Synthesis of Compatibilizers and Characterization of the Compatibilized and Noncompatibilized Blends of PP/Rodrun LC3000

M. T. Cidade,[1] S. Filipe,[1*] A. P. Duarte,[1,2] J. C. M. Bordado[2,3]

[1]Departamento de Ciência dos Materiais and CENIMAT, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Campus da Caparica, 2829-516 Caparica, Portugal
[2]ICTPOL, IST – Departamento de Engenharia Química e Biológica, Torre Sul, 1049-001 Lisboa, Portugal
[3]Departamento de Engenharia Química e Biológica, Instituto Superior Técnico, 1049-001 Lisboa, Portugal

ABSTRACT: The addition of a liquid crystalline polymer (LCP) to a matrix of a flexible thermoplastic (TP) has been used in the last two decades as an *in situ* reinforcement of the matrix. Owing to the immiscibility of the two phases and the high degree of orientation typical of LCPs, the dispersed phase is, after processing, essentially constituted by fibrillar structures, which are responsible for the reinforcement of the matrix and the decrease of viscosity with respect to the matrix. The low degree of adhesion typical of LCP/TP blends often requires the use of compatibilizers, which will act reducing the interfacial tension between the two components. In this work, we present the synthesis of three different compatibilizers, as well as the mechanical characterization of the corresponding compatibilized blends. Some scanning electron microphotographs will be also presented to better explain the mechanical results. The mechanical properties of these blends were compared with the noncompatibilized blend, as well as with the ones presented by blends obtained with two commercial compatibilizers, leading to the conclusion that, considering our compatibilizer C, the one that leads to the higher enhancement of the Young's modulus, when compared with the noncompatibilized blend, we obtain a Young's modulus 27% higher than the one presented by the noncompatibilized blend. Comparing this result with those presented by the blends compatibilized with the two commercial compatibilizers, D and E, we conclude that this enhancement is higher than those presented by those blends (increase in Young's modulus of 16% for both compatibilizers). © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3001–3009, 2007

Key words: synthesis; compatibilization; blends; mechanical characterization

INTRODUCTION

In the last two decades, considerable interest has been focused on liquid crystalline polymers (LCPs) and olefinic thermoplastic (TPs) blends, due to their improved mechanical properties, easier processability, and cost efficiency.[1–20]

One of the advantages of LCP/TP *in situ* composites arise from the high level of macroscopic molecular orientation developed in these blends (which leads to the formation of fibrillar structures oriented along the flow direction, with consequent mechanical performance enhancement). Another advantage is related with the decrease of viscosity, when compared with other reinforced thermoplastics, like, for instance, those with glass fibers.[21–23]

Nevertheless, in these blends, the LCP and the thermoplastic blends often present a low degree of adhesion, which arise from the fact that, owing to their high aromatic content, LCPs typically have high interfacial tension towards aliphatic polymers. The addition of compatibilizers that promote a decrease of the interfacial tension between the matrix and the dispersed phase, and a better dispersion of the LCP in the matrix, is a strategy to partially overcome this problem.[5–7,12,15,16,18,19,24]

The compatibilization is usually achieved by physical or chemical interactions between the components of the blend and the compatibilizer, which are performed by adding small amounts of functionalized graft or block copolymers to the LCP/thermoplastic blends.[5–7,15,16]

In principle, the degree of adhesion can be improved by using compatibilizers with chemical structures consisting of segments similar to those of the LCP and the thermoplastic blends, which will migrate to the interface, and thus, reduce the interfacial tension between the two components.

Compatibilizers like maleic anhydride-grafted-PP (MAGPP), triblock copolymer of styrene/ethylene–butylene styrene (SEBS), maleic anhydride-grafted-SEBS, ethylene–propylene–diene monomer (EPDM),

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and maleic anhydride-grafted-EPDM (MA-*g*-EPDM) are some of the compatibilizers that have been successfully used in blends of PP/Rodrun LC3000.[4,18,22]

A novel strategy has appeared recently,[25] in which the blends are prepared in such a way that a finely dispersed cocontinuous morphology is obtained for the blend. This is possible through reactive blending between the component with higher content, to which reactive groups along the backbone were added, and the component with lower content which presents end reactive chains. During reactive blending, random graft copolymers are formed and the mixture of these graft copolymers and unreacted backbones (major component) and grafts (minor component) results in thermodynamically stable microstructures. Pernot et al.[25] applied this technique to a blend of polyethylene (PE) and polyamide (PA), the funtionalization of the PE obtained by copolymerization, at high pressure and high temperature and using free-radical initiators, of ethylene, ethylacrylate, and maleic anhydride (MAH), while the functionalized PA was synthesized by polycondensation, and was terminated at one end by the reactive functional group NH_2, and at the other end by a nonreactive group CH_3. These functionalized groups were chosen to obtain a fast coupling reaction, which is the case between MAH and NH_2 groups.

The blends obtained by Pernot et al.,[25] with a functionalized PE with 1% weight fraction of MAH, a number–average molecular weight of 9300 g/mol and a polydispersity index of 5.5, and with a PA with a number–average molecular weight of 2500 g/mol, a polydispersity index of 2 and 20 wt % content in the blend, present improved material transparency, creep and solvent resistance, and an increase in the stress at break while keeping ductility.

One problem concerning this method is that, to avoid phase separation, homopolymers have to be short, crystallizable, and with an appropriate polydispersity, which turned impossible to use this method for our blends, since the synthesis of compatibilizers was just a continuation of a work that we had already started[20,26,27] and our matrix, as will be described in the Material section, was a isotatic polypropylene with a weight–average molecular weight ($\overline{M_w}$) of 1200,000 g/mol.

In this work, we present the synthesis of structure designed compatibilizers, which are mostly linear structures and were prepared with a part of the backbone compatible with the PP (matrix) and another part, with an oligomeric aromatic structure, compatible with the liquid crystal molecules structure. Both size and composition of these two components were varied, to change the compatibility with each one of the components.

Blends of PP/Rodrun LC3000 were prepared adding three synthesized compatibilizers and their me-

chanical properties measured. Additionally blends with two commercial compatibilizers were also prepared and characterized to compare the different compatibilizer performances.

EXPERIMENTAL

Materials

The LCP/TP blends were produced by using an isotatic polypropylene (Stamylan P 12E62, from DSM) as thermoplastic and Rodrun LC3000 (from Unitika) as liquid crystalline polymer. The thermoplastic possess a weight–average molecular weight ($\overline{M_w}$) of 1200,000 g/mol (obtained by GPC), a melt flow index of 0.8 g/10 min (at 230°C and for 21.6N), and a melting temperature of 160°C. Rodrun LC 3000 is an aleatory copolyester of 60 mol % of *p*-hydroxybenzoic acid (HBA) and 40 mol % of polyethylene terephthalate (PET), with a nematic transition temperature of 189°C. The molecular weight for the LCP could not be estimated due to solubility problems of Rodrun LC3000 (no solvent could be found for this polymer).

To improve the compatibility between the liquid crystalline polymer and the thermoplastic, five different compatibilizers were used. Of these, three compatibilizers (A, B, and C) were prepared in the framework of the present work, and their synthesis will be presented later. The fourth compatibilizer (D) is a commercial material constituted by maleic anhydride-grafted polypropylene (Epolene G-3003 Wax) and was supplied by Eastman. Compatibilizer E, the fifth compatibilizer, is an ethylene–propylene copolymer grafted with maleic anhydride (0.3% by weight), with the commercial name Exxelor VA 18020 and was supplied by Exxon Mobil Chemical. Compatibilizer E has an elastomeric nature, while all the others have a thermoplastic nature. The chemical structures of compatibilizers D and E, along with the one for Rodrun LC3000 are presented in Figure 1.

Methods

Extrusion and injection molding

A corotating twin-screw extruder from Leistritz, model LSM 30.34 was used for the preparation of the blends. Before extrusion, all the materials were dried in an oven at 90°C for 24 h. The blends were processed at 4 kg/h, 220°C (the temperature was set constant all over the die length), and with a screw speed of 150 rpm, and the final extrudates were immediately quenched in a water bath (to freeze the morphology obtained at the die exit) and subsequently pelletized.
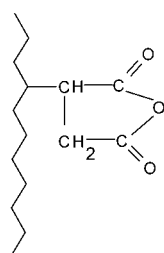
The resultant pellets were dried at 90°C for a period of 24 h and injection molded specimens for tensile and impact properties were produced by using an injection molding machine ENGEL model ES200/45
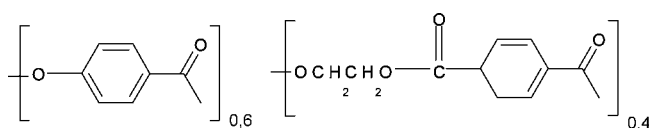
Rodrun LC3000
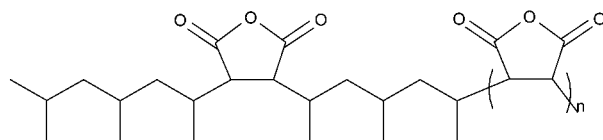
Compatibilizer D

Compatibiliser E

Figure 1 Chemical structures of Rodrun LC 3000 and compatibilizers D and E.

HL-V. The processing conditions are described in more detail elsewhere.[28,29]

Morphological characterization

The morphological characterization was performed by scanning electron microscopy (SEM) using a scanning electron microscope ZEISS DSM 962. All the cryogenically fractured samples were previously coated using a POLARON SC502 and then examined by SEM at an accelerating voltage of 10 kV. These observations were performed for the cryogenically longitudinal cuts of the final extrudates.

Mechanical characterization

Tensile and impact measurements were carried out using a Rosand Instrumented Falling Weight Impact Tester, Type 5 for the impact measurements and an Instron Universal Tester Machine model 1.16 for tensile measurements. The impact mass used was 25 kg, and the impact velocity was set at 2 m/s. A set of five measurements was performed for each blend, and the final results were obtained by the mean value of the different measurements.

More details about the measurement conditions are available elsewhere.[28,29]
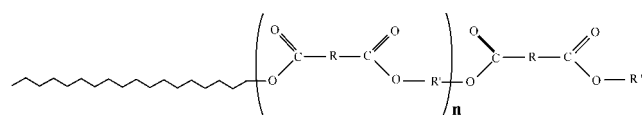
Aliphatic segment
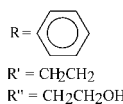(low polarity and very hydrophobic)

Polyester segment

with

$R = $

$R' = CH_2CH_2$
$R'' = CH_2CH_2OH$

Figure 2 Representation of the compatibilizer structure (aliphatic and aromatic segments).

Synthesis of the compatibilizers

Design of the molecular structure

The compatibilization of LCP in the PP matrix should be achieved by promotion of adhesion, better described in the liquid phase as dispersability of the LCP microcrystal domains.

This surface modification can, conceptually, be achieved by rather small oligomers with sufficient mobility in the melt to "adhere" to the surface of the LCP fibrils.

A - Lifting platform
B - Heating System
C - Reactor
D - Stirring Motor
E - Condensation finger
F - Vigreux column
G - Termometer
H - Dean-stark adaptor
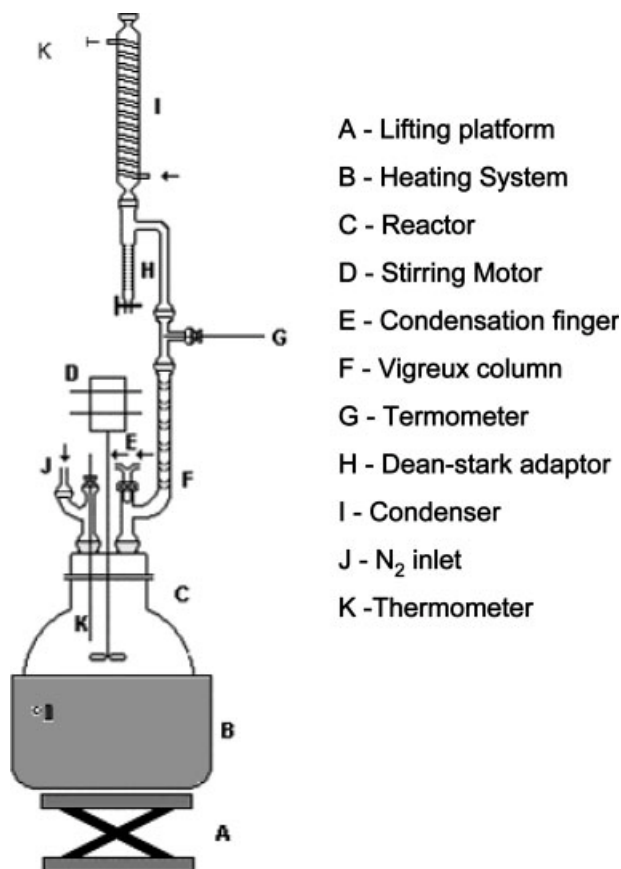I - Condenser
J - N₂ inlet
K - Thermometer

Figure 3 Schematic representation of the reactor used for the synthesis of compatibilizers A, B, and C.

The PP matrix, with a marked polyolefinic character would not easily admit a rather polar oligomer and their molecules should migrate to the LCP surface creating an interphase with different typology.

In the melt state, the behavior of the oligomeric compatibilizer should be somewhat analogous to the behavior of surfactants in the presence of two different liquid phases.

We decided therefore to prepare oligomers with two main segments, one aliphatic chain, compatible with the matrix, and one aromatic (polyester segment), compatible with the LCP (Fig. 2).

This type of structures open room to iterative optimization since the length of the two segments can be varied to increase the affinity to the LCP (longer polyester chain), or to the matrix (longer aliphatic segment).

It is also possible to increase the mobility of the compatibilizer molecules by reducing the overall molecular weight (length) of the synthesized compatibilizer.

Synthesis procedure for compatibilizers A, B, and C

The chemical synthesis of compatibilizers A, B, C was performed using the same reactor system;[29] the scheme is presented in Figure 3.

The chemical synthesis of compatibilizer A was based on the following reactants: linear dodecanol, dimeric acid, and an oligomeric polyester diol (with commercial name Terol[TM]). The experimental procedure was performed as follows (for the chemical structures see Fig. 4): 1 mol of terol and 1 mol of dimeric acid were mixed and heated up to 240°C in a
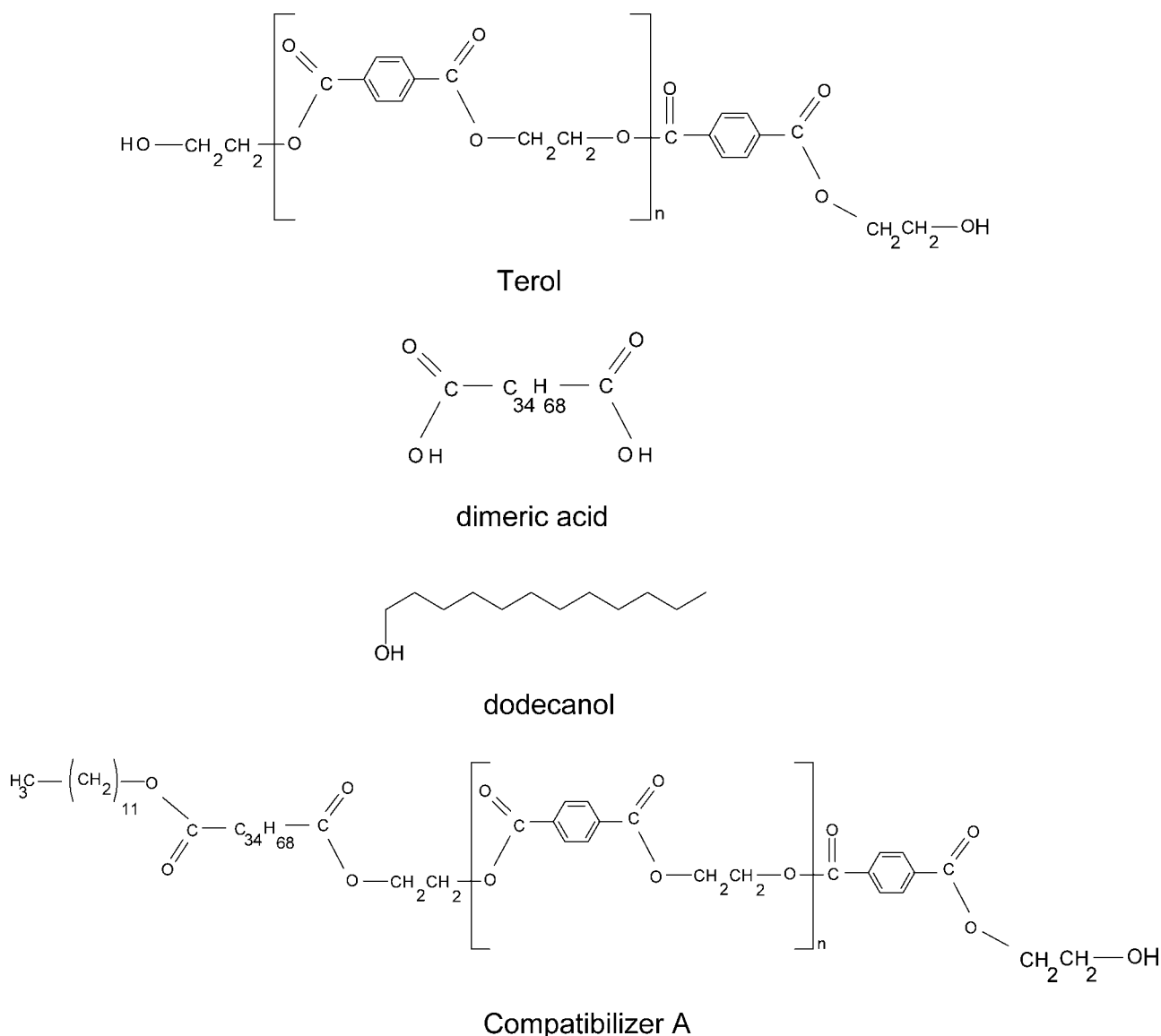

Terol

dimeric acid

dodecanol

Compatibilizer A

Figure 4 Chemical structures of the oligomeric acid, Terol[TM], dimeric acid, dodecanol, and compatibilizer A.
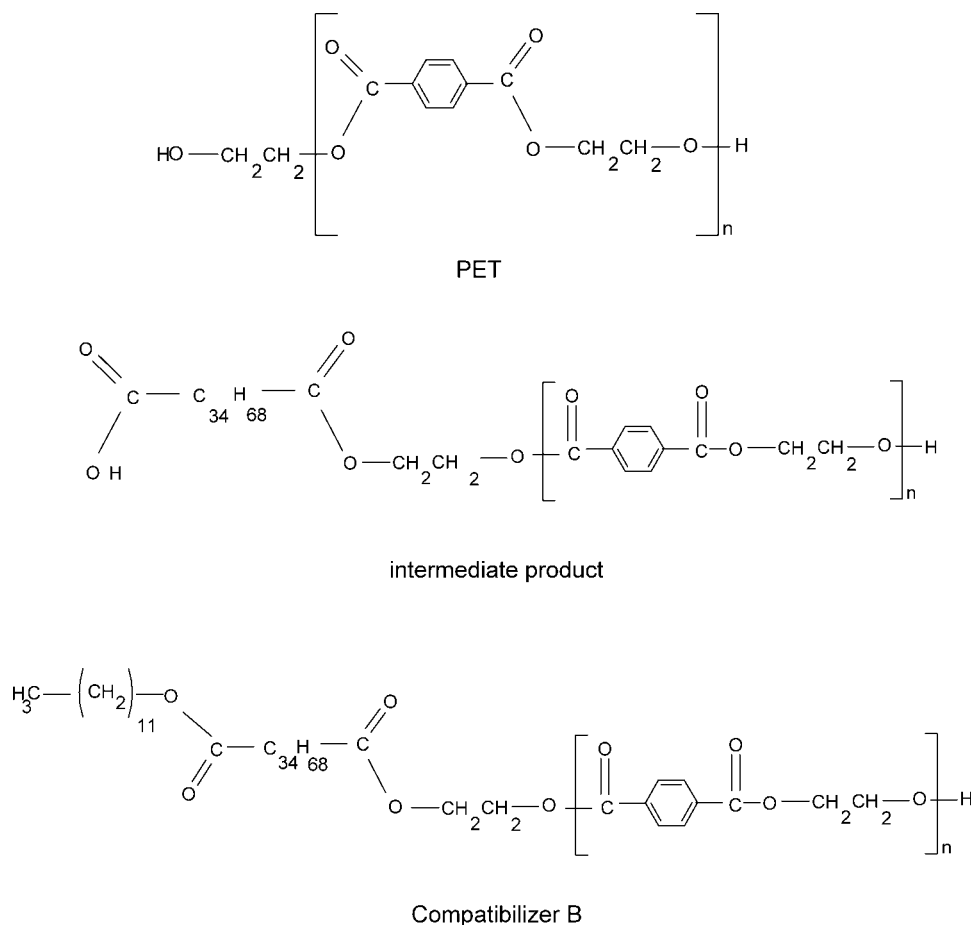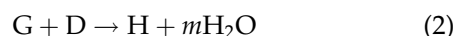
Figure 5 Chemical structures of PET, intermediate product, and compatibilizer B.

chemical reactor (2 dm³). The reaction temperature was kept until the end of formation of water, which took around 4 h. After that, the temperature was lowered to 200°C, and after stabilization of temperature, 1 mol of dodecanol was added. After this step, the temperature was again raised to 240°C, and the reaction continued until no further progress is detected (at the end of the reaction the acid value, obtained by an adaptation of the method described in International Standard ISO 2554, was bellow 1 mg KOH/g). The final product was compatibilizer A.

As described later, no improvement on the mechanical properties were obtained by adding this compatibilizer, which we attributed to a high level of affinity between the compatibilizer and the matrix. To overcome this problem, we decided to replace Terol by polyethylene terephthalate (PET), to increase the affinity between the compatibilizer and the LPC.

For the chemical synthesis of compatibilizer B, dodecanol, dimeric acid, and PET were used. The reaction was carried out by mixing 0.04 mol of PET, 0.04 mol of dimeric acid, and 50 mL of xylene. The mixture was kept under nitrogen atmosphere at 250°C, until total removal of water. After this procedure 0.04 mol of dodecanol were added and the reaction proceeded at the same temperature. After distillation of the formed water, the temperature was lowered until 200°C and 0.05% (with respect to the mass of dimeric acid) of a catalyst tetraisopropyl orthotitanate were added to the resultant products and the reaction continued until an acid value below 1 mg KOH/g was obtained. The reactional scheme for the preparation of compatibilizer B can be described by:

$$F + B \rightarrow G + nH_2O \tag{1}$$

$$G + D \rightarrow H + mH_2O \tag{2}$$

where B and D are the dimeric acid and dodecanol depicted in Figure 4, whereas F (PET), G (intermediate product), and H (compatibilizer B) are depicted in Figure 5.
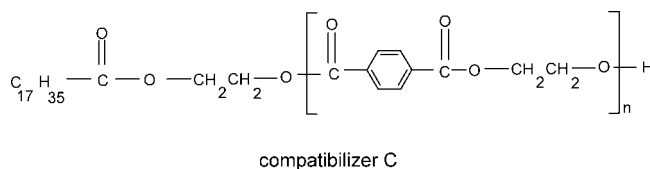

compatibilizer C

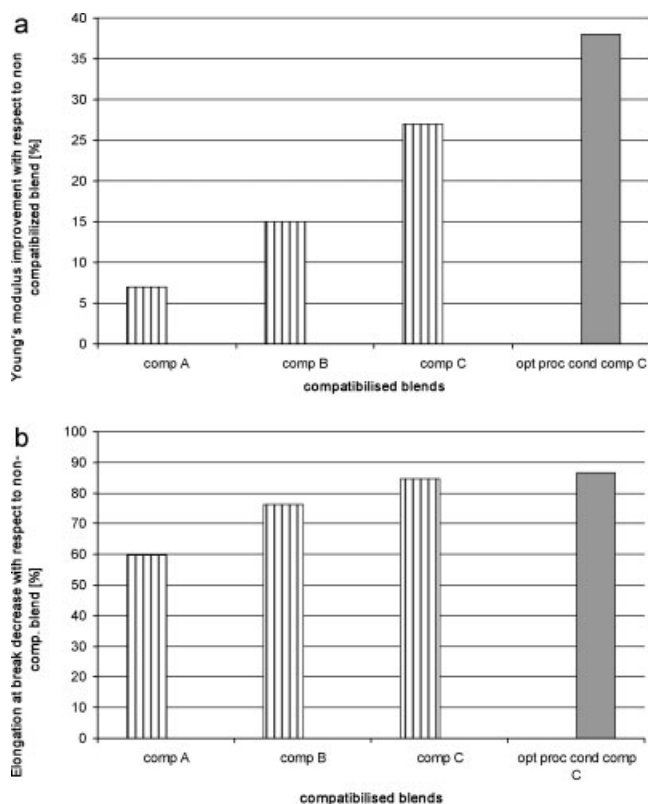**Figure 6** Chemical structure of compatibilizer C.

Figure 7 Young's modulus improvement (a) and decrease of the elongation at break (b) with respect to the noncompatibilized blend, for blends containing 10 wt % LCP and 2 wt % compatibilizer A, B, and C, processed at 150 rpm and for a blend with 10 wt % LCP and 2 wt % comp. C, processed at 100 rpm (opt proc cond comp C).

Blends prepared with compatibilizer B, as described later, presented better mechanical properties than those prepared either with compatibilizer A or with noncompatibilized ones; however, the enhance-

ment of the properties were not sufficiently significant, and so we decided to further decrease the affinity of the compatibilizer with the matrix by reducing the size of the aliphatic part.

Compatibilizer C was prepared using 0.04 mol of PET, 0.04 mol of TOFA (tall oil fatty acid), and 50 mL of xylene. This mixture reacted under nitrogen atmosphere at 250°C until no further water could be distilled off. Afterwards, 0.03% of tetraisopropyl orthotitanate (catalyst) was added to the resultant products (the amount of catalyst was calculated on the basis of the mass of TOFA). The reaction was finished after achievement of an acid value lower than 1 KOH/g. Tall oil fatty acid is a complex mixture of fatty acids obtained as a subproduct of the Pulp Industry, and its composition although variable can be expressed by an average around C_{18} (mostly saturated). Therefore, the structure of the compatibilizer although being a mixture can be represented by the average structure presented in Figure 6.

Mechanical characterization

Blends with compatibilizers A–C

The mechanical characterization was performed for blends with 10 wt % LCP and 2 wt % compatibilizer content of each of the different compatibilizers, and has been already reported by us.[28] However, to be able to compare the compatibilization effect of the different compatibilizers, and to turn it easier for the reader, we decided to present, again, the results obtained. The discussion of these results will be, however, much more simplified that that presented in Ref. 28.

The addition of compatibilizers A, B, and C to the blend with 10 wt % LCP resulted in an improvement

TABLE I
Young's Modulus for Other Compatibilized Systems

Thermoplastic	LCP	Compatibilizer	Young's modulus (PP/LCP)	Young's modulus (Comp. blends)	Reference
PP (extrusion film casting from pellets obtained with injection molding) ($E = 616$ MPa)	10 wt % Rodrun LC3000	2 wt % SEBS (tri-block copolymer of styrene/ ethylene-butylene styrene)	$\cong 1,200$ MPa	1,556 MPa (30%)[a]	18
PP (extrusion film casting from pellets obtained with injection molding) ($E = 616$ MPa)	10 wt % Rodrun LC3000	2 wt % MA-SEBS (maleic anhydride-grafted SEBS)	$\cong 1,200$ MPa	1,333 MPa (11%)[a]	18
PP (injection molded) ($E = 1,600$ MPa)	10 wt % Vectra B 950	2 wt %PEMA-Zn (ethylene-methacrylic acid copolymer with methacrylic acid partially neutralized with Zn)	1,900 MPa	2,100 MPa (11%)[a]	30

[a] Percentage increase of the Young's modulus of compatibilized blends with respect to the noncompatibilized blends.
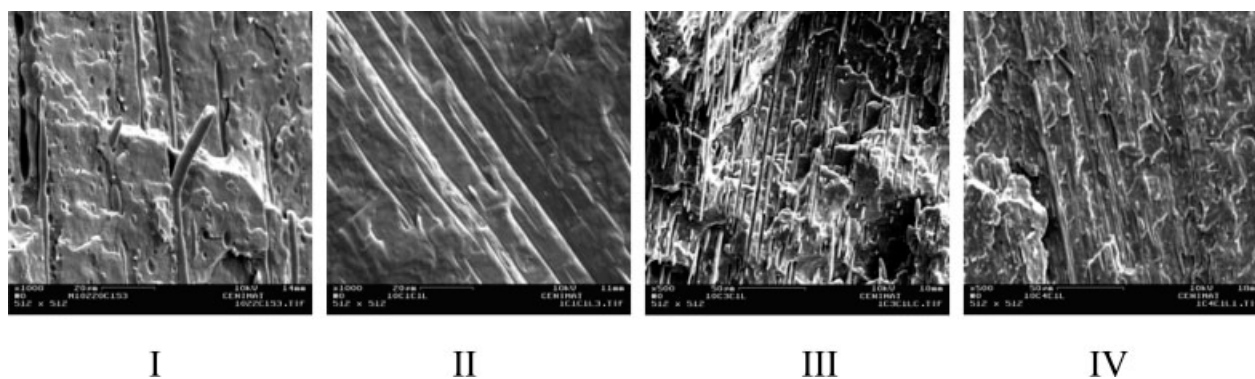
Figure 8 SEM images for the longitudinal cuts performed to the final extrudates of blends with 10 wt % LCP- I without compatibilizer; II with compatibilizer A; III with compatibilizer B and IV with compatibilizer C (Figs. 1 and 2 with magnification of ×1000, and Figs. 3 and 4 with magnification of ×500).[28]

of the Young's modulus and a decrease of the elongation at break, with respect to the noncompatibilized blend. This improvement was 7, 15, and 27% for compatibilizers A, B, and C, respectively [Fig. 7(a)]. Although the increase in the Young's modulus obtained by the addition of compatibilizers A, B, and C are from the same order of those obtained in the past by other researchers, with different compatibilizers,[18,30] as can be seen in Table I, we should point out that the mechanical improvement (in what concerns the Young's modulus) of the blend with compatibilizer C can, under appropriate processing conditions, be increased from 27 to 38%, with respect to the noncompatibilized blend.[29] In fact, the application of a lower screw speed, 100 rpm, revealed to be beneficial for the fibrillation process, giving rise to blends with a higher Young's modulus, than those obtained for a screw speed of 150 rpm.

The lower Young's modulus obtained by the use of compatibilizer A is probably due to its high chemical compatibility with the matrix (PP), arising from the presence of a long aliphatic chain and low compatibility with the LCP. Under these conditions, the compatibilizer will have tendency to act as a plasticizer.

As expected, a decrease of the elongation at break, with respect to both noncompatibilized blend (ε_r = 192%) and the thermoplastic (ε_r = 298%), occurred for all the blends compatibililized with compatibilizers A, B, and C (ε_r = 77, 46, and 30%, respectively), as can be seen in Figure 7(b).

As expected, the improvement of the Young's modulus for the compatibilizers with a thermoplastic nature is gained at the expenses of a decrease in the elongation at break, which means that the blend which present the higher Young's modulus, the one which is more brittle, is the one that present the lower elongation at break. The reason for this must be the better fibrillation observed in the case of compatibilizer C, when compared with the ones observed for

other compatibilizers, as can be observed in Figure 8. The better the fibrillation obtained when passing through the die of the extruder, the higher the Young's modulus and the lower the elongation at break.

The impact measurements (peak force) showed that the impact resistance decreases with the addition of the compatibilizer, for all compatibilized blends, and can be seen on Figure 9.

Comparision between the results obtained with the synthesized compatibilizers and the blends obtained with the commercial ones

To be able to evaluate the ability of our synthesized structures to act as compatibilizer, and as we have already told, we have also prepared samples with two commercial compatibilizers (note that, once again, the results obtained with blends compatibilized with the two commercial compatibilizers, D and E, were also reported before, in Refs. 28 and 29). To do so, Table II resumes the results obtained for all five blends studied.
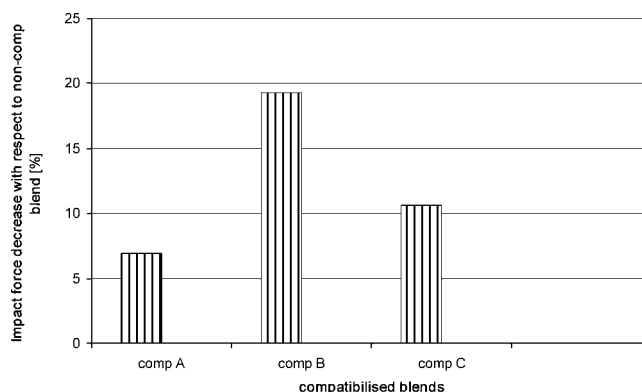

Figure 9 Decrease of the impact strength with respect to the noncompatibilized blend, for blends containing 10 wt % LCP and 2 wt % compatibilizer A, B, and C.

TABLE II
Mechanical Properties of Blends Compatibilized with Different Compatibilizers

Mechanical property	Young's modulus (MPa)	Elongation at break (%)	Peak force (N)
Compatibilizer			
A	1,953	77	201
B	2,098	46	175
C	2,317	30	193
D	2,126	88	204
E	2,118	165	260
Opt. Proc. Cond. C	2,521	26	–
Opt. Proc. Cond. E	2,652	120	–

From Table II, we conclude that the mechanical improvement (in terms of the Young's modulus) obtained by the blends compatibilized with compatibilizers D and E is smaller than those obtained with the blend with compatibiliser C, even though the contrary is found for the impact strength (actually, due to the experimental errors, compatibilizers C and D may be considered very similar, in this respect) as well as for the elongation at break. Considering the elongation at break, we must point out that the elastomeric nature of the compatibilizer E allows a significant increase of this property relatively to the blends with compatibilizers having a thermoplastic nature (A–D), as would be expected. In fact, the elongation at break obtained for the blend compatibilized with compatibilizer E is much closer to that of the noncompatibilized blend (192%) than those obtained for the blends with compatibilizers A, B, C, and D.

In earlier studies,[27,29] we have performed the optimization of the compatibilizer contents for compatibilizers C and E, those that presented (with a 2 wt % compatibilizer content) better mechanical properties. From this study, we concluded that the optimum compatibilizer content for compatibilizers C and E were 2 and 4 wt %, respectively. Considering the results obtained for a blend with 4 wt % compatibilizer E, we conclude that the Young's modulus of this blend becomes slightly higher than those with compatibilizer C. Also the optimization of the processing conditions leads to an increase of the Young's modulus of the blend with compatibilizer E, similarly to what happens with the blend with compatibilizer C.

Finally, it is important to point out that the only blend for which an improvement of the impact strength was obtained, within experimental error, relatively to that observed for the noncompatibilized blend, and the one for each the impact strength, measured by the peak force, is above the predicted by the rule of mixtures is the one obtained for the blend with compatibilizer E. This is not unexpected, since compatibilizer E acts as an impact modifier for the liquid crystalline and thermoplastic blend.

CONCLUSIONS

From the results obtained, we can conclude that our successive trials to obtain a chemical structure that can act as a compatibilizer for the blend 90 wt % PP/10 wt% Rodrun LC3000 were relatively successful.

Considering compatibilizer C used in this study, the one that leads to the higher enhancement of the Young's modulus, when compared to the noncompatibilized blend, we obtain a Young's modulus 27% higher than the one presented by the noncompatibilized blend, enhancement that can be further increased if we use more appropriate processing conditions, as we have done in another work,[29] obtaining an increase of the Young's modulus of 38%, instead of the 27%. Comparing this result with those presented by the blends compatibilized with the two commercial compatibilizers D and E, we conclude that this enhancement is higher than those presented by the former blends (increase in Young's modulus of 16% for both compatibilizers). The increase of the Young's modulus of our blend with compatibilizer C is also higher than the ones obtained in the past by other researchers with different compatibilizers.[18,30] We must point out, however, that the Young's modulus of blends compatibilized with 4 wt % of compatibilizer E (which is the optimum content of this compatibilizer for our blend, contrary to what happens to the optimum content of compatibilizer C, which is 2 wt %, as we have proved in another work[27]) becomes slightly higher than the Young modulus of the blend with 2 wt % of compatibilizer C.

Additionally, the higher increase of the impact strength is observed for the blend with compatibilizer E, which is not unexpected since it works as an impact modifier, and the corresponding decrease of the elongation at break is smaller than the one with compatibilizer C, which is due to its elastomeric nature.

Finally, we may state that, even though we have been able to synthesize a relatively good compatibilizer, the enhancement of the mechanical properties are far away from what we expected to obtain, which means that a novel strategy for the synthesis must be faced in a near future.

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