

Blends of Polyamide 6, Polycarbonate, and Poly(propylene oxide). II. Reactive Compatibilization–Thermal Degradation Relationships

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ABSTRACT: The thermal degradation of some blends of polyamide 6/polycarbonate (PA6/PC) and polyamide 6/polycarbonate/poly(propylene oxide) (PA6/PC/PPO) were investigated. The copolymer formed during the mixing of polyamide 6 and polycarbonate, at 240°C, for 30 min, increases the thermal stability of PA6/PC and of PA6/PC/PPO blends. This increase in the thermal stability occurs due to the plasticizing effect of PPO, which increases the mobility of the molecules of PA6 and PC, and consequently increases the probability of the reaction between the —NH₂ and —O—CO—O groups of polyamide 6 and polycarbonate, respectively. The ternary blends with PPO (5–10% w/w) have lower thermal stability than PA6/PC blends. This is due to the decrease of miscibility between these polymers and the rise of the diluting effect. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2556–2562, 2001

Key words: polyamide 6; polycarbonate; poly(propylene oxide); blends; reactive mixtures; copolymer; miscibility; thermal degradation

INTRODUCTION

The compatibilization of polyamide 6 (PA6) and polycarbonate (PC) can be performed through the PA6–PC block copolymer, synthesized *in situ* during a long melt mixing process.^{1–13} The internal carbonate groups of PC may react with the amino terminal groups of PA6, during the melt mixing process, at 240°C. The formation of PA6–PC copolymers suggests that they can act as

compatibilizers inducing the compatibility of the heterogeneous blends of PA6/PC.^{1,2,8}

Polymers containing an alcohol group show some miscibility with PA6.³ The compatibility of the PA6/PPO blends improves as the PPO interacts with PA6, due to hydrogen bonding between C=O and C—OH groups of PA6 and PPO, respectively.^{11–13}

The study of thermal degradation of the PA6/PC blends, performed by thermogravimetry, shows the possibility of the intermolecular exchange reactions occurring through the inner amide groups, and of the amino end groups of PA6 and the carbonate group of PC similar reactions are known to occur easily at 240°C.¹⁰

This work verified the influence of PPO on the thermal degradation of PA6/PC/PPO blends.

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Table I Processing Conditions and Compositions of the PA6, PC, PA6/PPO, PA6/PC, and PA6/PC/PPO Blends at 240°C and 30 min

Blends	Composition (%) and (phr)
PA6	100
PC	100
PA6/PPO	97/3
PA6/PC	95/5, 90/10, 85/15
PA6/PC/PPO (%)	87/10/3, 85/10/5, 80/10/10
PA6/PC/PPO (phr)	85/15/3, 85/15/5, 85/15/10

EXPERIMENTAL

Materials

The commercial homopolymers used in this study were: PA6 (NYLODUR, NT 2700) with relative viscosity (η_r) = 2.65–2.75 (with H₂SO₄ as solvent), NH₂ = 35–40 mEq/kg, melt flow index (MFI) = 4.13 ± 0.12 g/10 min (235°C, 1 kg), supplied by De Millus S.A.; PC (LEXAN 141,111) with an average molecular weight (M_n) ≅ 45,000, supplied by Coplen Ind. and Com. (General Electric Co.) and PPO with M_n ≅ 1000, supplied by Dow Química S.A. The homopolymers were dried over 72 h before processing.

Preparation of the Blends

The blends were prepared in a Haake Rheomix 600 cam mixer at $T = 240^\circ\text{C}$, at 30 rpm, for 30

min. The samples were analyzed by means of torque–time curves and thermogravimetry (TG, DTG, and isothermal curves). The processing conditions and compositions of the blends are presented in Table I. Some of the blends were prepared with a constant PA6/PC mass ratio (85/15) and a variable amount of PPO. The composition of these blends will be expressed in parts per hundred constant mass ratios of resin (phr).

Thermogravimetry

The thermal degradation of the blends was observed on a Perkin-Elmer thermal analyzer TGA-7. These analyses were carried out on samples of 4 mg under a nitrogen flow of 32 cm³/min and a heating rate of 10°C/min up to 700°C. The temperature of the maximum rate of polymer degradation (PDT) corresponds to the temperature (°C) at which the DTG reaches their maxima.

Isothermal Thermogravimetry

The thermal stability of the homopolymers and of the blends was assessed by isothermal thermogravimetry. These analyses were carried out on 5 mg samples under a nitrogen flow of 32 cm³/min and a heating rate of 240°C/min up to 240°C, for 30 min.

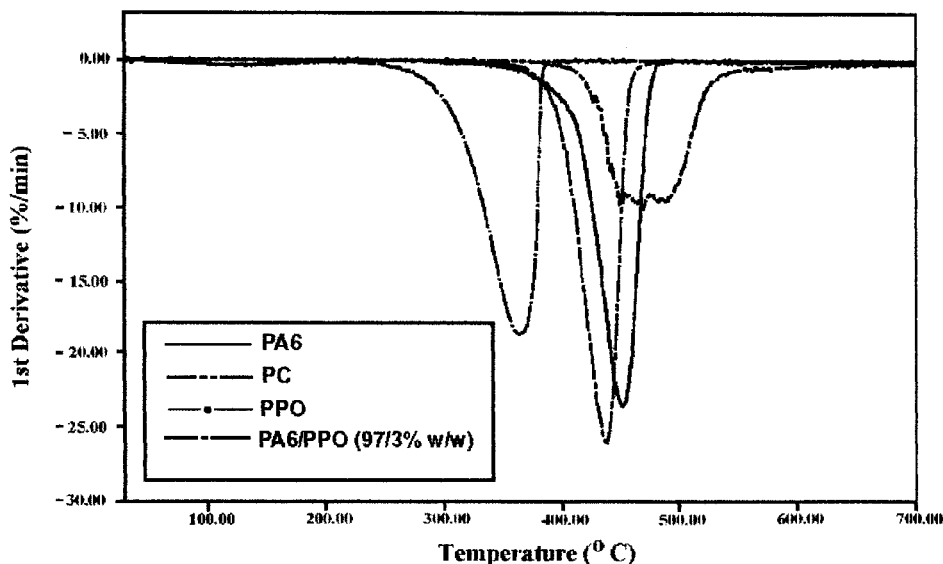


Figure 1 Thermogravimetric curves of PA6, PC, PPO homopolymers, and PA6/PPO blend.

Table II Thermal Degradation Temperatures of PA6, PC, PPO Homopolymers, and PA6/PPO Blend

Homopolymers and PA6/PPO Blend (%)	Thermal Degradation Temperatures (°C) Peak	Weight (%)
PA6	438	97.3
PC	479	78.6
PPO	362	99.3
PA6/PPO (97/3)	451	94.7

RESULTS AND DISCUSSION

Torque

The measurements of the torque of the PA6 and PC homopolymers, PA6/PPO, PA6/PC, and PA6/PC/PPO blends processed at 240°C, 30 min show that the PA6/PC and PA6/PC/PPO blends present an increase in the torque after 15 min of processing. The rise in the torque indicates the occurrence of a chemical reaction. This equimolar reaction takes place as an exchange process between the amino terminal groups of PA6 (NH₂) and the internal carbonate groups of PC (O—CO—O).¹⁴

Thermal Degradation

The first derivatives of the thermogravimetric curves of the PA6, PC, PPO homopolymers, and

PA6/PPO (97/3% w/w) blend are reported in Figure 1.

The decrease in the degradation temperatures of PA6 homopolymer and PA6/PPO blend, observed around 100°C, can be attributed to the loss of humidity by PA6. The presence of 3% w/w of PPO in the PA6/PPO blend increased the degradation temperature of the PA6. This small PPO percentage and the long time of mixing have a plasticization effect, increasing the crystallinity effect of PA6. Table II presents the thermal degradation temperatures (TG) of the PA6, PC, PPO, and the PA6/PPO blend.

Figure 2 shows the first derivatives of the thermogravimetric curves of PA6/PC blends. It can be observed in this figure that there is a weight loss, around 100°C. This is attributed to the loss of humidity by PA6. These blends present two periods of thermal degradation temperatures. These periods are related with the degradation temperature of the PA6-PC copolymer formed during the mixing process, and with the thermal degradation temperature of the PA6/PC blends (≈325 and 460°C, respectively). The rise in the PC proportion increases the formation of PA6-PC copolymer, indicated by the loss of weight and by a degradation temperature around 320°C (Table III). The degradation temperatures of the PA6/PC blends are higher than the degradation temperature of PA6. This change can be associated with the presence of the copolymer acting as an interfacial agent that increases the thermal stability of the PA6/PC blends.

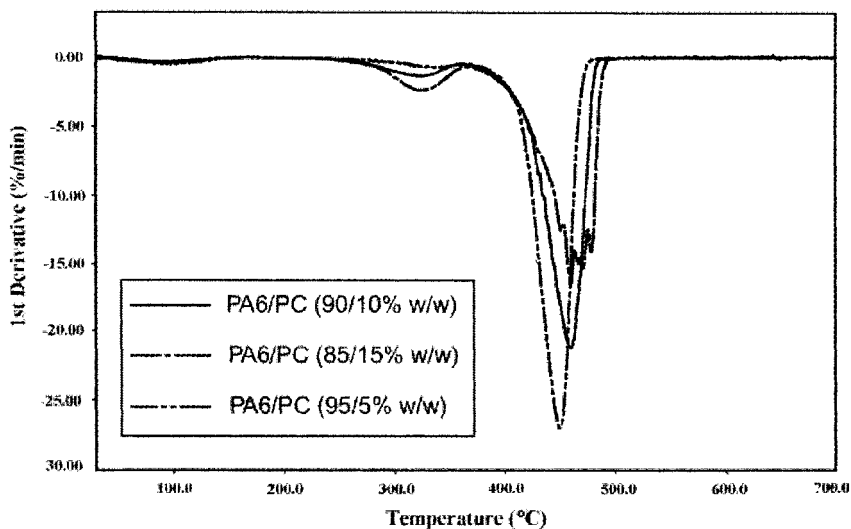


Figure 2 Thermogravimetric curves of PA6/PC blends.

Table III Thermal Degradation Temperatures of PA6/PC Blends

PA6/PC (%)	Thermal Degradation Temperatures (°C) Peaks	Weight (%)
95/5	334/457	5.2/89.9
90/10	325/460	10.5/86.9
85/15	324/460	18.3/81.3

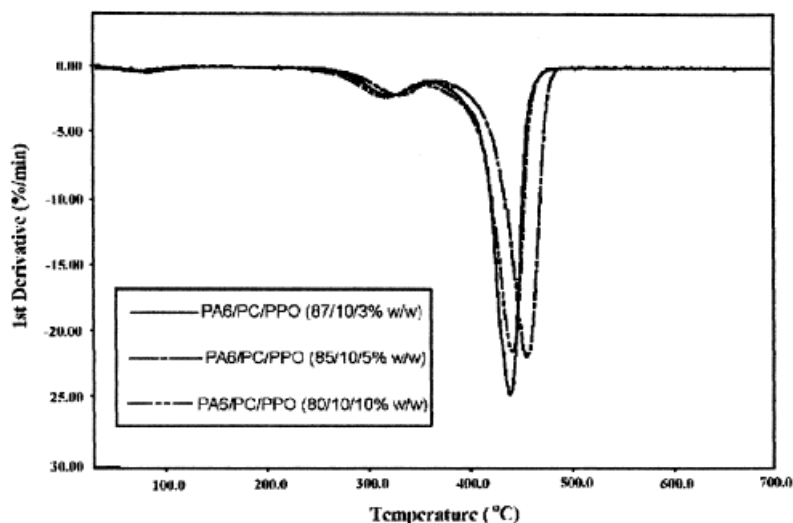
Figure 3 and Table IV show the first derivatives of the thermal degradation curves and the degradation temperatures of the PA6/PC/PPO blends (3–10% w/w of PPO), respectively. It can be verified in Table IV that the 85/10/5% w/w blend presents higher degradation temperature than the 87/10/3% and 80/10/10% w/w blends. This result can be connected with the PPO plasticizing effect, with a different interaction between PA6 and PPO, and with the formation of the PA6–PC copolymer. The presence of PPO may cause a modification in the interactions between the active groups of PA6 and PC homopolymers present in the PA6/PC/PPO blend systems. The presence of PPO in the ternary blends increases the mobility of PA6 molecules sufficiently to change the reaction rate between PA6 and PC, and to modify the percentage of PA6–PC copolymer formed. When the PPO percentage is above 5% w/w, the plasticizing effect of the poly(propylene oxide) decreases the degradation temper-

Table IV Thermal Degradation Temperatures of PA6/PC/PPO Blends

PA6/PC/PPO (%) (phr)	Thermal Degradation Temperatures (°C) Peaks	Weight (%)
87/10/3% w/w	359/437	14.7/82.3
85/10/5% w/w	360/453	13.2/83.3
80/10/10% w/w	360/440	14.8/81.0
85/15/3 phr	333/467	17.4/79.9
85/15/5 phr	330/469	19.0/77.4
85/15/10 phr	334/471	19.6/76.0

atures of the blend. This result can be associated with the heterogeneity between the PA6 and PPO molecules in these ternary systems.

Figure 4 shows the first derivatives of the thermal degradation curves of the PA6/PC/PPO blends (with 3–10 phr of PPO). The results in Table IV indicate that the PA6 proportion is very important for the occurrence of the exchange reactions in the ternary blends and on the formation of the PA6–PC copolymer and, consequently, for the thermal stability of the blends. In these systems, the constant PA6/PC mass ratio (85/15%) can cause a decrease in the apparent viscosity of the PA6/PC/PPO blends. These results are related to the difference of interaction between PA6/PPO and PA6/PC. The increase in the PPO proportion inhibits the exchange reactions between PA6 and PC (equimolar reaction


Figure 3 Thermogravimetric curves of PA6/PC/PPO blends.

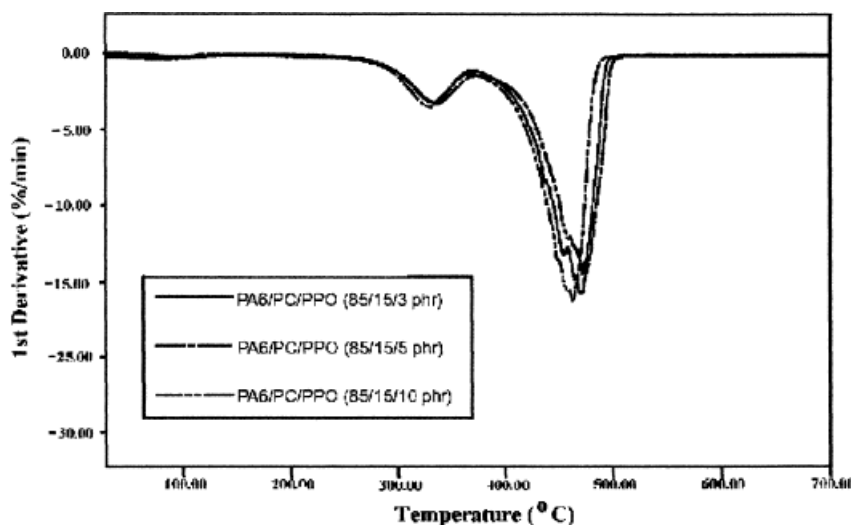


Figure 4 Thermogravimetric curves of PA6/PC/PPO (3–10 phr of PPO) blends.

with respect to repeated units), changing the thermal stability and reducing the weight values of these blends.

Isothermal Thermogravimetry

The homopolymers and the blends were analyzed by the loss of weight during isothermal degradation, at 240°C. Table V shows the loss of weight during the isothermal degradation of PA6, PC, and PPO

homopolymers. It can be observed that the highest loss of weight is caused by PPO homopolymer. The loss of weight caused by PA6 could indicate the presence of humidity. Figure 5 shows the variation of the loss of weight with time for these homopolymers. It can be seen that the PPO presents a lower thermal stability than PA6 and PC.

One can see from the data in Table V that the loss of weight for the PA6/PC blends is smaller

Table V Weight Values of Isothermal Degradation of the PA6, PC, and PPO Homopolymers and the PA6/PC and PA6/PC/PPO Blends

Composition (% and phr)	Loss of Weight (wt %)					
	5 min	10 min	15 min	20 min	25 min	30 min
Homopolymers (240°C, 30 min)						
PA6 (100)	0.66	1.18	1.50	1.88	2.27	2.58
PC (100)	0.13	0.19	0.22	0.25	0.27	0.28
PPO (100)	1.23	2.19	2.91	3.76	4.46	5.11
PA6/PC blends (240°C, 30 min)						
90/10	0.57	0.95	1.34	1.70	2.04	2.32
85/15	0.53	0.92	1.28	1.63	2.02	2.32
PA6/PC/PPO blends (240°C, 30 min)						
87/10/3%	0.45	0.81	1.14	1.43	1.72	1.97
85/10/5%	0.51	0.94	1.33	1.75	2.19	2.57
80/10/10%	0.86	1.47	1.74	2.26	2.75	3.18
85/15/3 phr	0.83	2.22	3.65	5.10	6.45	7.67
85/15/5 phr	0.47	0.87	1.21	1.54	1.86	2.14
85/15/10 phr	0.56	1.1	1.50	1.90	2.27	2.57

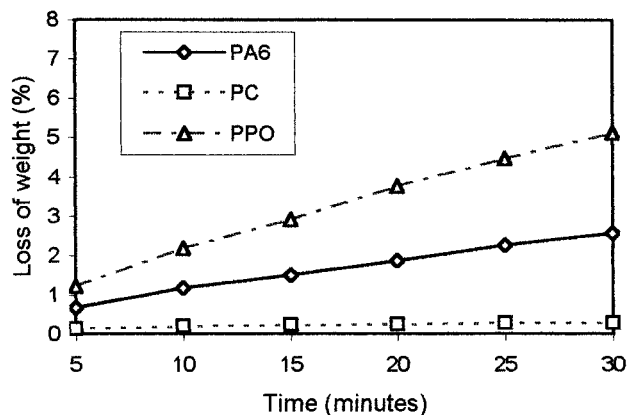


Figure 5 Isothermal degradation curves of PA6, PC, and PPO homopolymers.

than that for the PA6 homopolymer. This may indicate that the humidity in the PA6/PC blends is smaller than in the PA6 homopolymer. Added to this, the PA6-PC copolymer may be acting as an interfacial agent, leading to an increase in the thermal stability of the PA6/PC blends. The losses of weight in both blends are similar, and can be inferred from the data in Figure 6.

The loss of weight of the PA6/PC/PPO (3–5% w/w of PPO) blends confirms the antiplasticization effect caused by the small percentage of PPO that will also increase the thermal stability of the ternary blends. Besides this, the presence of the PA6-PC copolymer decreases the loss of weight of the PA6/PC/PPO blends. The plasticization effect of the ternary blends with PPO percentage above 5% w/w decreases the thermal stability of the mixture and, consequently, increases the loss of

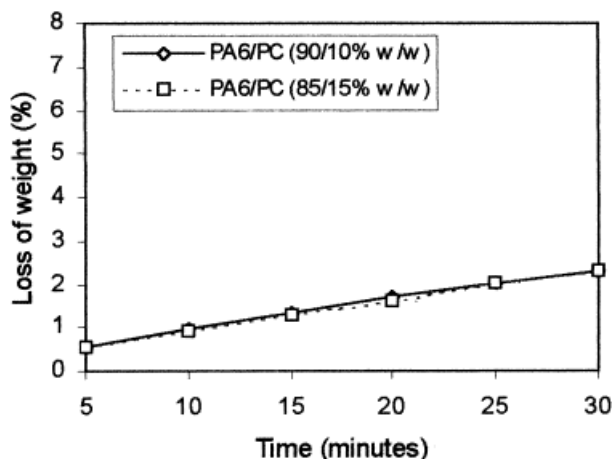


Figure 6 Isothermal degradation curves of PA6/PC blends.

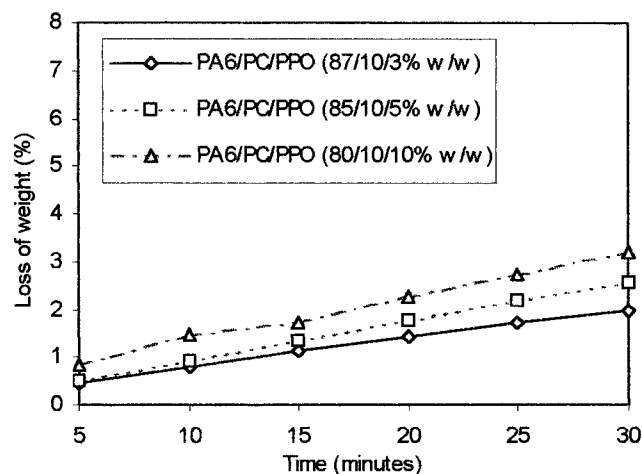


Figure 7 Isothermal degradation curves of PA6/PC/PPO blends.

weight of the blend (Table V and Fig. 7). The presence of the PPO is very important for the blends with constant mass ratio of PA6/PC (85/15% w/w), because it changes the thermal stability of these blends. It can be observed (Table V and Fig. 8) that the blend (85/15/3 phr) has a higher loss of weight than the blends with 5–10 phr of PPO. The results also confirm the difference of interaction between PA6/PPO and PA6/PC, leading to a decrease in the apparent viscosity of the PA6/PC/PPO blends. This can be due to the smaller mobility of the PA6 and PC molecules, when small proportions of PPO are present in the blends, decreasing the PA6-PC copolymer formation and, consequently, decreasing the thermal stability of these ternary blends.

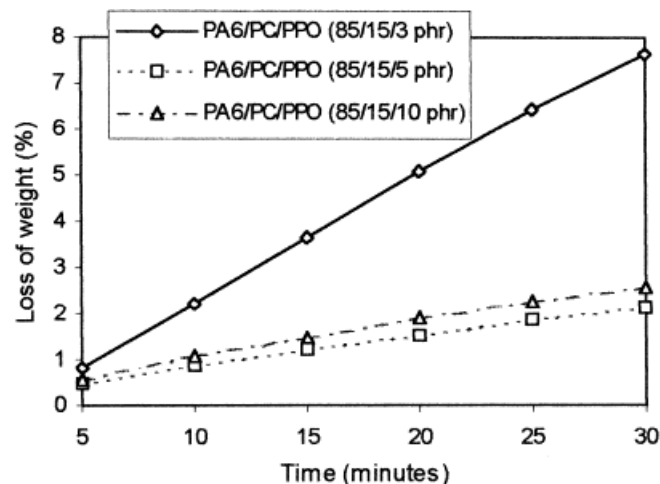


Figure 8 Isothermal degradation curves of PA6/PC/PPO blends.

CONCLUSION

In the PA6/PPO (97/3% w/w) blend, the presence of a small PPO percentage and a long time of mixing increase the degradation temperature of the PA6/PPO blend. This fact may be related to an antiplasticization effect of PPO on the PA6. The PA6/PC blends show two periods of thermal degradation temperatures that are related with the thermal degradation temperature of the PA6-PC copolymer formed during the mixing time, and the thermal degradation temperature of the PA6/PC blends. Increase in the PC percentage in the blends increases the formation of the PA6-PC copolymer, and this copolymer can act as an interfacial agent, increasing the thermal stability of the PA6/PC blends. The formation of PA6-PC copolymer and the plasticizing and diluting effects due to the PPO are very important for the thermal stability of the ternary blends (PA6/PC/PPO). The loss of weight of the PA6/PC/PPO (3-5% w/w of PPO) blends confirms the plasticization effect with a small percentage of PPO, which increases the thermal stability of the ternary blends. Besides this, when 5% w/w of PPO is present in the blend, the increase in the mobility of the molecules of PA6 and PC is sufficient to raise the reaction speed, increasing the formation of the PA6-PC copolymer. The presence of this copolymer decreases the loss of weight of the PA6/PC/PPO blends. The diluting effect for the PA6/PC/PPO blend with 10% w/w PPO is the highest and, consequently, decreases the degradation temperature and the thermal stability of this blend. To the ternary blends with 3-10 phr of PPO, the PA6/PC constant mass ratio causes a difference of interaction between PA6/PPO and PA6/PC blends, due to a change in the mobility of these molecules with the presence and percentage of PPO. This difference of interactions between

PA6/PPO and PA6/PC decreases the exchange reactions between PA6 and PC (equimolar reaction with respect to repeated units) changing the thermal stability and the loss of weight of these blends.

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