

# Solid-State Nuclear Magnetic Resonance of the PA6/PC, PA6/PPO, and PA6/PC/PPO Blends

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**ABSTRACT:** The effect of mixing time is very important to plasticization and/or occurrence of chemical reaction between polyamide 6/poly(propylene oxide), polyamide 6/polycarbonate, and polyamide 6/polycarbonate/poly(propylene oxide) blends. The systems were investigated through solid-state carbon-13 cross-polarization magic angle spinning with variable contact time in the NMR experiment. In the systems, polycarbonate can prevent the antiplasticization effect already observed in the polyamide 6/poly(propylene oxide) blend. Therefore, it was verified that the addition of polycarbonate in the polyamide 6/poly(propylene oxide) system causes a hardening of the blend. This fact can be attributed to the restriction of the mobility of the NH group, probably influenced by the type of interaction that occurs in the polyamide 6/polycarbonate/poly(propylene oxide), due to the effect of poly(propylene oxide), which can be act as an interfacial agent promoting a better interaction between polyamide 6 and polycarbonate. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 129–133, 1998

**Key words:** NMR; solid state; PA6/PPO blends; PA6/PC/PPO blends

## INTRODUCTION

Blends with polyamide 6 (PA6), polycarbonate (PC), and poly(propylene oxide) (PPO) have been studied to characterize the heterogeneity of the blends through high-resolution solid-state nuclear magnetic resonance (NMR).<sup>1–3</sup> The magic angle spinning (MAS), cross-polarization/MAS (CP/MAS), variable contact time experiment, and  $T_{1\rho}^H$  and  $T_{CH}$  values can be used to interpret the motion and compatibility of polymer blends.<sup>4,5</sup> The NMR techniques described were used to obtain information on the PA6/PC, PA6/PPO, PC/PPO, and PA6/PC/PPO systems. The high-resolution, cross-polarization magic angle individual

proton and carbon rotating frame relaxation times ( $T_{1\rho}$ 's) were used to characterize chain motions in the kilohertz frequency range. In these experiments, proton  $T_{1\rho}$ 's were obtained from a series of identical matched cross-polarization transfers from protons to carbons initiated at variable times after the protons are spin locked. This way, these transfers track the decay of the protons after they have been placed in the rotating frame. These proton  $T_{1\rho}$ 's 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. The result is that the cross-polarization transfers between protons in the two components can be used to characterize the homogeneity of the mixture. In this work, heterogeneous blends formed by PA6/PPO containing PC have been analyzed by NMR techniques as described previously to obtain informa-

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**Table I Proton Spin-Lattice Relaxation Time in the Rotating Frame of the PA6/PPO, PA6/PC, and PA6/PC/PPO Systems**

Systems	Composition (%)	$T_{1\rho}^H$ (ms)		
		173.5	36.6	30.0 $\delta$ (ppm)
PA6	100/0/0 (220°C, 5 min)	2.9	2.7	2.6
	100/0/0 (240°C, 10 min)	3.7	3.1	2.9
PA6/PPO	97/3 (240°C, 10 min)	3.9	2.9	2.8
	97/3 (240°C, 30 min)	1.8	1.6	1.5
	97/3 (220°C, 5 min)	2.2	2.3	2.0
	95/5 (220°C, 5 min)	2.2	2.3	2.0
	90/10 (220°C, 5 min)	2.4	1.9	1.9
PA6/PC	90/10 (240°C, 10 min)	4.7	3.1	3.0
	90/10 (240°C, 30 min)	1.5	1.7	1.8
	90/10 (240°C, 65 min)	5.1	3.1	2.9
	95/5 (240°C, 30 min)	2.6	2.8	2.7
	90/10 (240°C, 30 min)	1.5	1.7	1.8
	85/15 (240°C, 30 min)	1.9	1.8	2.0
PA6/PC/PPO	92/5/3 (240°C, 10 min)	3.3	2.7	2.8
	92/5/3 (240°C, 30 min)	3.3	2.6	1.8
	92/5/3 (240°C, 65 min)	3.0	2.5	2.6
	92/5/3 (240°C, 65 min)	3.0	2.5	2.6
	90/5/5 (240°C, 65 min)	3.1	2.5	2.4
	85/5/10 (240°C, 65 min)	2.7	2.5	2.5
	85/10/5 (240°C, 10 min)	3.2	2.6	2.4
	85/10/5 (240°C, 30 min)	3.5	2.6	2.6
	85/10/5 (240°C, 65 min)	3.5	2.5	2.5
	87/10/3 (240°C, 65 min)	6.0	3.6	3.5
	85/10/5 (240°C, 65 min)	3.5	2.5	2.5
	80/10/10 (240°C, 65 min)	3.8	2.9	2.6
	82/15/3 (240°C, 65 min)	2.7	2.7	2.7
	80/15/5 (240°C, 65 min)	2.2	2.4	2.5

tion on the behavior of the PA6/PC, PA6/PPO, and PA6/PC/PPO systems.

## EXPERIMENTAL

### Materials

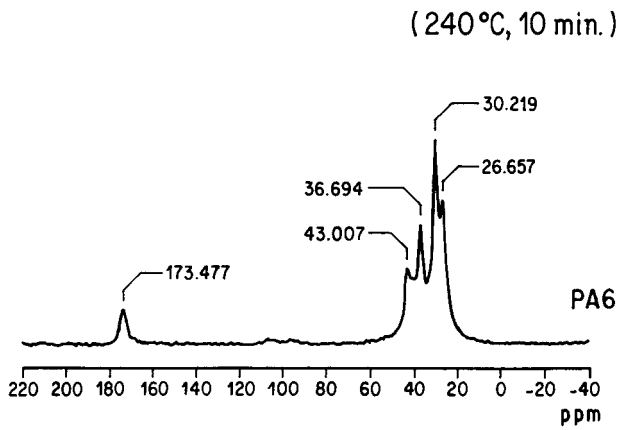
Homopolymers used in this study were commercial: PA6 (NYLODUR, NT2700) of relative viscosity ( $\eta_r$ ) = 2.650–2.750 ( $H_2SO_4$ ),  $NH_2 = 35$ – $40$  mEq/kg, and melt flow index =  $4.13 \pm 0.12$  g/10 min (235°C, 1 kg). They were supplied by DeMil-lus S.A. PC (LEXAN 141,111) of a numerical average molecular weight ( $M_n$ )  $\cong 45,000$  was supplied by Coplen Ind. and Company (General Electric Co.) and PPO of  $M_n \cong 1000$  was supplied by Dow Química S.A.

### Preparation of the Blends

Blends of the homopolymers PA6, PC, and PPO were prepared in a Haake Rheomix 600 cam mixer at  $T = 220^\circ$  and  $240^\circ C$ , at a rotational speed of 30 rpm for 5, 10, 30, and 65 min. Blends of PA6/PPO were obtained with the compositions of 97/3, 95/5, and 90/10% (w/w). PA6/PC blends were obtained with the compositions of 95/5, 90/10, and 85/15% (w/w). PA6/PC/PPO blends were obtained with the compositions of 94/3/3, 92/3/5, 92/5/3, 90/5/5, 85/5/10, 87/10/3, 85/10/5, 80/10/10, 82/15/3, and 80/15/5.

### NMR Spectroscopy

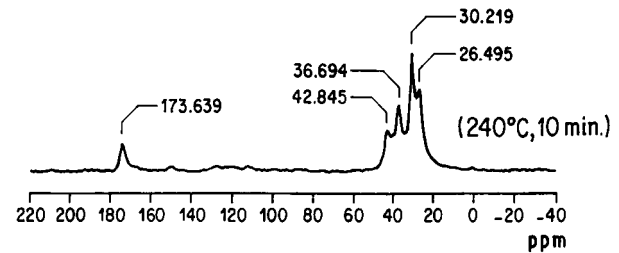
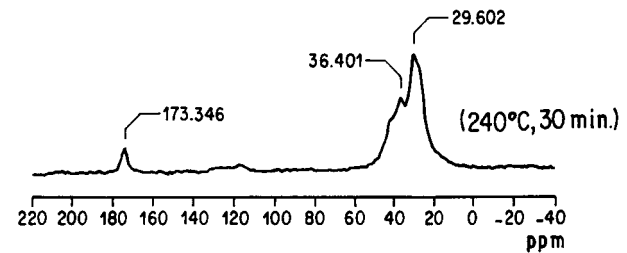
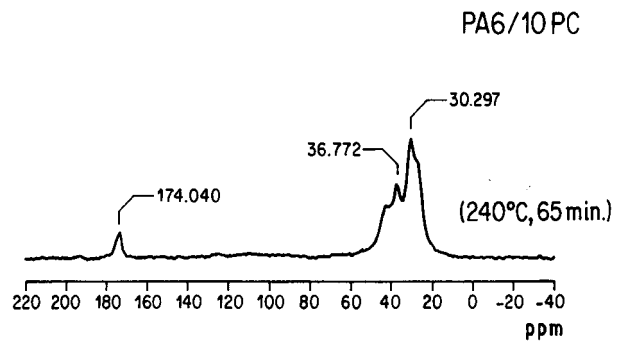
Solid-state  $^{13}C$  CP/MAS NMR spectra were obtained as described in ref. 2.



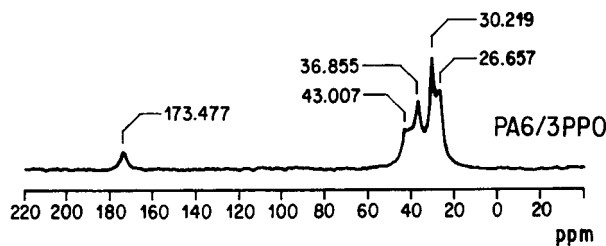
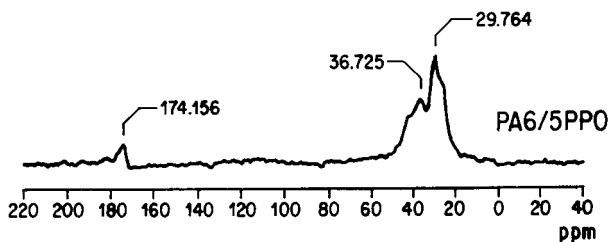
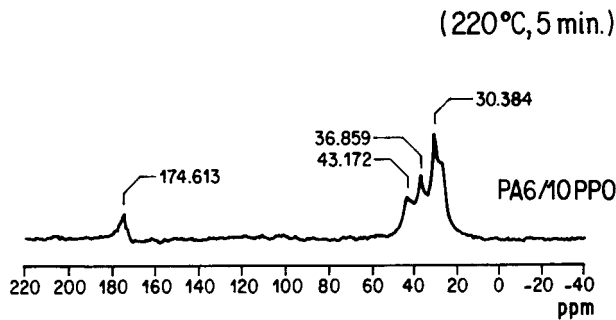
**Figure 1** <sup>13</sup>C NMR CP/MAS spectrum of PA6 film obtained by fusion at 240°C for 10 min.

**RESULTS AND DISCUSSION**

By analyzing the series of CP/MAS spectra, some interesting information was extracted. First, a



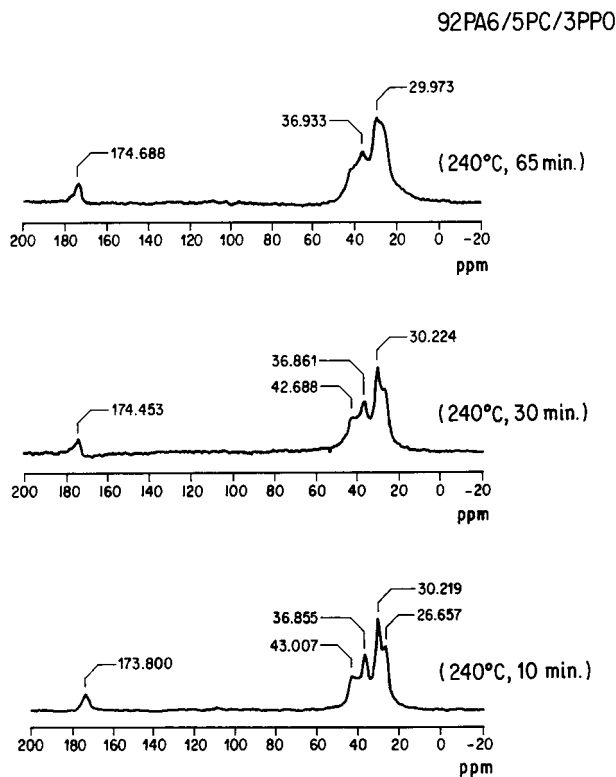
**Figure 3** <sup>13</sup>C NMR CP/MAS spectra of PA6/PC films obtained by fusion for the same composition at different processing times at 240°C.



**Figure 2** <sup>13</sup>C NMR CP/MAS spectra of PA6/PPO films obtained by fusion at different compositions processed at 220°C for 5 min.

broadening of resonance lines in the <sup>13</sup>C CP/MAS spectra for samples prepared at 240°C for 30 and 65 min was detected when chemical reaction occurred between PA6 and PC. It was important to consider the <sup>13</sup>C CP/MAS spectra at short contact times. A displacement in the signals was also observed as a consequence of rigid domains. This was confirmed by a decreasing of  $T_1^H \rho$  values showed in Table I. Figures 1–5 show the CP/MAS spectra of the PA6, PA6/PPO, PA6/PC, and PA6/PC/PPO blends, respectively.

Table I shows, for the PA6/PPO system obtained at 220°C (5 min), a slight decrease in the  $T_1^H \rho$  values when compared with PA6 prepared under the same conditions. This decrease can mean that the mixing time is not enough for the plasticization of PA6. However, the <sup>13</sup>C CP/MAS spectrum of PA6/PPO shows a broadening that may come from a hardening of the sample caused by an antiplasticization effect (Fig. 2).



**Figure 4**  $^{13}\text{C}$  NMR CP/MAS spectra of PA6/PC/PPO films obtained by fusion for the same composition at different processing times at 240°C.

The PA6/PPO system obtained at 240°C (10 min) presents an increase in the  $T_1^H\rho$  value, which can mean a plasticization effect between PA6 and PPO, compared with PA6 obtained under the same conditions. Variation in the  $T_1^H\rho$  parameters shows that the plasticization effect depends much more on the temperature and mixing time than the composition of blends. When the time is equal to 30 min, the system shows a large decrease in the  $T_1^H\rho$  values, which can be related to a strong interaction between PA6 and PPO homopolymers.

Comparing the PA6/PC compositions obtained at distinct times, it is clear that, after 30 min of mixing, there is a large decrease in the value of  $T_1^H\rho$ . Considering different compositions of 95/5, 90/10, and 85/15, the 90/10 proportion showed a large decrease in this parameter, as well. This decrease comes from the formation of rigid domain. Thus, the behavior of these blends can be associated with the occurrence of chemical reaction between the components.

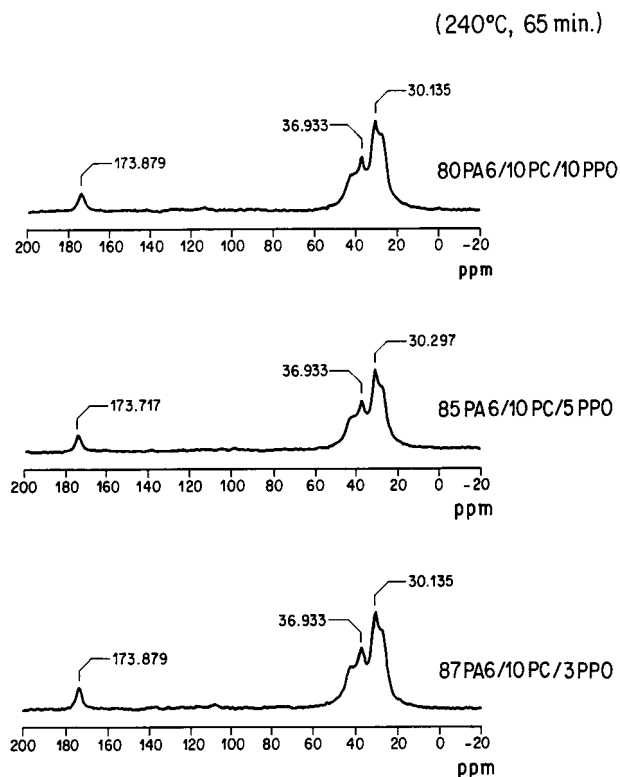
In relation to the blends mixing at 240°C, an interesting observation in the  $T_1^H\rho$  values can be made for the different mixing times. Comparing the values of  $T_1^H\rho$  PA6, it can be seen that, for 10

and 65 min, the values of this parameter increases. In relation to that, two situations can happen to plasticization of PA6, induced by PC or the decrease of molecular weight of the blend components.

Figure 2 exhibits the CP/MAS spectra of the PA6/PC system (90/10% w/w) *versus* mixing time. Broadening in the spectra of the blends processed at 30 and 65 min is observed, which can occur by the chemical reaction between PA6 and PC.

Table I presents the  $T_1^H\rho$  values of the PA6/PC/PPO system, with varying compositions and mixing times. The systems with 5% w/w of PC show an increase in the  $T_1^H\rho$  values when compared with PA6/PC. This increase comes from the PPO effect, which acts as an interfacial agent promoting a better interaction between PA6 and PC.

For the systems that contain 10% w/w of PC, and different proportions of PA6 and PPO, an increase in the  $T_1^H\rho$  value was observed for the lower quantity of PPO, which can be associated with an improvement in the interaction between of PA6 and PC.



**Figure 5**  $^{13}\text{C}$  NMR CP/MAS spectra of PA6/PC/PPO films obtained by fusion at different compositions processed at 240°C for 65 min.

## CONCLUSIONS

In the systems investigated, PC acts as an interfacial agent preventing the antiplasticization effect already observed in the PA6/PPO blend.<sup>1</sup> Therefore, it was verified that the addition of PC in the system PA6/PPO causes hardening of the blend. This fact can be attributed to the restriction of the mobility of the NH group, probably due to the influence of the type of interaction that occurs in the PA6/PC/PPO system.

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