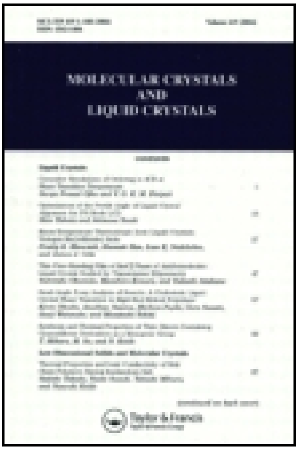

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Effect of the Orientation on the Properties of Compatibilized Polypropylene/Liquid Crystal Polymer Blends

Francesco Paolo La Mantia [a] , Roberto Scaffaro [a] , Rosa Spoto [a] , Pierluigi Magagnini [b] & Massimo Paci [b]

[a] Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Università di Palermo, Viale delle Scienze, 90128, Palermo, Italy

[b] Dipartimento di Ingegneria Chimica, Chimica Industriale Scienza dei Materiali, Università di Pisa, Via Diotisalvi 2, 56126, Pisa, Italy

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Effect of the Orientation on the Properties of Compatibilized Polypropylene/Liquid Crystal Polymer Blends

FRANCESCO PAOLO LA MANTIA[a], ROBERTO SCAFFARO[a], ROSA SPOTO[a], PIERLUIGI MAGAGNINI[b] and MASSIMO PACI[b]

[a]*Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Università di Palermo, Viale delle Scienze, 90128 Palermo, Italy and* [b]*Dipartimento di Ingegneria Chimica, Chimica Industriale e Scienza dei Materiali, Università di Pisa, Via Diotisalvi 2, 56126 Pisa, Italy*

Blends of polypropylene and a semirigid liquid crystal polymer have been compatibilized with an acrylic acid modified polypropylene and with an *ad-hoc* synthesized graft copolymer made from polypropylene and from the monomers of the liquid crystal polymer. The two compatibilizers improve the adhesion and the mechanical properties of the two incompatible phases. The two compatibilizers give about the same results. The effect of the compatibilization improve also the orientation of the liquid crystalline polymer particles and the mechanical properties.

Keywords: blends; liquid crystal polymer; modified polypropylene; orientation

INTRODUCTION

In the last few years, blends of liquid crystalline polymers (LCPs) with thermoplastic resins have received considerable interest by academic and industrial research laboratories because of their potential as processing aids and reinforcing agents [1,2].

Unfortunately, most commercial thermoplastics are incompatible with LCPs and although the incompatibility gives rise to the segregation of fibers of the dispersed phase and then to a reinforcing effect, this is also the cause of for poor properties of the blends due to the lack of adhesion between the phases.

In particular, if LCP-polyolefins (polyethylene, PE and polypropylene, PP) blends are concerned, the interphase adhesion is too low to grant acceptable mechanical properties.

The addition of additives to improve compatibilization may lead to enhanced adhesion and may also solve the problems of poor dispersion in polymer blends.

Recently, commercial functionalized polymers, such as maleic anhydride grafted PP [3-12] or acrylic acid grafted PP [13-16], have been used as compatibilizers for PP-LCP blends. It was shown that only a slight improvement of adherence between the matrix and the dispersed phase was realized, due to polar interactions (such as hydrogen bonding) between the components and not to the formation of covalent bonds. We found a similar behavior in blends of PE with a semiflexible LCP, compatibilized with maleic anhydride grafted PE.

A new strategy, based on the synthesis of block or graft copolymers carrying segments with chemical structure and solubility parameters similar to the blend components, seemed to be more attractive. In previous papers [17-18], we described the compatibilizing ability with respect to HDPE-LCP blends of a PE-g-LCP copolymer synthesized by polycondensation of the LCP monomers in the presence of functionalized PE as well as of similar PE-g-LCP copolymers obtained by reactive blending with preformed LCP. The studies have shown that both products improved the interfacial adhesion and phase dispersion when added to PE-LCP blends.

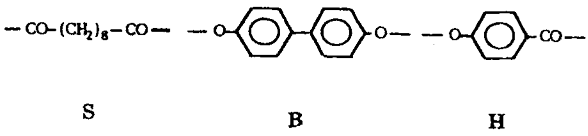
In this work, a new PP-g-LCP copolymer, recently synthesized in our laboratories [19] has been evaluated as a compatibilizer for blends of PP with a semirigid liquid crystalline polymer. An acrylic acid grafted PP of fairly high molar mass was used for comparison.

EXPERIMENTAL

Materials

PP was an injection molding grade material (X30G) manufactured and kindly provided by Montell Italy. The melt flow index is about 8 g/10 min.

The LCP, referred to herein as SBH, Scheme 1, was a copolyester of sebacic acid (S), 4,4'-dihydroxybiphenyl (B), and 4-hydroxybenzoic (H), in the molar ratio 1:1:2, developed by Eniricerche S.p.A., San Donato Milanese, Italy[20] whose characterization of SBH has been described elsewhere [1-2, 21].



SCHEME 1 Chemical formulas of the components of SBH

The acrylic acid grafted PP (PPAA), was a commercial sample (Polybond 1001 manufactured and kindly provided by Uniroyal). This polymer has a weight average molar mass of about 100,000 and contains 6% w/w of acrylic acid branches. This corresponds approximately to 0.7 mmols of carboxyl groups per gram. PPAA was used either directly as a compatibilizer or as a precursor for the synthesis of the PP-*g*-SBH copolymer.

PP-g-SBH synthesis

PP-*g*-SBH (COPP) was synthesized in a Pyrex reactor equipped with a stainless steel stirrer and vacuum outlet, by melt polycondensation of appropriate amounts of the SBH monomers in the presence of PPAA.

The composition of the mixture was calculated in such a way as to obtain a graft copolymer containing 50% w/w PPAA. A minute amount of sodium acetate was added as a catalyst.

Details on the synthesis and the characterization of this copolymer have been provided in a previous paper[19].

Blends and samples preparation

Blends were prepared in a Brabender internal mixer attached to a Brabender Plasticorder PLE 330. The mixing temperature was 240°C, the rotational speed 60 rpm, and the mixing time about 5 min (until constant torque was measured).

The composition of the blends was designed so as to reach a total SBH content, calculated as the sum of the weighed amount of neat SBH plus that contained in the PP-*g*-SBH copolymer (if any) equal to 20% w/w. The amount of added compatibilizers was 5.0 phr.

The samples for the tensile tests were obtained by compression molding and by melt spinning. The compression molding was performed in a laboratory Carver press at T ~ 240°C.

Fibers were prepared, from all the blends, using the tensile module of a capillary viscometer, Rheoscope 1000 (CEAST, Italy), with a capillary of 1 mm diameter and length-to-diameter ratio of about zero.

The extruded monofilament passes through a pulley system and is then drawn by two counter-rotating rolls, the rotational speed of which continuously increases with a linear acceleration of 1 rpm/s.

The spinning temperature was about 280°C. The draw ratio, DR, was evaluated as the ratio between the cross section of the die and of the filament.

Rheological Properties

The viscosity curves of pure polymers and blends were determined using a Rheometrics Dynamic Analyzer RDA2. The tests were carried out in the dynamic mode with the plate and plate geometry, at 240°C.

Mechanical properties

The Young's modulus (E), the tensile stress (TS) and the elongation at break (EB) of all the investigated materials were measured using an Instron mechanical testing machine mod.1122. All the values were determined as the average of at least 7 measurements.

Morphology

The morphology was studied by scanning electron microscopy (SEM) using a Philips mod. 501 apparatus. The samples were fractured in liquid nitrogen and coated with gold using an SPI sputter coater.

RESULTS AND DISCUSSION

The viscosity curves of the pure components measured at 240°C are shown in Figure 1.

The acrylic acid grafted PP and the pure PP samples show the lowest flow curves and an almost Newtonian behavior. SBH and COPP samples show the highest viscosities in the whole shear rate range, a strong non-Newtonian behavior and no Newtonian region is revealed. This behavior can be attributed to the "structured morphology" of these materials in the melt [17-18].

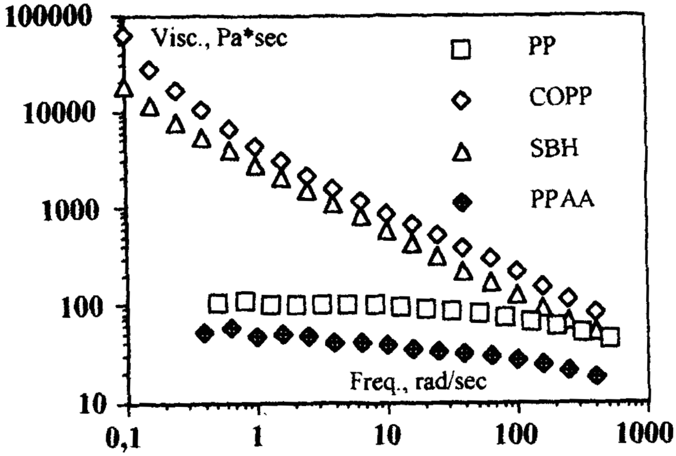


FIGURE 1 Flow curves of pure components

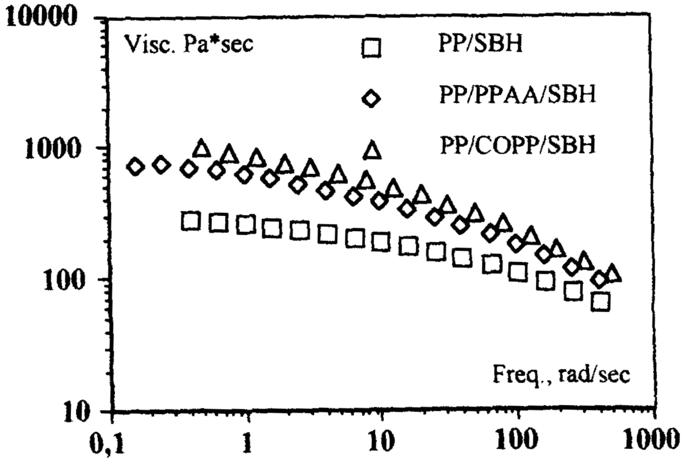


FIGURE 2 Flow curves of the blends

The effect of the two compatibilizing agents into the blends with 20% of SBH is shown in Fig. 2, where the flow curves of the compatibilized blends (5% of compatibilizing agent) are plotted together with that of the uncompatibilized one.

The viscosity of the two compatibilized blends is higher than that of the uncompatibilized one in the whole frequency range investigated, showing that a compatibilizing effect is in fact exhibited by both additives. Actually, the better adhesion between the two phases, giving rise to larger and well connected flow units, is responsible for the viscosity increase. This is larger for the blend compatibilized with COPP. It is also worth noting that the addition of PPAA into the PP/SBH blend causes a viscosity increase, though being far thinner than the blend components (cf. Fig. 1).

To confirm the foregoing statement, the morphology of the binary and ternary blends was studied and the relevant SEM micrographs are reported in Figs. 3 a-c.

The morphology of the uncompatibilized PP/SBH blends, Fig. 3a, is typical for a biphasic material characterized by poor dispersion (droplets size ranging between 1 and 80 μm) and by almost no adherence (none of the droplets involved in the fracture).

The poor mechanical properties exhibited by this blend are in good agreement with those expected for a material showing such a morphology.

The SEM micrograph of the fracture surface of the ternary blend containing COPP, Fig. 3b, shows that the addition of the graft copolymer improves the distribution of the LCP minor phase; the drawback is that the adhesion between the matrix and the droplets is only slightly increased. A clearer indication of an enhanced dispersion (particle size lower than 15-20 μm) and an improved adhesion is provided by Figure 3c, showing the fracture surface of the blend compatibilized with PPAA.

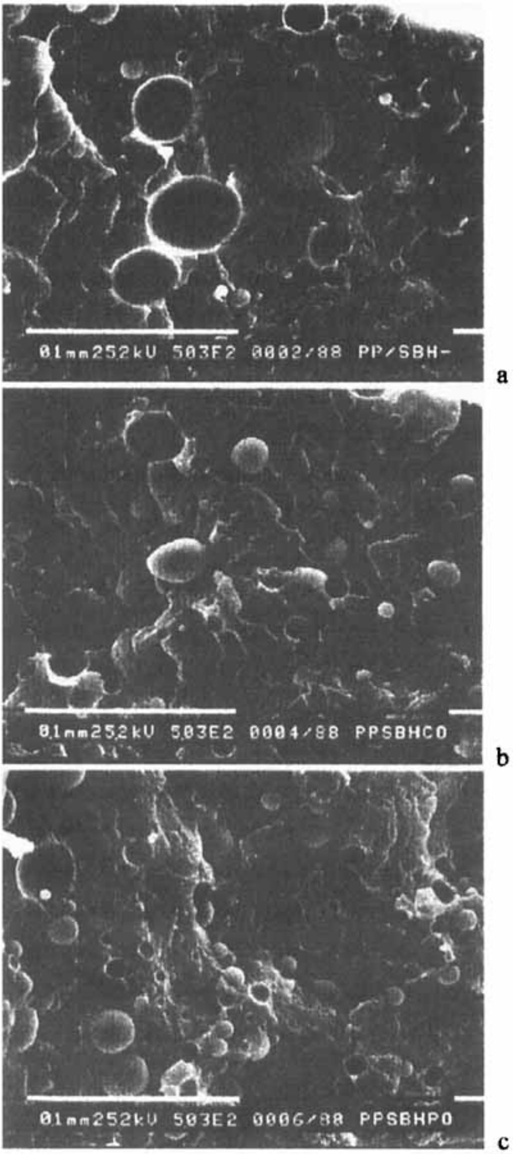


FIGURE 3 SEM micrographs of compression molded blends

One might expect the improved adhesion between the two polymers, as revealed by both rheological and morphological analyses, to be accompanied by an increase of mechanical properties. In Table I the tensile properties, elastic modulus, E, tensile stress, TS, and elongation at break, EB, for the three systems are reported.

TABLE I Tensile properties of uncompatibilized and compatibilized blends

Blend	E, MPa	TS, MPa	EB, %
PP/SBH	800	22	7
PP/SBH/PPAA	860	24	8.5
PP/SBH/COPP	850	24.5	9.5

The addition of PPAA and COPP into the blends leads to an improvement of all the tensile properties that is similar for both the compatibilizers. It is worth noting, however, that the measured improvements are quite poor (6-7 % for the modulus, about 10% for the tensile stress and 20-30% for the elongation at break) and lower than that one would expect from the viscosity results. This behavior has already been reported for other blends[19-20] and the suggested explanation considers the different contraction undergone by the two materials during cooling, that can "stress" the interphase and reduce the adhesion.

The enhanced mechanical behavior of the compatibilized blends is also evidenced by the creep curves reported in Fig. 4 .

The creep curves of the two compatibilized display lower values with respect to those of the uncompatibilized blend; this behavior is an indication of an improved resistance to the deformation. This tendency can be due either to the higher values of the elastic modulus and to the better adhesion between the two phases. The latter is probably responsible also for the larger values of the deformation at break measured for the compatibilized blends.

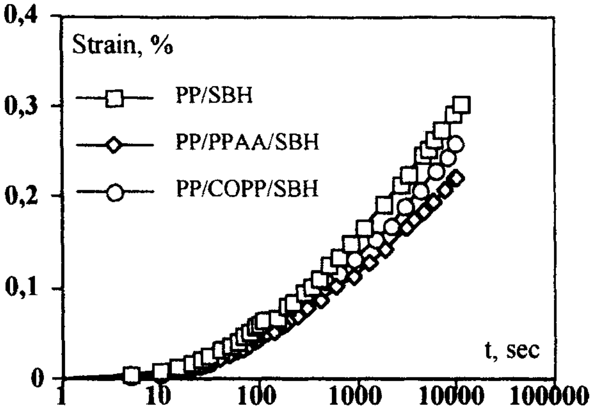


FIGURE 4 Creep curves of the blends

In Figs. 5-6 the elastic modulus, E, and the tensile stress, TS, are reported, as a function of the draw ratio, DR, for fibers of the binary and ternary blends.

The modulus, Fig. 5, and the tensile stress, Fig. 6, increase with the increase of the draw ratio, µp to about 3 GPa and about 100 Mpa, respectively.

The properties of the compatibilized blends are slightly better than those of uncompatibilized one. In particular, the modulus and the tensile strength of the PPAA containing blend are about 35% larger than those of the uncompatibilized one.

The SEM micrographs of the fibers, reported in Figs 7a-c confirm the mechanical results. The blend compatibilized with PPPA shows quite long

SBH fibrils, Fig. 7a, whereas the latter are shorter for the blend with COPP, Fig. 7b.

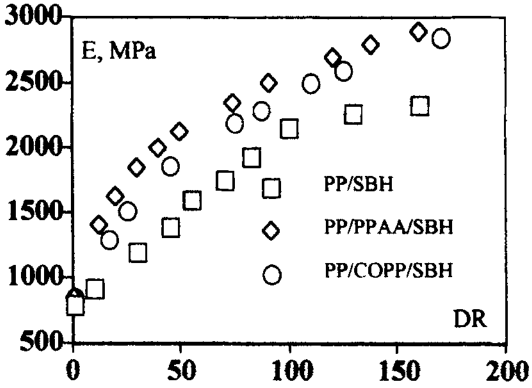


FIGURE 5 Elastic modulus of the blends as a function of draw ratio

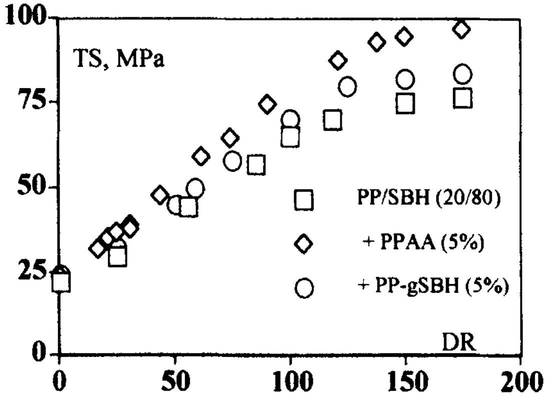


FIGURE 6 Tensile stress of the blends as a function of draw ratio

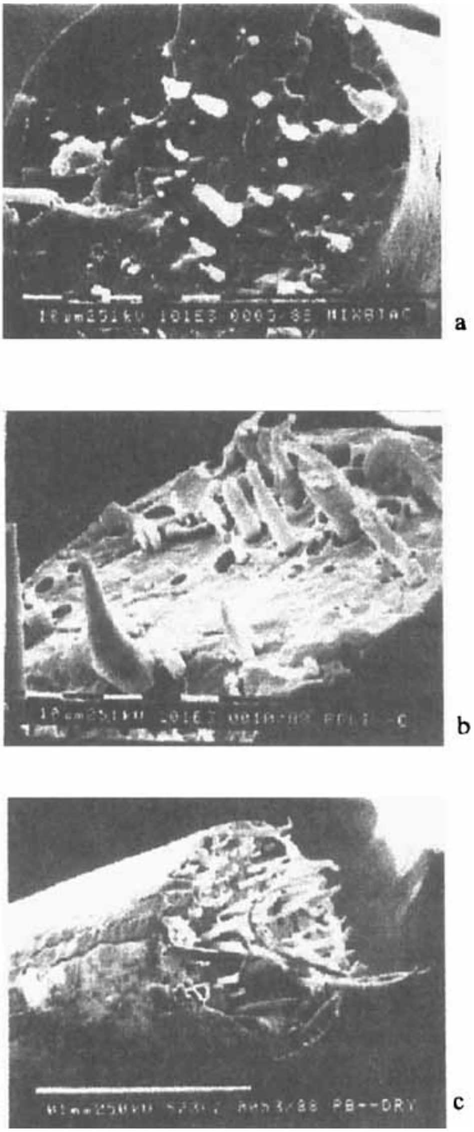


FIGURE 7 SEM micrographs of compatibilized and uncompatibilized PP/SBH blends

In the uncompatibilized blend fiber, almost no fibrillation of the minor phase has occurred, as it is shown by Fig. 7c, where only slightly elongated droplets are visible.

The morphology of these fibers indicates that the adhesion is not particularly improved as a result of the compatibilizer addition. Indeed, the SBH fibrils visible in the micrographs of Fig.s 7a and 7b appear to have been pulled-off as a result of fiber rupture. Nevertheless, the better fibrillation of the SBH particles in the compatibilized blends suggests an improved stress transmission between matrix and dispersed particles and, therefore, enhanced interfacial adhesion.

CONCLUSIONS

In this work the effect of the compatibilization on the properties of oriented and unoriented PP/LCP blends has been investigated.

The addition of an ad-hoc synthesized PP-g-LCP copolymer or of an acrylic acid modified PP as compatibilizers allows to enhance the adhesion between the two phases and the dispersion of the LCP particles into the matrix with a consequent improvement of the mechanical and thermomechanical properties.

The compatibilization also improves the orientation of the LCP particles.

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