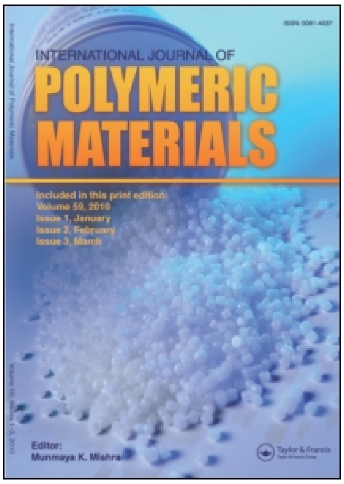

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Kinetic studies of the reactive compatibilization of polyamide 6, polycarbonate and poly(propylene oxide)

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KINETIC STUDIES OF THE REACTIVE COMPATIBILIZATION OF POLYAMIDE 6, POLYCARBONATE AND POLY(PROPYLENE OXIDE)

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The kinetics of the reactive blending process occurring during the stirred melting of polyamide 6/polycarbonate (PA6/PC), polyamide 6/polycarbonate/poly(propylene oxide) (PA6/PC/PPO) in a Haake internal mixer at 240°C were investigated. In the PA6/PC blends the formation of copolymers can be observed and they act as compatibilizing agents, raising the miscibility of these blends. In the PA6/PC/PPO blends, the composition is very important in creating the PA6-PC copolymers. The rise of the PPO percentage increases the mobility of the PA6 molecules and the probability of formation of PA6-PC copolymers in PA6/PC/PPO blends with 10% w/w of PC. The PPO percentage (3–10 phr) influences the kinetics of reaction of PA6/PC/PPO ternary blends with a constant PA6/PC mass ratio (85/15).

Keywords: poly(carbonate of bisphenol A), polyamide-6, nylon-6, reactive processing, copolymers, compatibilizer

INTRODUCTION

Small amounts of a polymer with a polar functional group added to polyamide 6 can chemically react, forming block or graft copolymer. This copolymer will increase the compatibility of the blends, enhancing their dispersability and mechanical properties [1], as reported about the blends of polyamide 6-polycarbonate [2–5], polyamide 6-poly(phenylene oxide) [6], polystyrene–polyamide [7].

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Polyamide 6 (PA6) and polycarbonate (PC) are two incompatible polymers but after long periods of a melting process, their blends showed evidence of some degree of compatibility. During the stirred melting of PA6/PC blends at 240°C an equimolar reaction occurs due to an exchange between the amino terminal groups of PA6 and the internal carbonate groups of PC [3, 8, 9].

Polymers containing ether groups have been found to show some miscibility with polyamides. Poly(propylene oxide) (PPO), polyether polyols, of low molecular weight derived from propylene oxide can be used as plasticizers in polymer blends. The plasticizers increase the mobility of the polymer chain resulting in a decrease of the glass transition temperature. The addition of the plasticizer to the crystalline polymer gives rise to a variation in the amorphous phase of the components of the blend, decreasing the melting temperature as well as the crystallinity of the polymer [7, 10].

In this work, the reactive compatibilization processes of the PA6/PC and PA6/PC/PPO blends were investigated through kinetic studies using the torque values.

EXPERIMENTAL

Materials

The commercial homopolymers used in this study were: PA6 (NYLODUR, NT2700) of $M_w \cong 30{,}900$, $NH_2 - 12.43$ meq/Kg, supplied by De Millus S. A.; PC (LEXAN 141,111) 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 homopolymers were dried for 72 h before processing.

Preparation of the Blends

The blends were prepared in a Haake Rheomix 600 cam mixer at $T = 240°C$, at a rotational speed of 30 rpm, for 30 and 65 min. The samples were analyzed using torque-time curves and kinetic studies. The PA6 and PC were processed at 240°C, for 10 minutes. The compositions of blends are PA6/PPO (97/3, 95/5 and 90/10% w/w) PA6/PC (95/5, 90/10 and 85/15% w/w) and PA6/PC/PPO (87/10/3, 85/10/5, 80/10/10% w/w) and PA6/PC/PPO (85/15/3, 85/15/5 and 85/15/10 phr). These blends were prepared during 30 minutes at 240°C.

Torque *Versus* Time

The blends were analyzed using the dependence of the torque of each blend on the mixing time and composition. After attaining the initial steady torque, the changes of the torque values were registered. Therefore, it was

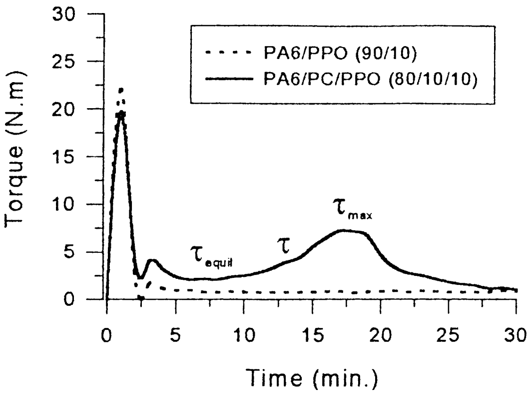

FIGURE 1 Torque curves of PA6/PPO and PA6/PC/PPO blends.

possible to separate the rise in torque due to reaction from that due to the mixing process.

Kinetic Studies

The nylon-6-PC blends showed an amine/carbonate reaction with the formation of a graft copolymer *in situ*. The torque curves of these blends were used to calculate the increase in the torque due only to the reaction. The equilibrium torque (τequilibrium) before or without any reaction taking place, is subtracted from the torque registered after the reaction ($\tau - \tau$ equilibrium) and it is normalized by dividing it by the maximum difference (τmax $-$ τequilibrium). This ratio ($\tau - \tau$ equilibrium)/(τmax $-$ τequilibrium) $= \Theta$, varies between 0 (no reaction) and 1 (complete reaction). Figure 1 shows the torque curves where the τ, τequilibrium and τmax values were calculated. The parameter S is defined by Eq. (1). The reaction slows down and can be represented by a second or a third degree polynomial [11].

$$\mathrm{S} = (1 - \Theta) = (\tau\,\mathrm{max} - \tau)/(\tau\,\mathrm{max} - \tau\,\mathrm{equil}) \qquad (1)$$

RESULTS AND DISCUSSION

Torque Values

The torque measurements gave information concerning the PA6 and PC homopolymers and the PA6/PPO, PA6/PC and PA6/PC/PPO blends through the mixing time and composition of these blends. Figure 2 shows the torque curves of PA6 and PC homopolymers processed at 240°C, for

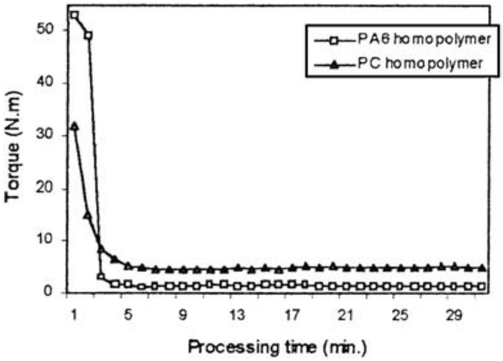

FIGURE 2 Torque curves of PA6 and PC homopolymers processed at 240°C, 30 min.

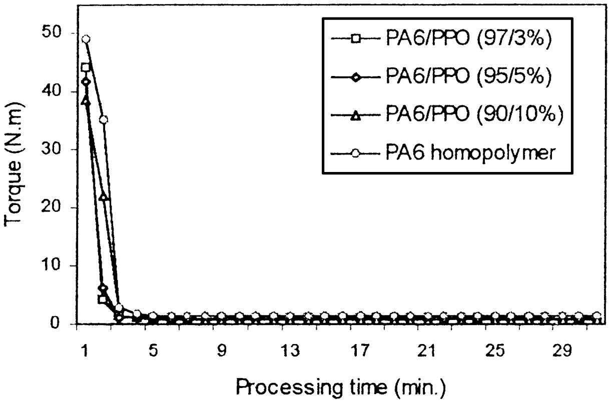

FIGURE 3 Torque curves of PA6/PPO blends processed at 240°C, 30 min.

30 min. The PA6 curve presents torque values smaller than the torque values of PC. This result shows the high stiffness of the PC.

The PA6/PPO (97/3, 95/5 and 90/10% w/w) blends, processed at 240°C for 30 minutes (Fig. 3), presented the lowest torque values, even smaller than those for PA6. These results indicate that the PPO reduces the apparent viscosity of the PA6/PPO blend system.

One can observe in Figure 4 (torque curves of the PA6/PC blends) that after 10 minutes of mixing there is an increase of the torque values for these blends. This result means that a chemical reaction is occurring between the amino terminal groups of PA6 and the internal carbonate groups of PC, with the formation of block copolymers that act as compatibilizers of the PA6/PC blend system. The increase of the torque values of the PA6/PC

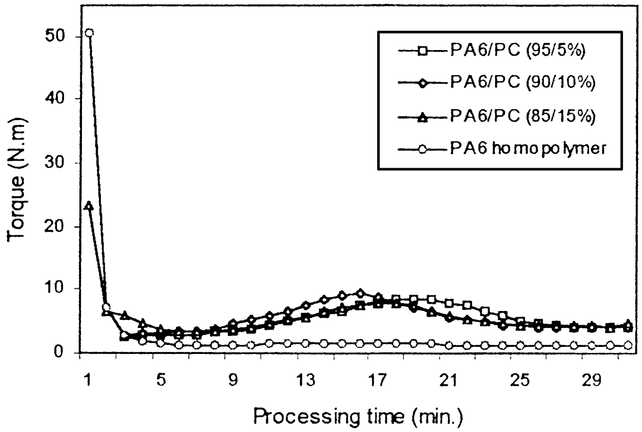

FIGURE 4 Torque curves of PA6/PC blends processed at 240°C, 30 min.

blend system (up to 10% PC) processed at long mixing times (30 minutes) indicates that this is the best composition for the occurrence of a chemical reaction between these homopolymers.

The torque curves of PA6/PC/PPO of the compositions (87/10/3, 85/10/5 and 80/10/10% w/w) and (85/15/3, 85/15/5 and 85/15/10 phr) blends processed for 30 minutes at 240°C, are presented on Figures 5 and 6, respectively. One can observe in Figure 5 an increase of the torque values after 13–20 minutes of processing the blend system. This increase is larger when the proportion of PPO reaches the value of 10% w/w. These results indicate the formation of PA6-PC copolymer and the different interaction between PA6 and PPO, due to the decrease of the apparent viscosity of the heterogeneous PA6/PPO blend system. From the analysis of Figure 6

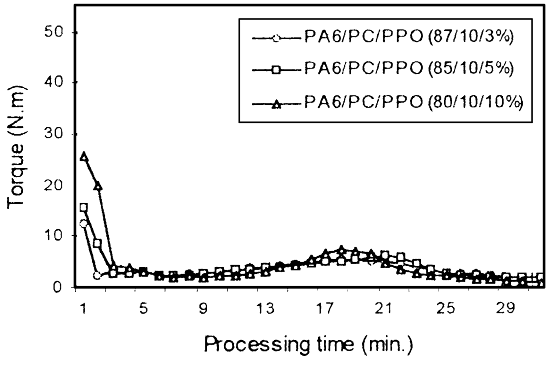

FIGURE 5 Torque curves of PA6/PC/PPO blends processed at 240°C, 30 min.

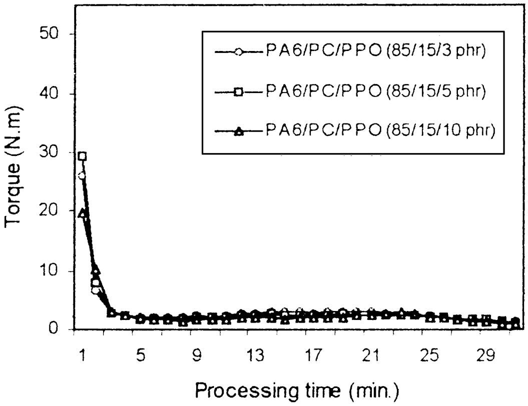

FIGURE 6 Torque curves of PA6/PC/PPO blends (with 3 – 10 phr PPO) processed at 240°C, 30 min.

(85/15/3, 85/15/5 and 85/15/10 phr blends) one can see that at constant mass ratio of PA6/PC, the increase of the PPO proportion cause a decrease on the torque values of these blend systems. In this case, the interactions between PA6 and PPO are greater than those encountered in ternary blends with 10% of PC, decreasing the chemical reaction between the active groups of PA6 and PC and therefore reducing the torque values of the blends.

Kinetic Studies

Figure 7 shows a plot of the parameter S *vs.* time for the PA6/PC blends. It can be observed that for the PA6/PC (90/10% w/w) blend the formation of block copolymers occurs at a processing time shorter than that for the PA6/PC (95/5 and 85/15% w/w) blends. The reaction between the active groups of PA6 and PC seems to begin after 6 minutes of processing. It is also observed that these blend systems only attain high reaction rates after 15 minutes of processing. After this time the reaction rate between these groups starts to decrease.

The curves presenting the kinetics of reaction for PA6/PC/PPO blends, with 10% of PC and variable PPO proportion (3 – 10%) (Fig. 8) show that the increase of the PPO proportion causes a decrease of the reaction rate between the active groups of PA6 and PC homopolymers in the PA6/PC/PPO blend system. This result can be related to the heterogeneity between the PA6 and PPO molecules in these ternary systems. The presence of PPO modifies the interaction between PA6 and PC.

In the PA6/PC/PPO (80/10/10% w/w) system, the curve shows that the reaction rate is low until 10 minutes of processing. After this time, the

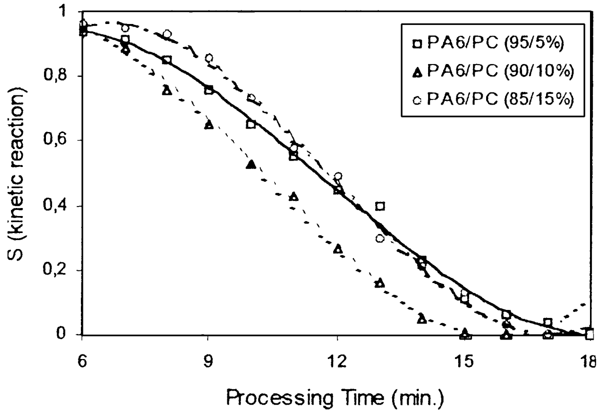

FIGURE 7 Curves for the kinetics of reaction for PA6/PC blends.

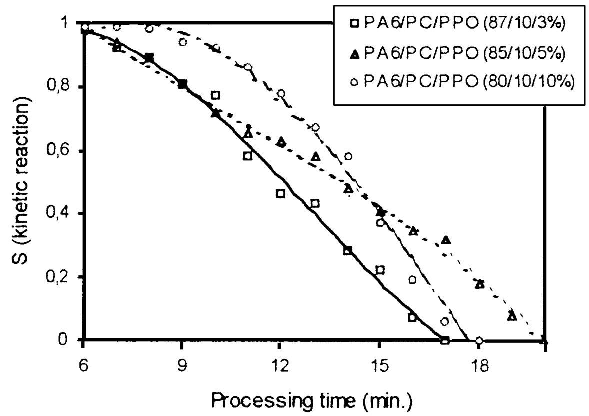

FIGURE 8 Curves for the kinetics of reaction for PA6/PC/PPO blends.

reaction rate increases considerably. This behavior can be related to the composition of this blend that presents a considerable amount (10%) of PPO and that can increase the heterogeneity between PA6 and PPO in the ternary systems.

Figure 9 shows curves for the kinetics of reaction of the PA6/PC/PPO blends of compositions (85/15/3, 85/15/5, 85/15/10 phr). It can be seen from this figure that the increase of PPO proportion in the blends with a constant PA6/PC mass ratio causes a decrease on the apparent viscosity of the PA6/PC/PPO blend system. This result could be related to the difference of interaction between PA6/PPO and PA6/PC, due to the active groups present

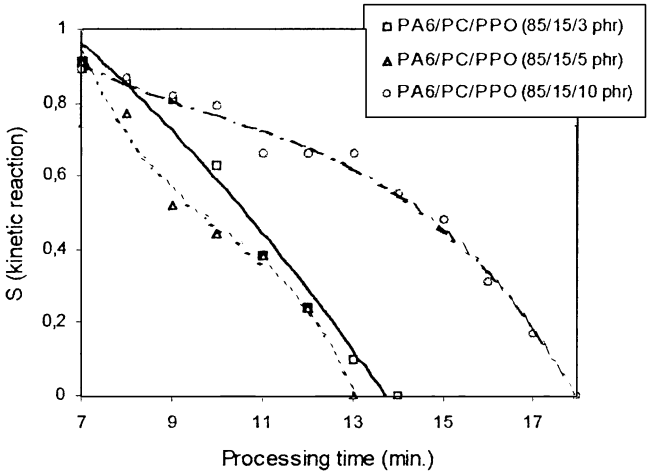

FIGURE 9 Curves for the kinetics of reaction for PA6/PC and PA6/PC/PPO blends (with 3 – 10 phr PPO).

in the PA6 and PC homopolymers, promoting the reaction between these homopolymers. These results show that the PA6 proportion is very important for the occurrence of exchange reactions in the ternary blends. The presence of a high PPO proportion PA6/PC/PPO (85/15/10 phr) makes the exchange reactions between PA6 and PC (equimolar reaction with respect to repeated units) hard to occur. This blend presents a very low rate of reaction. The PA6/PC/PPO (85/15/3 and 85/15/5 phr) blends present a reaction rate higher than the PA6/PC (85/15% w/w) blend. These results suggest that the presence of PPO in low percentage is capable of promoting the chemical reaction between PA6 and PC homopolymers.

CONCLUSIONS

The composition and the stirred melting time modified the torque values for PA6/PPO, PA6/PC, and PA6/PC/PPO blends. In the PA6/PPO blends, the PPO acts as plasticizers to PA6, decreasing the torque values of these blends. The best composition for the occurrence of chemical reaction between PA6 and PC is 90/10, with these homopolymers processed for long periods of mixing (30 minutes). The modifications of the torque values for the PA6/PC/PPO (with 10% of PC) blends, means that the increase of the proportion of PPO to 10% in these blends increases the mobility of the PA6 molecules (PPO plasticizing effect) increasing the probability of the formation of the PA6-PC copolymers. For the PA6/PC/PPO ternary blends with a constant

PA6/PC mass ratio (85/15) and variable PPO proportion (3 – 10 phr), this constant ratio of PA6/PC changes the kinetics of reaction of these blends. The rise of the PPO percentage is not beneficial for the reaction between the active groups of PA6 and PC homopolymers. The presence of a high PPO proportion decreases the occurrence of exchange reactions between PA6 and PC (equimolar reaction with respect to repeat units). However, for blends with a low proportion of PPO (until 5%), this amount is enough to aid in the chemical reaction between PA6 and PC homopolymers.

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