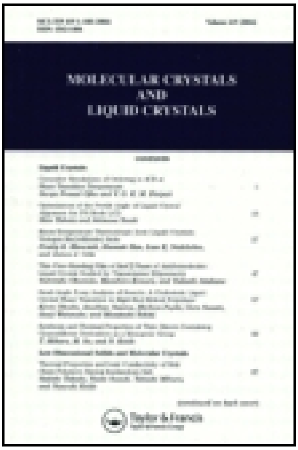

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Use of PP-g-OXA in the Compatibilization of PP/LCP Blends

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Adding small amounts of liquid crystalline polymers (LCP) to flexible thermoplastic matrices (FTP) allows to enhance the mechanical and thermomechanical properties. Therefore it is possible to obtain materials with new properties only by simple mixing. A strong shortcoming is the incompatibility between LCP and FTP that leads to materials with very poor properties unusable for commercial pourposes. The presence of a compatibilizer is therefore required. Oxazoline functionality is known to be highly reactive toward many other functional groups and then oxazoline functionalized polymers can be efficiently used as compatibilizer precursors. In this work the compatibilizazion of polypropylene (PP) with a semirigid LCP by using an *ad hoc* tailored oxazoline functionalized PP has been studied.

Keywords: LCP; blends; compatibilization; oxazoline; functionalization

INTRODUCTION

In the last years there has been an ever growing interest in blending existing polymers, rather than synthesizing new ones, to get new materials with enhanced properties. In most cases polymeric couples are immiscible and consequently the final properties are poor, hindering any practical application. In these cases compatibilization is a fundamental step to produce materials with good final properties an then with a commercial interest [1-2].

One of the most common methods used to compatibilize immiscible polymer blends is to add block or graft copolymers previously synthesized. Such copolymers have the function to reduce the interfacial tension, enhancing the particle dispersion and the phase adhesion beyond reducing the average dimension of the dispersed phase. This system has been used already also for liquid crystal polymers (LCP) containing blends.[3-6] Other methods consist in using functionalized polymers that during processing in conventional apparatuses react to form, *in situ*, copolymers that can act as compatibilizing agents. In particular, in these last years, there has been a strong interest toward a new method, the so called one step compatibilization. The aim is to produce a compatibilized blend starting from commercially available polymers and introducing in the processing apparatus the functionalizing agents,and the catalyst if requested, achieving in a single passage the functionalization, i.e. the formation of compatibilizer, and the compatibilization as well.[7-9] Oxazoline ring is one of the most indicate to give rise to compatibilizer as it easily and rapidly react with several other functional groups[10] allowing the fast formation of graft copolymers at the interface of the two incompatible phases.

Polypropylene (PP) and liquid crystal polymers (LCP) form incompatible blends, because of the strong difference in their macromolecular structure, and present narrow processing windows. Several attempts have been carried out to compatibilize LCP containing blends by using functionalized polymers [11-13] or graft copolymers *ad hoc* synthesized[4-6]. The results have not been ever encouraging. One route is to use semirigid LCP, i.e. LCP with flexible units in the main chain. This allows to lower processing temperature and to enhance

In this work an oxazoline modified polypropylene has been used as compatibilizer precursor for blends between PP and a semirigid LCP. The study has been carried out in order to evaluate the compatibilizing of the modified polypropylene on the rheological, mechanical, morphological and calorimetric properties of the blends.

EXPERIMENTAL

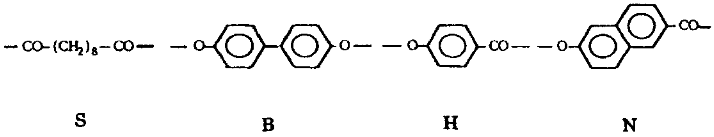
Materials

Two PP samples containing different amounts of grafted oxazoline have been used. In the sample having a larger concentration of OXA groups, (Hu 11) the grafted oxazoline is about 1.51 phr, while in the other sample (Hu4) is about 0.94 phr.

The samples have been purificated by dissolving them in boiling xylene and then by precipitating in acetone. To completely remove the solvents, the samples have been placed in a vacuum oven for at least 24 hours at 40 °C.

For comparison pourposes, a sample of virgin PP has been used. The sample (Moplen X30G) supplied by Montell, is an injection moulding grade.This sample has been chosen in order to use a non functionalized PP having a molecular weigth, Mw, quite similar to that of the two functionalized samples. Indeed, during the functionalization reactions a strong decrease of Mw occurs

The LCP was a semirigid sample named SBHN 1135. The letters indicate the components and the figures the molar ratios. S stands for sebacic acid, B for 4,4' dihydroxybiphenyl, H for 4-hydroxybenzoic acid, N for 2-hydroxy-6-naphtoic acid. A complete characterization of these materials can be found elsewhere.[14-15]



SCHEME 1 Chemical formulas of the components of SBHN

In scheme 1 the formulas of the components have been reported.

Synthesis of the modified PP

The grafting reaction of oxazoline onto PP has been carried on using a procedure similar to that used for grafting of glycidyl metacrylate on the same polymer [10].

Proper amount of an extrusion grade PP (Himont Valtec CL101D with MFI= 0.3 g/10 min) have been fed to a co-rotating twin screw extruder together with the functionalizing agent (ricinoloxazolin maleinate, Henkel Loxamid V-EP 8515), styrene as a comonomer and 1,3 bis (tert-butylperoxy-isopropyl) benzene (Akzo Perk-14, lifetime at 210 °C about 15 sec) as iniziator. The amounts of all these components have been chosen to have the maximum yield in OXA grafting onto the PP backbone, according to the results of a previous work[7] in which the grafting of oxazoline on PP was studied in a batch mixer.

Those results indicated that a grafting yield of OXA up to 1.5 phr could be obtained with a conversion that could be up to 50 %. Adding the styrene as a comonomer did not increase the yield.

Other details of this experimental part can be found elsewhere .[7-9]

Preparation

Blends (PP/SBHN, Hu4/SBHN, Hu11/SBHN 70/30 wt/wt and 0.3% of an antioxidant, P-EPQ by Sandoz) have been prepared using a Brabender Plasticorder mod. PLE 330 equipped with a mixing chamber of 50 cm^3 at a rotor speed of 60 rpm. The processing temperature was 210 °C, and the mixing was carried out for a time enough to reach a constant value of the torque (about 5 minutes for all the blends).

To prevent hydrolitic phenomena during mixing, the OXA grafted samples and the LCP have been dried for at least 24 hours at 70°C under vacuum.

Morphological characterization

The morphology has been studied using a scanning electron microscope Philips mod. 501. The samples have been fracturated in liquid nitrogen and covered with gold to make them electrically conductive using a SPI sputter coater.

Rheological characterization

Rheological measurements have been carried out on dried samples in a parallel plate rheometer (Rheometrics RDAII, diameter of plates 25 mm) at 210 °C in the frequency range 0.1-500 rad/sec with a strain of 5%.

RESULTS AND DISCUSSION

Processability and rheological characterization

In Fig. 1 the flow curves of the pure materials are displayed. The SBHN sample shows the highest viscosity in the whole range of the investigated frequencies. The crystal-nematic transition temperature for this sample is around 200 °C. Therefore - although the very low value of the crystallinity of this materials - at the testing temperature the morphology of this LCP is expected to be essentially biphasic, with zones that are "liquid-like" (that is in the nematic state) and some zones that are "solid-like" (crystalline zones melting at higher temperatures). This can be considered the reason why the viscosity of this sample is so high, showing a yield at low frequencies and a very strong non-Newtonian behaviour.

As for the other samples, the virgin PP shows a higher Newtonian viscosity and a stronger non-Newtonian behavior.

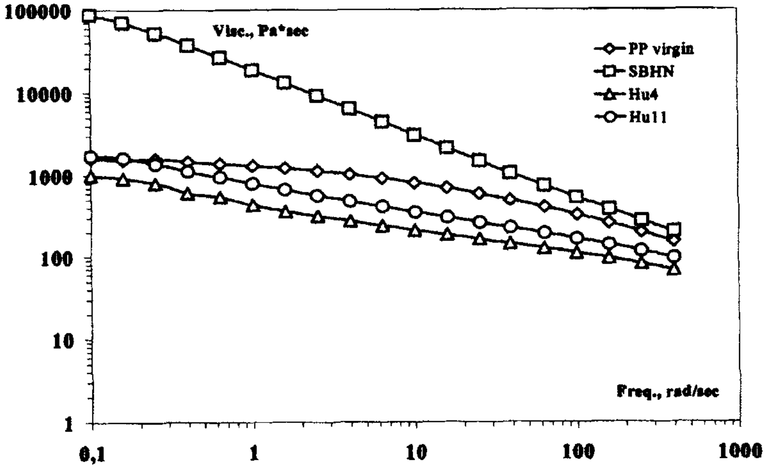


FIGURE 1 Flow curves of the pure materials

In Fig. 2 the curves of the torque as a function of time for the PP/SBHN and for the PP-g-OXA/SBHN blends are reported. The torque shows a decreasing trend approaching a steady state value for all the blends, due to the thermal and fluodynamical equilibrium of the materials inside the chamber.

Even if the viscosity of the Hu11 sample is lower than that of the virgin PP (see Fig. 1), the Hu11 based blend shows the highest values of torque, probably due to an extended reaction between the oxazoline ring grafted onto the PP main chain of Hu11 and the end groups of SBHN.

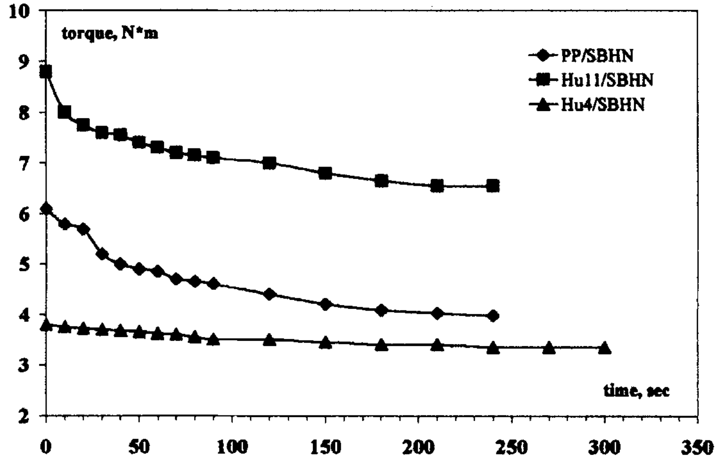


FIGURE 2 Flow curves of the torque as a function of time for the blends

During mixing PP-g-SBHN copolymers are produced at the interface giving rise to a better adhesion between the two incompatible phases The low value of torque for the Hu4 based sample indicates that in this case the reaction does not occur extensively. Moreover, the lower torque is also due to the lower viscosity of the Hu4 sample with respect to pure PP and with respect to the Hu11 sample (see Fig. 1). In Fig. 3 the viscosity curves as a function of frequency for the blends are reported. The results coming out from the mixing torque analysis are confirmed by the analysis of the curves there displayed.

The Hu11/SBHN blend shows the highest viscosity and moreover a yield can be detected at low frequencies. The viscosity at high frequencies is, on the contrary, similar to that of the unmodified PP based blend. The high viscosity at low frequency and the strong non-Newtonian behaviour can be considered typical of materials having a "structured morphology".

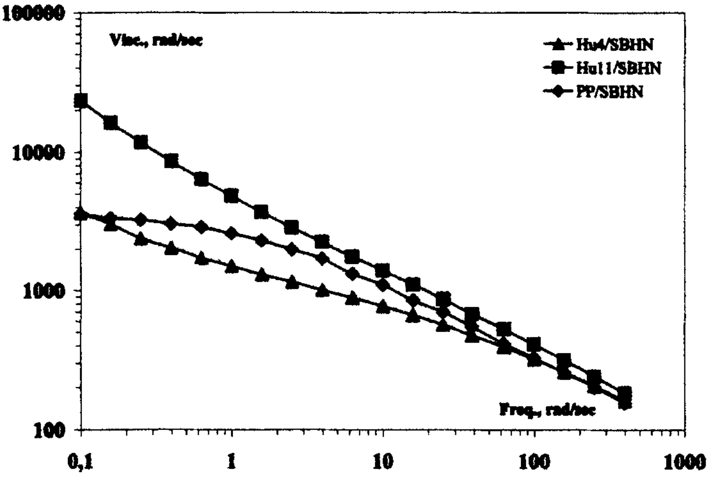


FIGURE 3 Flow curves of the blends

This suggests the presence of PP-*g*-SBHN copolymers at the interface that act as compatibilizer.

At low frequencies, that means at low shear stress, the presence of the compatibilizers allows to achieve a strong adhesion between the phases. In these conditions the material needs a yield stress to start to flow. On increasing the frequency, and then the shear stress, the effectiveness of these compatibilizers is lower and the material starts to flow showing a strong non-Newtonian behavior. A polar interaction between PP-*g*-OXA and SBHN cannot be, however, excluded.

The lower viscosity of the Hu4 based blend agrees with the mixing torque analysis. Although the lower viscosity of the PP modified matrix, it is reasonable to consider that in this case a lower amount of PP-*g*-SBHN copolymers are produced according to the minor content of oxazoline groups.

Morphology

In Figs. 4-6 the SEM micrographs of the blends have been reported. The uncompatibilized blend PP/SBHN, Fig. 4, shows a morphology typical of an incompatible blend

FIGURE 4 SEM micrograph of uncompatibilized PP/SBHN 70/30 blend

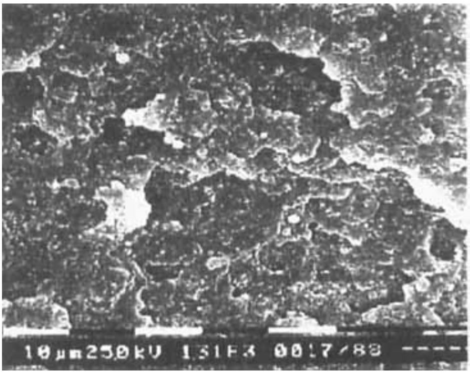


FIGURE 5 SEM micrograph of Hu11/SBHN 70/30 blend.

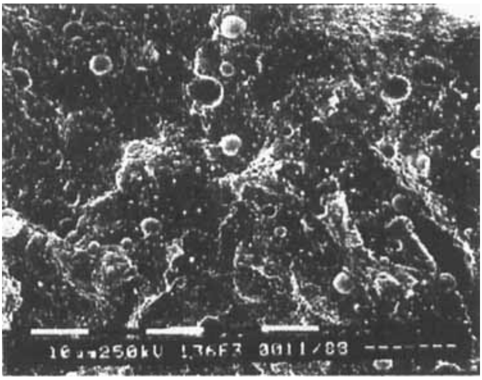


FIGURE. 6 SEM micrograph of a Hu4/SBHN 70/30 blend

The particles of dispersed phase are bad distributed, the adhesion is extremely poor, the average dimension is relatively large (about 20 μm). In the Hu11/SBHN blend, Fig. 5, the situation is completely different.

The average dimension of the particle has fallen down to no more than 0.5 mm, and both the adhesion and the dispersion are extremely good.

The situation for the Hu4 based blend, Fig. 6, is qualitatively similar to the last blend, but the particles are larger and the adhesion appears sligthly worse. We have a confirmation of the lower compatibilizing effect obtained using this PP modified sample

Mechanical properties

In Tab. I the main tensile properties (Young's modulus, E, tensile stress, TS, elongation at break, EB) have been reported for the pure materials. SBHN shows the higher modulus but a brittle behavior.

However, the modulus is quite low for a liquid crystal polymer and this is

TABLE I Tensile properties of the pure components

Material	E, MPa	TS, MPa	EB, %
SBHN	1440	27.2	2.3
PP	1315	31.0	18.8
Hu4	886	21.8	8.6
Hu11	1175	24.6	11.9

due both to the presence of flexible segments in the chain and to the fact that only in the anisotropic state these materials show very high values of the modulus. The three PP samples show different mechanical properties due both to the different molecular weight and to the presence of the oxazoline groups. The values of the elongation at break of all the samples are very low and this depends on the low molecular weight.[17-18] In this range of molecular weight, indeed, the elongation at break is decreasing with decreasing the molecular weight. Modulus and tensile strength follow the same trend and then the different values of these properties seem in good agreement with this behaviour. However, from a quantitative point of view, the large differences between the mechanical properties of these threee samples having similar molecular weight suggest some influence of the oxazoline groups.

In Tab. II the tensile properties of the blends are reported together with the ratios between the properties of the blend (subscript b) referred to those of the relative matrix (subscript m). The uncompatibilized blend shows the value of the modulus intermediate between those of the two components while the ultimate properties are below those of PP and SBHN. This behavior is well expected considering the deep incompatibility between the two components. Particularly impressive is the strong reduction of the elongation at break (less than half of the value of the PP matrix).

The behavior of the compatibilzed blends is very different.

TABLE II Tensile properties of the blends

Material	E, MPa	E_b/E_m	TS, MPa	TS_b/TS_m	EB, %	EB_b/EB_m
PP/SBHN	1395	1.06	22.3	0.72	7.8	0.42
Hu4/SBHN	956	1.08	22.1	1.01	9.2	1.07
Hu11/SBHN	1295	1.10	24.7	0.99	14.3	1.20

Indeed, although the absolute values of the mechanical properties are not so high as expected on the basis of the morphology, for the blends with the modified PP quite good properties have been measured and, in particular, no decrease of the mechanical properties with respect to those of the matrix is observed. The tensile properties are better for the blend with Hu11 confirming the better adhesion between the two phases induced by the presence of the oxazoline groups.

As already said, the tensile properties of compatibilized blends are not so high as expected on the basis of the good morphology observed for these samples. This behaviour has been noticed for many blends[3-4] and can be probably attributed to the different cooling conditions of the two materials leading to some dewetting with consequent rupture of the "bridges" between the two phases and reduction of the adhesion.

CONCLUSIONS

Blends of PP and LCP are deeply incompatible and their properties are in general modest and, in some case, lower than those of the two components. Oxazoline modified PP gives rise to blends with better properties and, in particular, with a very fine morphology. This behaviour has been attributed to the possible occurrence of reactions between the oxazoline group of the PP matrix and the end groups of the LCP dispersed phase. The ultimate tensile properties of the uncompatibilized blends show a minimum with respect to

those of the pure components but this minimum desappears for the compatibilized blends.

It is therefore demonstrated that the oxazoline groups, already used for compatibilizing blends of flexible polymers, can be usefully employed for the compatibilization of LCP based blends.

ACKNOWLEDGEMENTS

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