All solution NMR spectra were obtained on a Varian Mercury 300 (Varian Associates, Palo Alto, CA) and the solid spectra on a Inova 300 spectrometer, operating at 75.4 MHz for ^{13}C. The solution ^{13}C spectra were obtained in quantitative conditions. All solid NMR experiments were obtained at the ambient probe temperature and were performed using gated high decoupling. A zirconium oxide rotor (7-mm diameter) was used to acquire the NMR spectra at rates of 5.8 kHz. The ^{13}C-NMR spectra were carried out in the magic-angle spinning (MAS) and cross polarization (CP)/MAS. For the variable-contact time (VCT), a range of contact time was established from 0.2 to 8 ms. $T_1^H \rho$ values were determined from the intensity decay of ^{13}C peaks with increasing contact times and also from the delayed-

contact time (DCT), with a spin-locking range from 1 to 8 ms.

RESULTS AND DISCUSSION

Solution NMR

From the ^{13}C-NMR solution spectra of PVP/PEO blends (Fig. 1), all NMR signals from both polymers were detected and no influence or overlapping signals were observed. From the integration area of all types of carbons that probably are taking place in the interaction, no change in the microstructure was detected, showing that the interaction process occurs in the same way for all the microstructure sequences. By analyzing the form of carbonyl signal (Fig. 2), it was observed that up to 30% of PEO no significant change in the form was detected. Therefore, when the PEO is around 50% a very small change in the form could be observed, in which the signal becomes slightly wider, which can be a consequence of phase separation.

Solid-State NMR

The PVP was investigated by the basic MAS ^{13}C-NMR, routine CP/MAS ^{13}C, and by protons spin–
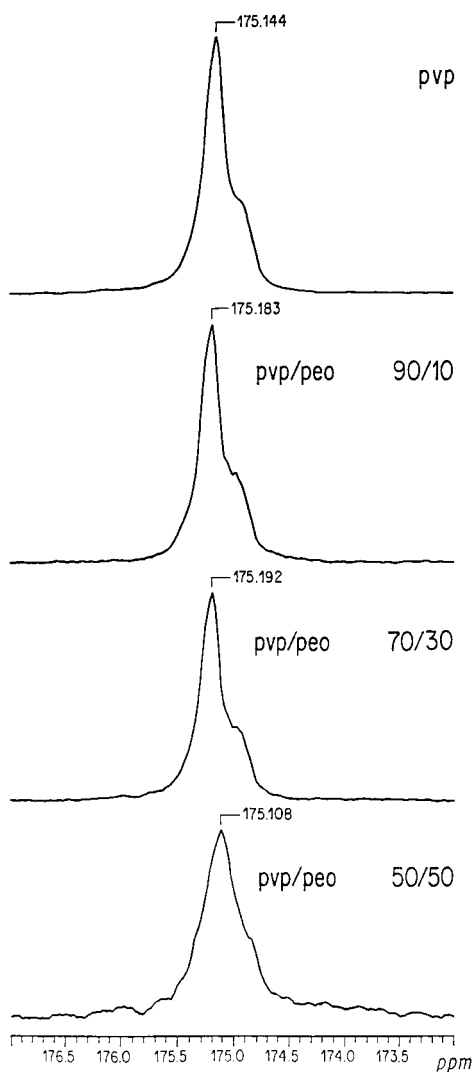
Figure 2 ^{13}C-NMR solution spectra of the carbonyl signal for the PVP and their blends with PEO at 90/10, 70/30, and 50/50 proportions.

lattice relaxation time in the rotating frame. The MAS and CP/MAS showed wide signals that are common for amorphous materials, and corroborate what was observed by solution NMR with regard to the detection of the different microstructure sequences. The $T_1^H\rho$ for the carbonyl group is 2.3 ms, which is a typical value for amorphous rigid materials.

PEO was also analyzed by MAS ^{13}C and CP/MAS ^{13}C, and in both NMR spectra one sharp signal located at about 70 ppm was attributed to the CH$_2$—O from the backbone chain assigned to the crystalline phase, and a small signal at about 69.5 ppm assigned to the CH$_2$—O in the amorphous or mobile phase.

MAS ^{13}C-NMR spectra of the binary blends were obtained using a short delay time between 90° pulses to observe only the mobile region. In this case, just the PEO signal was detected. The value of the chemical shift of the signal was 71.0 ppm.

CP/MAS ^{13}C-NMR spectra showed signals from both polymers (Fig. 3). The chemical shifts detected for the polymer blends did not change the values in relation to those of the pure polymers. In solids the linewidths are greater than those in liquids, which makes it difficult to detect small differences in the chemical shift resulting from specific interaction.

A series of VCT CP/MAS ^{13}C-NMR spectra were also recorded and the rate of intensity decay provided evidence of homogeneity of the blends and also permitted us to measure the proton spin–lattice relaxation time in the rotating frame. The $T_1^H\rho$ value for the carbonyl group (178.2 ppm), obtained for PVP, was 2.3 ms and the values of this parameter for the samples changed to high values, indicating that PEO can act as a
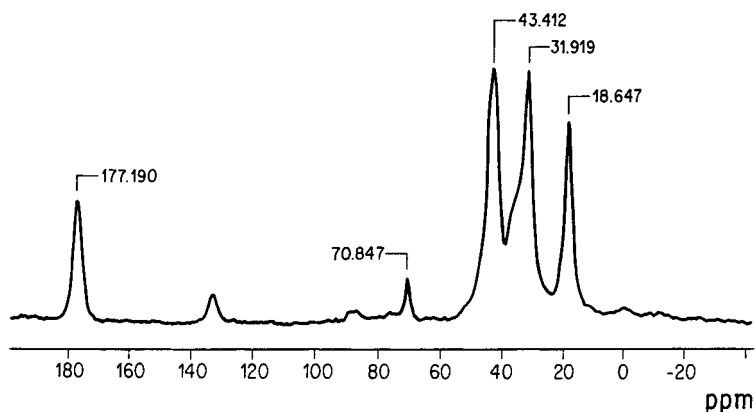
Figure 3 CPMAS ^{13}C-NMR spectrum of 70/30 proportion.

plasticizer for PVP while a phase-separation process is also occurring.

The $T_1^H\rho$ relaxation parameter for the carbonyl group was measured by two distinct experiments, that is, VCT and DCT. These two experiments give the response of molecular miscibility and molecular homogeneity. Values of the $T_1^H\rho$ parameter for PVP/PEO blends, obtained by VCT and DCT, are listed in Tables I and II, respectively. From the values found for $T_1^H\rho$, it is clear that all compositions are highly plasticized.

By analyzing the relaxation data listed in Table II, we can see that for the 80/20 and 70/30 blends two phenomena are simultaneously taking place, one related to the plasticization effect and the other one referring to the homogeneity of the blends, confirming that these binary blends are partially miscible. However, in the 50/50 blend the value of $T_1^H\rho$ decreased at least to one half of the values for the other compositions, which establishes that these blends are not homogeneous and the plasticization effect is not as strong as that for the other two, while a phase separation can also be occurring.

Comparing both $T_1^H\rho$ measurements, the difference between the values of 80/20 and 70/30 blends did not change. However, for the 50/50 composition this difference is higher, which can be attributed to the phase-separation process.

CONCLUSIONS

The NMR results allowed us to acquire information on the microstructure and molecular dynamic behavior of polymer blends. From the NMR solution it was possible to evaluate the microstructure: PVP presented a preferential syndiotactic distribution sequence and PEO presented two regions, one crystalline and the other amorphous. Considering the solid-state NMR results it was possible to evaluate the molecular dynamics and all binary blends, showing that PEO behaves as a plasticizer. From this study it was determined that these binary blends are characterized by partial miscibility.

Table I $T_1^H\rho$ Values for the Carbonyl Group, Obtained by VCT

PVP/PEO (%)	$T_1^H\rho$ (ms)
100/0	2.3
80/20	16.2
70/30	15.0
50/50	17.5

Table II $T_1^H\rho$ Values for the Carbonyl Group, Obtained by DCT

PVP/PEO (%)	$T_1^H\rho$ (ms)
100/0	2.3
80/20	9.1
70/30	8.0
50/50	4.0

REFERENCES

1. Souza, C. M. G.; Pacheco, C. R.; Tavares, M. I. B. J Appl Polym Sci 1999, 73, 221.
2. Stejskal, E. O.; Memory, J. D. High Resolution NMR in the Solid State; Oxford Univ. Press: New York, 1994.
3. Bovey, F. A.; Mirau, P. A. NMR of Polymers; Academic Press: New York, 1996.
4. Simmons, A.; Natanshon, A. Macromolecules 1991, 24, 3651.
5. Schaefer, J.; Stejskal, E. O.; Buchdhal, R. Macromolecules 1977, 10, 384.
6. Schaefer, J.; Sefcik, M. D.; Stejskal, E. O.; McKay, R. A. Macromolecules 1984, 17, 1118.
7. Silva, N. M.; Tavares, M. I. B.; Stejskal, E. O. Macromolecules 2000, 33, 115.
8. Stejskal, E. O.; Schaefer, J.; Sefcik, M. D.; McKay, R. A. Macromolecules 1981, 14, 275.
9. Edbon, J. R.; Huckerby, T. N.; Senogles, E. Polymer 1983, 24, 339.