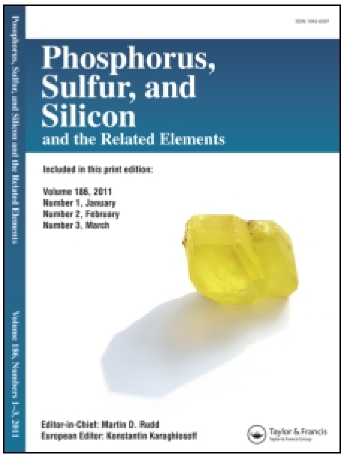

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Hexakis(4-Oxazolinophenoxy) Cyclophosphazene as a Novel Compatibilizer for Polycarbonates and Polyamides

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Hexakis(4-oxazolinophenoxy)cyclophosphazene has been used to promote the compatibility between polycarbonate and polyamide-6 polymers. The resulting blends were characterized by a variety of method to assess the occurred compatibilization between the two types of macromolecules.

Keywords: phosphazenes; blends; oxazolines; polycarbonate; polyamide; compatibilization

INTRODUCTION

Polycarbonate/polyamide-6 (PC/N6) blends are reported to be immiscible in the whole range of composition[1]. However, the possibility to blend polyamide (excellent thermo-mechanical properties, good solvent resistance, good adhesion to inorganic fillers) with polycarbonate (high resilience, low sensitivity to moisture) would give very interesting new materials, providing that suitable compatibilizing agents are found[2-5].

Polyamides contain terminal COOH and NH_2 groups. Partial degradation occurring during processing causes an increase of end groups. Polycarbonate usually lacks of end groups, because monophenols are used during synthesis to control the molecular weight. However, phenolic OH are generated during processing due to partial thermal-hydrolytic scission of carbonate groups.

$$\text{---Ph-O-CO-O-Ph---} + H_2O \text{ ---> } 2 \text{ ---Ph-OH} + CO_2$$

Oxazolines are organic molecules able to react with both carboxylic and phenolic groups[6], that appear very suitable to chemically link polycarbonate and polyamides through their end groups. In this paper we report on the use of a cyclophosphazene-based hexafunctional oxazoline derivative, i.e. hexakis(4-oxazolinophenoxy)cyclophosphazene (as obtained by reacting hexachlorocyclophosphazene with 4-hydroxyphenyl-2-oxazoline[7]), and on its ability to form the compatibilizing agent *in situ* during blending PC and N6.

EXPERIMENTAL

Hexakis(4-oxazolinophenoxy) cyclophosphazene (C6OXA)[7] and (1,4-phenylene)bis-2-oxazoline (Φ2OXA)[8] were synthesized as reported elsewhere. Blends of Bisphenol-A polycarbonate (EniChem) and polyamide-6 (Radici Chimica) were prepared with a Haake internal mixer at 245-250°C and compression molded at the same temperature. Blends extraction was performed in Kumagawa extractors. Mechanical properties were determined on Dumbell samples (DIN 53448) with an Instron Tester 4502. Infrared spectra were registered with a Perkin Elmer FTIR 1800 spectrophotometer. Scanning electron microscopic analysis was performed with a Stereoscan 360 apparatus (Cambridge Inst.).

RESULTS AND DISCUSSION

Three 50:50 PC/N6 blend compositions have been prepared, containing no additives, C6OXA and Φ2OXA (in similar amount based on the moles of oxazoline functional groups), respectively.

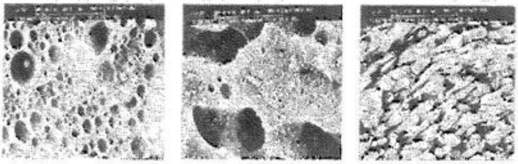

Figure 1. SEM micrographs of PC/N6 blends etched with $CHCl_3$ (2000x). Left: PC/N6; center: PC/N6+Φ2OXA; right: PC/N6+C6OXA.

PC/N6 blend (without any additive) shows a biphasic structure (Figure 1) with voids which are visible at domain boundaries. In disagreement with previously reported data[9], N6 is the matrix, and PC is dispersed as well defined spheroids. The PC globules present at the fractured surface dissolve after treatment with chloroform, leaving holes in the matrix. PC globules entrapped in the bulk, however, do not dissolve because they are not reached by the solvent. Indeed, the prolonged extraction with chlorinated solvent in a Kumagawa apparatus does not lead to the separation of the two blend components (only half of PC is extracted).

By adding Φ2OXA, large polymer domains are still evident, and the two polymeric phases become cocontinuous. With C6OXA, N6 is dispersed in form of microfibrilles in a PC matrix, as evident from the michrographs of the etched samples. In this case the extraction with chlorinated solvent is able to remove most of PC from the blend. Only a small amount of PC (about 3-4%) remains in the N6 phase, as confirmed by infrared spectroscopic analysis. Moreover, IR spectra show that both polymer fraction show small peaks attributable to C6OXA residues (945 cm^{-1}, ν P-O-Ar; 1651 cm^{-1}, ν C=N). IR analysis carried out at 230°C on the single polymer components treated with C6OXA shows that both components react with the oxazoline groups: the reaction is very fast and almost quantitative for COOH polyamide groups, much slower for the OH groups of polycarbonate generated during heating.

Therefore, it is plausible that some grafting of PC chains upon N6 can occur via the oxazoline-phosphazene trimer. This so formed compatibilizing agent can be present in very low amounts, near the limits of detection of IR, but still effective and sufficient to modify the interfacial tension of the two polymer phases, changing the morphology and improving the miscibility.

A similar behavior was found, for instance, in PPE/poly(styrene-co-maleic anhydride) blends compatibilized with amino-terminated polystyrene[10]. From the point of view of mechanical properties (Table 1), elastic modulus is greatly enhanced by the presence of C6OXA, possibly as a consequence of the phase inversion and the lower effect of water as a plasticating species. The toughness of the material is substantially kept at good levels, as indicated by the specific energy to break values; the thoughness of the blend containing Φ2OXA is very poor due to the phase cocontinuity.

Table 1.

Blend	Elastic Modulus (MPa)	Specific Energy to Break (J/mm^2)
PC/N6	1000	0.035
PC/N6 + Φ2OXA	1780	0.006
PC/N6 + C6OXA	2080	0.020

CONCLUSION

The addition of hexafunctional C6OXA to polycarbonate/polyamide blends was found to dramatically affect the properties of the final material. These effects are believed to be the result of the presence of small amounts of *in situ* formed compatibilizing agent, generated by grafting of PC chains upon N6 through the oxazoline-phosphazene trimer. It can be anticipated that even greater improvement of the final properties of the blend can be attained by increasing the amount of compatibilizing agent in order to reach full miscibility.

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