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Effects of mixing time and blend composition on properties and morphologies of polyamide 6/polycarbonate blends*

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SUMMARY

The role of the mixing time and the composition of polyamide 6/polycarbonate, PA6/PC, mixtures was investigated by torque and thermal measurements as well as by Molau test and morphological analysis.

PA6 and PC are clearly incompatible over the whole range of composition showing well segregated phases. However, at high PA6 content and long time of mixing no more phase separation is observed. This has been attributed to chemical reactions between PA6 and PC molecules, that give rise to some block copolymers, which act as interfacial agents between the two polymers.

The copolymer extracted from 75/25 PA6/PC blend, mixed for 45 min., shows T_g at about 65°C and two endotherm peaks at 127 and 211°C.

INTRODUCTION

It is well known that the morphology and the properties of polymeric blends strongly depend on processing conditions. In particular, temperature and mixing speed (and then the applied stress) play and important role in determining the size of dispersed phase (1,2).

On the other hand, a sistematic study of the influence of the mixing time has not been carried out. Indeed when this parameter is long enough, no remarkable influence of the mixing time seems to occur, if degradative phenomena do not intervene.

In this work the influence of the mixing time and the blend composition on the structure, rheological and thermal properties of polycarbonate/polyamide 6 blend is considered.

The choice of these two polymers has been made on the basis that, under severe processing conditions, they could react to give rise to copolymers, acting as surfactant agents of the blends, as reported for mixtures of polycarbonate with poly(ethylene terephthalate) (3) and poly(butylene terephthalate) (4).

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EXPERIMENTAL

The materials used in this work were a polyamide 6 (MFI=10.8 g/10 min.; $\bar{M}_w = 37 \cdot 10^3$; $\bar{M}_n = 17.6 \cdot 10^3$) and polycarbonate (MFI = 5.2 g/10 min.; $\bar{M}_w = 25 \cdot 10^3$; $\bar{M}_n = 8 \cdot 10^3$), manufactured and kindly supplied by SNIA and Enichem (Italy), respectively. The MFI of polyamide (PA6) was obtained following ASTM D1238/73 method, procedure R with T = 235°C and P = 2.16 Kg.; MFI of polycarbonate (PC) according to ASTM D1238/73 method, procedure O with T = 300°C and P = 1.2 Kg.

The homopolymers were mixed in a Brabender Plasticorder mod. PLE 330, equipped with a cam mixer at T = 240°C and at a rotational speed of 30 rpm. The maximum mixing time, τ_{mix}, was 45 min. The blend composition ranged from 0 to 100% w/w of PA6. For sake of simplicity, from here on,first figure of blend composition will indicate the PA6 weight percentage.

A pratical method to empirically asses the presence of copolymer in PA6 containing blends is the well known Molau test (5). Blends with 90,75 and 50% by weight of PA6, treated in Brabender for 15 and 45 min., were dissolved (2% w/v solution) in concentrated formic acid and allowed to rest for eight hours, at room temperature.

The solutions of the 50/50 blend were clear and showed a precipitate. The 75/25 blend gave turbid solutions; only by centrifugation at 20 K rpm for 3 hours, it was possible to separate the suspended material from the solution. The PA6-rich blend, 90/10, mixed for 45 min., gave clear, gel-like solution which did not change after centrifugation.

By selective dissolution, centrifugation and filtration the 75/25 blend was separated into three polymer fractions, one of which did not dissolve in the solvents of two homopolymers.These fractions were carefully washed with formic acid and/or methylene chloride, to purify each of them from the other components.

IR spectra were obtained with Perkin-Elmer spectrometer mod. 680; a Perkin-Elmer DSC 7 was used for thermal analysis, at a heating rate of 20°C/min.

Preliminary morphological observations of cold fractured 75/25 blends were performed using a Cambridge Stereoscan 250 MK2 electron microscope.

RESULTS AND DISCUSSION

The curves of the torque as a function of the time, recorded during mixing, are reported in Fig.1 for all the samples.

As for as the homopolymers and the polycarbonate-rich blends the shape of the M_t - t curves is similar to that shown by all the thermoplastic polymers, characterized by a rapid decrease of torque, followed by the attainment of a steady-state value. The 50/50 blend shows, on the contrary, a slight maximum after about 25 min. of mixing, than a slow decrease and, also after 45 min., no steady-state value is reached. The torque-time curves relative to the PA6-rich samples show a very complex behavior. They present several maxima that shift towards lower mixing time on increasing the PA6 percentage in the blend. For the sample with 90% PA6 at the end of

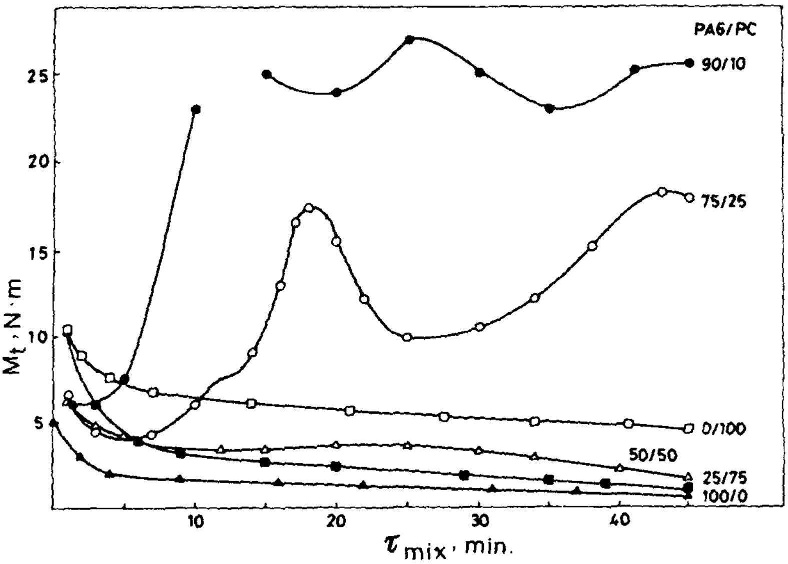

Fig.1 Torque as a function of the mixing time for pure PA6 and PC and their blends. T=240°C; rotational speed = 30 rpm.

the test no steady-state value seems reached.

As well known, the torque is indicative of the melt viscosity of the sample and then a maximum in the torque-time curve suggests that some new product with high viscosity or which stabilizes the blend be formed during mixing. This reaction takes place significantly only in the case of large excess of polyamide and/or long times of reaction.

Fig. 2 shows picture of 50/50 and 75/25 blend solutions, in formic acid for mixing times of 15 and 45 min., eight hours after the dissolution.

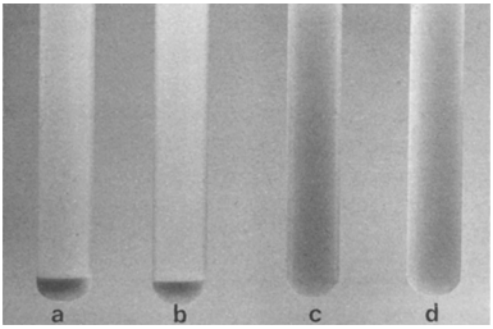

Fig.2 Solutions in formic acid of PA6/PC blend, after a rest of eight hours at room temperature.
Blend solutions: a) and b) 50/50; c) and d) 75/25;
Brabender mixing time: a) and c) 15 min.;b)and d) 45 min.

Following Molau, the persistent turbidity in the case of 75/25 blend should be due to the existence of PA6/PC copolymers, acting as interfacial agents between the chains of soluble (PA6) and insoluble (PC) homopolymers. We have not been able to obtain indication about copolymer formation in the 50/50 blend; the copolymer amount is probably too small to be put into evidence, as torque measurements would indicate.

The infrared spectrum of the polymer fraction, insoluble in formic adid and methylene chloride, is shown in Fig.3. Characteristic absorption bands of PA6 at 3300, 1450 and 1640 cm^{-1} and PC at 1770, 1240, 1080 and 1020 cm^{-1} are clearly present, thus confirming chemical reaction between the two homopolymers and the formation of some block copolymers.

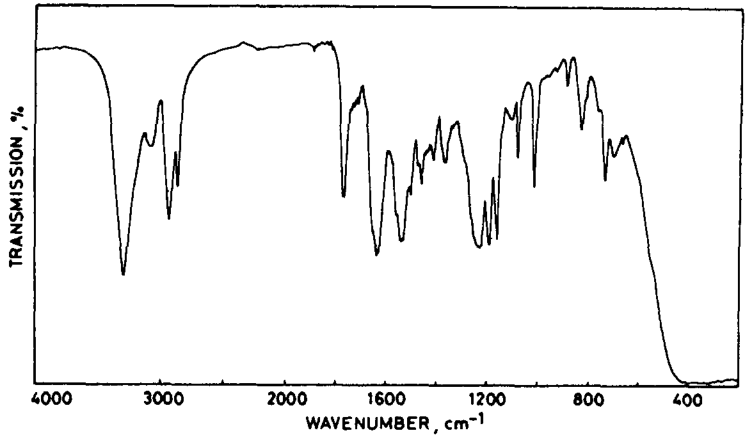

Fig.3 Infrared spectrum of fraction insoluble in formic acid as well as methylene chloride.

Further evidence of these phenomena comes out from the thermal analysis, as some tipycal thermograms show in Fig.4.

The results, collected in Table I, put into evidence the role played by the blend composition and mixing time in the degradative reactions. Under the same time of mixing (f.i.45 min.), the glass transition temperature, T_g, decreases from 154°C, for the pure PC, to 120°C when 75% PA6 is present. This is due to the degradation of polycarbonate macromolecules, which is directly dependent on the concentration of $-NH_2$ terminal groups of the polyamide chains. This interpretation is supported by our previous findings (6) and preliminary results about HPLC determination of the molecular weight of PC present in all the blends.

On the contrary, PA6 T_g practically does not change in the range of composition explored. In one case, the 75/25 blend-45 min., a transition at about 70°C is observed, very near to 65°C recorded for the copolymer fraction, extracted from the same blend. We consider this transition to be the T_g of the copolymer. However, the melting temperature T_m of polyamide is negatively affected by the chemical reactions which occur during the mixing. Maximum T_m decrease has been pointed out for the 90/10 blend, together with a melting region broader than those of the other mixtures (fig.4).

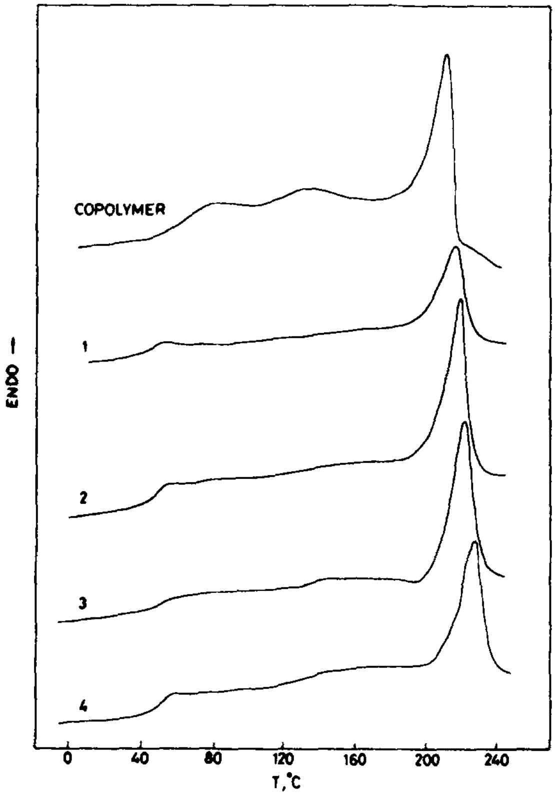

Fig.4 DSC traces of PA6/PC blends;
1) 90/10 - 45 min.;
2) 75/25 - 45 min.;
3) 50/50 - 45 min.;
4) 75/25 - 15 min.;
copolymer extracted from sample 2.

TABLE I

Glass transition and melting temperature of PA6 and PC as a function of blend composition and time of mixing.

PA6/PC w/w	τ_{mix}, min	$T_{g_{PC}}$,°C	$T_{g_{PA6}}$,°C	$T_{m_{PA6}}$,°C
100/0	< 0.5	-	50	221.0
90/10	45	-	45	214.0
75/25*	15	129	50	219.5
	45*	120	47/70	215.5
50/50	15	140	53	221.5
	45	138	52	219.0
0/100	45	154	-	-
Copolymer from (*)	-	-	65	127/211

The block copolymers enhance the interactions in the molten state between PA6 and PC molecules and hinder the typical development of the crystalline organization of the polyamide. Consenquently, PA6 crystals in the blends are less perfect and/or smaller, so that the melting happens before and in a wide range of temperature. These phenomena are more evident in the thermal behavior of the copolymer fraction, extracted from 75/25 blend-45 min.: two endotherm peaks at 127 and 211°C are shown.

Finally, SEM morphological analysis gives a further indication about the block copolymer formation (fig.5). After 15 min. of mixing the morphology of the 75/25 blend shows well segregated domains of PC in the PA6 matrix; at longer time an apparent homogeneous blend is obtained as a conquence of the interfacial action of the increasing copolymers which make more compatible the two homo-components.

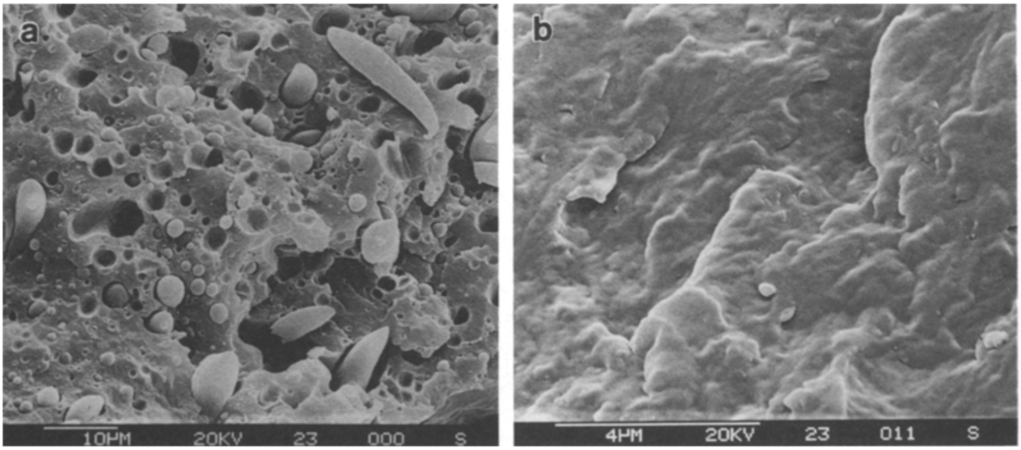

Fig.5.SEM micrographs of fracture surface of 75/25 PA6/PC blend, mixed for a) 15 and b) 45 min

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