Carbon-13 NMR High-Resolution Study at Solid of Polyamide 6/PPO Blends Containing Compatibilizer–Block Copolymer and Polycarbonate

DILMA ALVES COSTA,[1][2] EDEMILSON P. SILVA,[1] CLARA MARIZE F. OLIVEIRA,[1] MARIA INÊS B. TAVARES[1]

[1] Instituto de Macromoléculas Professora Eloísa Mano-IMA/UFRJ, Cidade Universitária, Centro de Tecnologia, Bloco J, Ilha do fundão, Rio de Janeiro, RJ, Brazil, C.P. 68525, CEP. 21.94-970

[2] Departamento de Tecnologia Química/IT/UFRRJ, Antiga Rio-S.Paulo, Km 47, Itaguaí, RJ, Brazil, CEP. 23.851-970

ABSTRACT: Two types of blends containing polyamide 6 and poly(propylene oxide) (PPO) were prepared. One of them was mixed with polycarbonate (PC) in a Brabender mixer. The other one was prepared in solution with the block copolymer as the interfacial agent. The blends were analyzed by ^{13}C nuclear magnetic resonance techniques at solid state, such as: magic angle spinning (MAS); cross-polarization MAS, and variable contact time experiment. It was observed that the addition of PC in the nylon 6/PPO system causes a hardening of it, which can be attributed to strong links, like a hydrogen bond. The ideal quantity of block copolymer added to a blend to improve the compatibility is between 5 and 10%. An increase of the quantity of this agent probably makes it act as a third component. Therefore, both PC and block copolymer can be used as an interfacial agent for nylon 6/PPO blends in an ideal composition. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 1635–1640, 1997

Key words: polyamide 6; poly(propylene oxide); polycarbonate; blend; melt mixing; block copolymer; NMR

INTRODUCTION

The compatibility of the binary system nylon 6/poly(propylene oxide) (NY6/PPO) has been studied previously by Maria I. B. Tavares and two other coauthors through solid-state nuclear magnetic resonance (NMR) measurements. Techniques such as magic angle spinning (MAS), cross-polarization (CP)/magic angle spinning, and CP/MAS with variable contact time experiment were used to characterize the compatibility of NY6/PPO blends.[1,2]

Two ranges of compatibility between NY6/PPO were found, one from 0.5 to 5% and the other from 10 to 20%. When the PPO content in the polymer is approximately 25% or more, the mixtures become immiscible. The results of differential scanning calorimetry have shown that when the PPO content increases in the blends, two values of glass transition temperature, T_g, were found. Thermogravimetric analysis (TG) has shown that the TG date increased (over NY6 by itself) when a low quantity of PPO was added. However, the values decreased when the PPO quantities increased in the blends. The proton spin-lattice relaxation time in the rotating frame was also registered, and the behavior found was equal to the T_g parameter.[1]

High-resolution solid-state NMR[3–8] has been widely used to characterize the heterogeneity of solid polymers. MAS, CP/MAS, variable contact time experiment, and $T_1^H\rho$ and T_{CH} values can be

---

used to determine the molecular motion and compatibility of blends.[1,3] The high-resolution magic angle techniques used to obtain ^{13}C NMR spectra in solids can be used to measure individual proton and carbon rotating frame relaxation times ($T_1\rho$ values), which are used to characterize chain motions in the kilohertz frequency range. In these experiments, proton $T_1\rho$ values were obtained from a series of identical, matched cross-polarization transfers from protons to carbons begun at variable times after the protons are spin locked. In this way, these transfers track the decay of the protons after they have been placed in the rotating frame. These proton $T_1\rho$ values 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 mixing. In this study, heterogeneous blends formed by polyamide 6 (PA6)/ PPO, containing polycarbonate (PC) or block copolymer, have been analyzed by NMR techniques as described before to obtain information on the behavior of the two systems under investigation.

EXPERIMENTAL

Materials

The homopolymers used in this study were commercial: two types of PA6 were used: NY6 of $M_n \cong 15,262$, supplied by Nitrocarbono S.A., and PA6 (NYLODUR, NT2700) of $\eta_r = 2,650–2,750$ (H_2SO_4); NH_2, 35–40 mequiv/kg; and MFI = 4, 13 ± 0, 12 g/10 min (235°C, 1 kg), supplied by DeMillus S.A. Also used were PC (LEXAN) of $M_n \cong 45,000$, supplied by COPLEN IND. and COM. (General Electric Co.), and PPO of $M_n \cong 1,000$, supplied by Dow Química S.A. The block copolymer of NY6/PPO was synthesized as described in the literature.[9]

Blend Preparation

Blends with the NY6 ($M_n \cong 15,262$) and PPO were prepared in solution state at 115°C for 15 min. The temperature was chosen on the basis of homopolymers to avoid degradation. A sample with 18% of polyoxide (PPO) represented as NY6/ PPO (82/18) was prepared, and the block copolymer was added up to 25% into blends with 10%

of polyoxides (as a rule, the weight percentage of the added copolymer was defined with respect to the total weight of the blend).

The blends of PA6/PPO were prepared in a Brabender mixer at 250°C and at rotational speeds of 45 and 60 rpm, for 3.5 min in a range of compositions of: 99/1, 97/3, 95/5, 90/10, and 85/15% (w/w). PA6/PC was used with compositions of: 99/1, 97/3, and 95/5% (w/w) and a ternary blend formed by PA6/PC/PPO, where the compositions have a different proportion between PC and PPO.

NMR Measurements

Solid-state ^{13}C CP/MAS NMR techniques were performed on a VARIAN VXR 300 spectrometer at room temperature. The hydrogen resonance frequency was 299.9 MHz, and the ^{13}C resonance frequency was 75.4 MHz. The Hartman-Hahn CP matching and dipolar decoupling filed was $\cong 40$ kHz, while a 5-μsec 90° pulse for the ^{13}C nucleus was used for the variable contact time experiment. The contact time varied from 50 to 8,000 μsec, and the MAS rate was 6 kHz. The $T_1^H\rho$ values were obtained from the ^{13}C CP/MAS intensity with increasing contact time. ^{13}C spectra were referred to the chemical shift of the methyl group carbons of hexamethyl benzene (17.3 ppm).

RESULTS AND DISCUSSION

Blends containing PA6 and other condensation polymers such as polyesters, PC, and other polyamides have a common feature. There has been a possibility of an occurrence of intermolecular reactions among the blend components during the mixing process, since the time and temperature of mixing are suitable.[10] The PA6/PC-blends with a relevant extent of interaction and interesting properties can be obtained, because a suitable mixing conditions are applied to increase this thermodynamic miscibility. The miscibility and the interchange reactions in PA6/PC blends prepared by melt mixing have been studied. The results indicate that the blends are partially miscible. An interchange reaction occurs between the two components when they are melt mixed.[10–13]

Because the MAS spectra were recorded in conditions such that only the flexible region can be detected, it was observed that the regions of PA6/ PPO, obtained by the mixing process, present

NYLON 6 / PPO

100 / 0

99 / 1

97 / 3

95/5

PPM

(a)

NYLON 6 / PPO

100 / 0

99 / 1

97 / 3

95 / 5

(b)
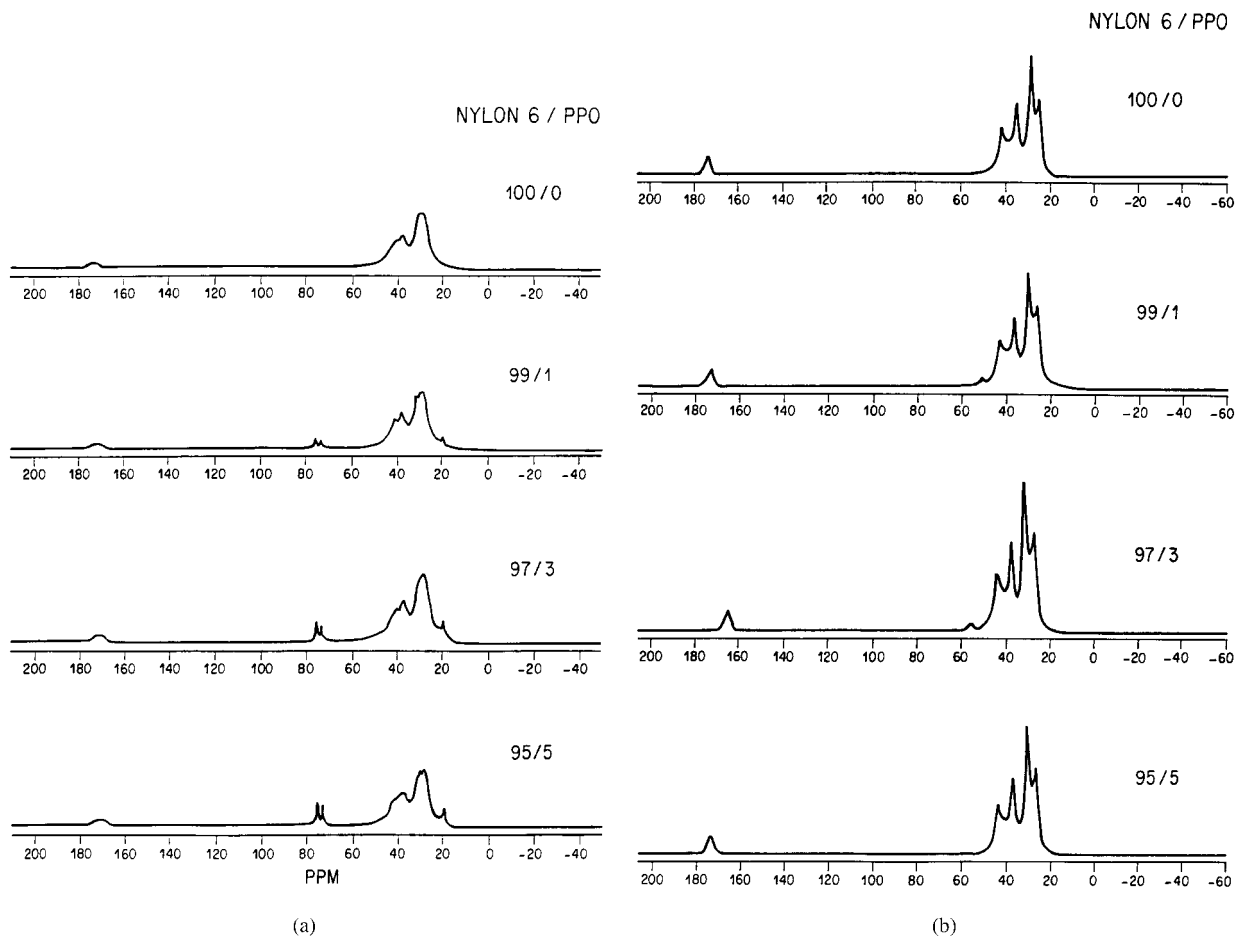
Figure 1 (a) ^{13}C-NMR spectra of PA6/PPO films obtained by fusion, at different compositions, by the MAS technique. (b) ^{13}C NMR spectra of NY6/PPO films obtained by solution, at different compositions, by the MAS technique.

more internal mobility and were detected even in samples that contain a small amount of PPO. In Figure 1(a), even for a small proportion of PPO, the NMR lines belonging to PPO can be detected. Comparing Figure 1(a) and 1(b), it is clear that the blends obtained by fusion present larger homogeneity, promoting more miscibility than the blends prepared in solution.

Figure 2 presents the array of contact time spectra of PA6/PPO prepared in fusion. In this figure, the antiplasticization effect is not noted, as was observed in samples prepared in solution (1). In our opinion, this happens because the solvent is absent and can not promote a nucleation process, which is responsible for the hardness of the sample. The better homogeneity in fusion blends comes from the mixing process, which does not give enough time for the PPO to induce nucleation.

Table I shows that the values of $T_1^H \rho$ for the

100 / 0

50   100   200   800   1000   2000   4000   8000 τ (ms)

99 / 1

97 / 3

95 / 5
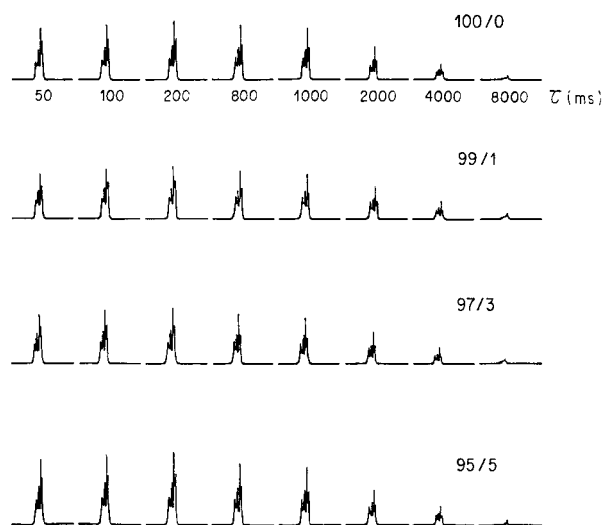
Figure 2 ^{13}C-NMR spectra of PA6/PPO films obtained by fusion, at different compositions, by the variable contact time experiment.

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

|		$T_1^H \rho$ (ms)			
System	Composition (%)	173.3	43.0	36.4	29.9 δ (ppm)
PA6	100/0/0	1.7	3.5	3.4	2.5
PA6/PPO	99/1	2.1	4.0	3.6	2.2
	97/3	2.8	4.6	3.2	3.1
	95/5	1.8	4.3	2.9	2.7
PA6/PC	97/3	2.5	1.8	2.8	2.9
	95/5	2.5	2.2	2.8	3.0
PA6/PC/PPO	99/3/1	3.1	1.7	3.1	2.8
	97/3/3	2.8	1.9	2.8	2.8
	99/5/1	3.3	2.6	2.1	2.6
	97/5/3	2.2	2.3	2.5	2.4

carbonyl group (located at 173.3 ppm) increase when 3% (w/w) of PPO is added in the system PA6/PPO. The incorporation of 3% (w/w) of PC in the same mixture raises the compatibility between the polyamide and PPO. In this case, PC acts as an interfacial agent, preventing the antiplasticization effect already observed in the system PA6/PPO.[1,2] The same behavior was observed when the quantity of PC was 5% (w/w). Observing the carbon, CH_2, attached at the group NH of PA6 (43.0 ppm), it was verified that the addition of PC in the system PA6/PPO causes a hardening of this group (reduction of the value of $T_1^H \rho$). This fact is 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 system PA6/PC/PPO. This decrease in the mobility can be caused by strong links, like a hydrogen bond, that promotes an induction of nucleaction or a formation of crosslinking.

Figure 3 verifies the increasing of the miscibility in the ternary system, confirmed by the identification of a mobile domain detected by MAS, for the systems of PA6 (I), PA6/PPO (II), PA6/PC (III), and PA6/PC/PPO (IV). In this domain lines from both PA6 and PPO were distinguished. This indicates that the plasticization effect occurs in the PA6 by PPO. The MAS spectrum of the ternary system formed by PA6/PC/PPO presents the NMR signals of PC, suggesting that the PC acts as a compatibilizer for the blends.

An NMR study obtained by proton spin-lattice relaxation time in the rotating frame (see Table II) shows that the incorporation of a copolymer promoted a better compatibility between polymers in the blend when the range of copolymer

was between 5 and 10%. This behavior was characterized by the increase of relaxation time, which is a function of an increase in the flexibility of the system. It is possible because the copolymer acts in the interface of the mixture, interacting with the homopolymers as a bridge.

It is known that the fragile thermoplastics have been modified to improve their capacity to obtain better impact resistance. However, the addition of a rubber material is not enough to increase the impact resistance of polymers due to weak interfacial adhesion between components. The addition of block or graft copolymers can promote
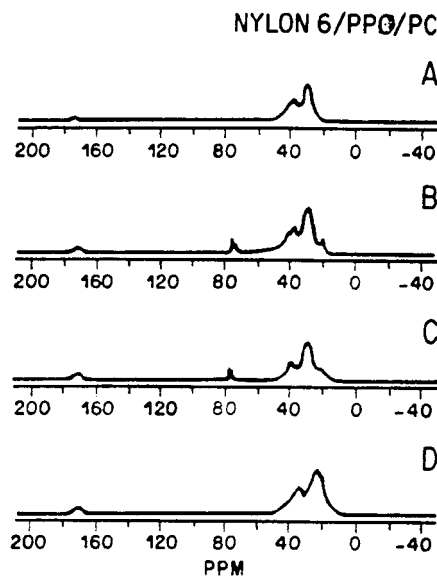
Figure 3 ^{13}C-NMR spectra of PA6, PA6/PPO, PA6/PC, and PA6/PPO/PC films obtained by fusion, at different compositions, by the MAS technique.

Table II   Proton Spin-Lattice Relaxation Time in the Rotating Frame of Three Types of CH$_2$ Groups of Nylon 6 Chain

System	Composition (%)	$T_1^H \rho$ (ms)			δ (ppm)
		30.2 (CH$_2$)	36.2 (CH$_2$)	43.3 (CH$_2$)	
NY6	100/0/0	3.1	2.8	3.5	
NY6/PPO	82/12	3.7	2.1	1.6	
NY6/PPO/block copolymer	82/12/5	4.1	4.0	3.2	
	82/12/10	4.2	4.1	2.6	
	82/12/20	3.1	2.6	2.3	
	82/12/25	2.6	2.2	2.1	

good effects in relation to impact resistance. In Table II, it was observed that the addition of a block copolymer improves the properties of the mixtures due to an increase of the compatibility of the system.
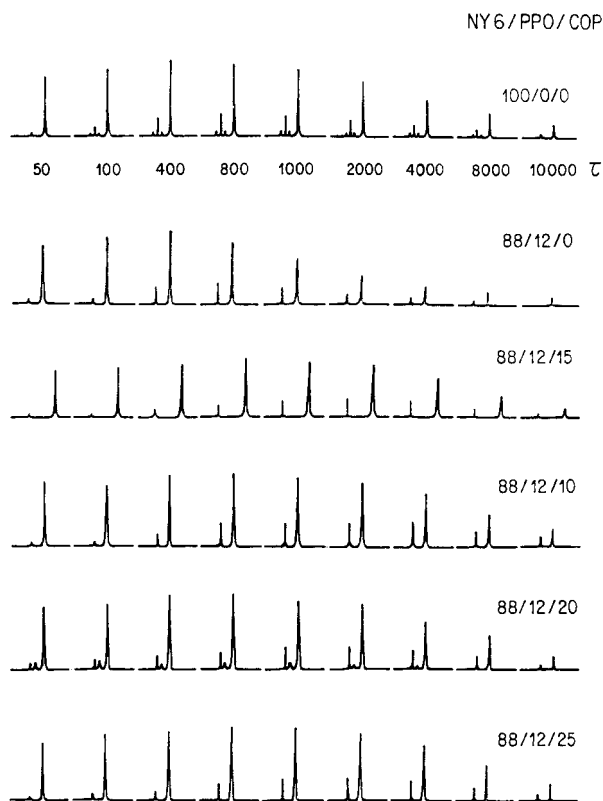
Figure 4 exhibits the spectra obtained by the variable contact time experiment for the NY6/PPO system. One can verify that the incorporation of the copolymer causes a shift in the distribution form of the resonance lines. The shift for a

Figure 4 ^{13}C NMR spectra of PA6/PPO/block copolymer (COP) obtained by solution, at different proportions, by the variable contact time experiment.

long contact time is due to the increase in the mobility of the system, which is in agreement with the $T_1^H \rho$ parameter already measured.

CONCLUSION

From the MAS technique, it was characterized that the regions of more internal mobility were detected even in a small amount of PPO in blends formed by PA6/PPO. This conclusion considers that the blends obtained by fusion present larger homogeneity than blends obtained by solution. In the blends obtained by fusion, the antiplasticization effect was not noted, because the solvent was absent. The incorporation of 3% (w/w) of PC in the those mixtures increases the compatibility between the PA6 and PPO. In this case, the PC acts as an interfacial agent, preventing the antiplasticization effect already observed in the system NY6/PPO. Therefore, it was verified that the addition of PC in the system PA6/PPO causes a hardening of this group. 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 system PA6/PC/PPO. The decrease in the mobility can be caused by strong links, like a hydrogen bond, that promotes an induction of nucleation or a formation of crosslinking.

Analyzing the NY6/PPO/block copolymer, the ideal quantity of copolymer to be added to the NY6/PPO blend to improve the compatibility is in a range of 5–10%. This occurs due to the better dispersion of the copolymer in the blend. An increase in the quantity of this agent probably makes it act as a third component. From the study, one observes that both PC and copolymer can be used as interfacial agents to improve the

properties of PA6/PPO blends, because the quantity of these components cannot be over the ranges already measured.

REFERENCES

1. M. I. B. Tavares, W. P. Castro, and D. A. Costa, *J. Appl. Polym. Sci.,* **55,** 1165 (1995).

2. M. I. B. Tavares, D. A. Costa, and S. M. C. Menezes, 4° SLAP/2° SIAP/6° IMC″, September, Gramado, RS, Brazil, **1,** 151 (1994).

3. M. I. B. Tavares, E. E. C. Monteiro, A. M. Kenwright, and R. K. Harris, *Polym. Bull.,* **30,** 637 (1993).

4. M. I. B. Tavares, E. E. C. Monteiro, R. K. Harris, and A. M. Kenwright, *Eur. Polym. J.,* **30,** 1089 (1994).

5. N. M. Silva and M. I. B. Tavares, *Polym. Testing,* **14,** 329 (1995).

6. J. Schaefer, E. O. Stejskal, and R. Buchdal, *Macromolecules,* **8,** 291 (1975).

7. D. E. Axelson and K. E. Russell, *Prog. Polym. Sci.,* **11,** 221 (1985).

8. E. O. Stejskal and J. D. Memory, *High Resolution NMR in the Solid State,* Oxford University Press, New York, 1994.

9. F. M. B. Coutinho and A. A. B. Sobrinho, *Eur. Polym. J.,* **27,** 105 (1991).

10. J. I. Eguiazábal and J. Nazábal, *Makromol. Chem., Macromol. Symp.,* **20/21,** 255 (1988).

11. E. Gattiglia, A. Turturro, E. Pedemonte, and G. Dondero, *J. Appl. Polym. Sci.,* **41,** 1411 (1990).

12. E. Gattiglia, F. P. Lamantia, A. Turturro, and A. Valenza, *Polym. Bull.,* **21,** 47 (1989).

13. E. Gattiglia, A. Turturro, F. P. Lamantia, and A. Valenza, *J. Appl. Polym. Sci.,* **46,** 1887 (1992).