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Fibres from polypropylene and liquid-crystal polymer blends using compatibilizing agents: 1. Assessment of functional and non-functional polypropylene–acrylic acid compatibilizers

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A graft polymer based upon acrylic acid-functionalized polypropylene (PP-AA) and PP-AA itself were assessed as compatibilizers for polypropylene/liquid-crystal polymer (PP/LCP) polyblend fibres. It was found that the functional compatibilizer improved interfacial adhesion and thus fibre properties, depending on the type of hot-drawing process used, as well as significantly enhancing the thermal stability of the fibre. Incorporation of PP–AA increased fibre crystallinity and orientation, with a slight enhancement of fibre properties observed. This was attributed to the promotion of specific polar interactions between the blend components.

(Keywords: polypropylene; liquid-crystalline polymer; polyblend fibre)

INTRODUCTION

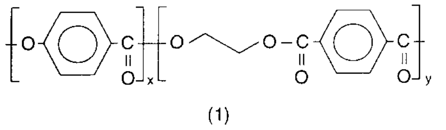
The blending and subsequent reinforcement of conventional thermoplastics with thermotropic liquid-crystalline polymers (LCPs) is an area of considerable scientific interest[1–3]. The concept of blending dissimilar polymers to obtain properties unattainable with the individual component polymers themselves[4] has been applied in order that the high longitudinal strength and orientation of the LCP component endows similar beneficial properties upon the resulting blend. The components of such blends are usually, however, immiscible owing to their fundamentally different chemical structures. In order to improve miscibility, and hence blend mechanical properties, compatibilizing agents may be added[5,6]. These are usually in the form of graft or block copolymers that possess segments capable of interaction with each blend component. Improved interfacial adhesion in the blend is promoted by the location of the compatibilizer molecules at the phase interface, in a surfactant-like manner. This also has the effect of reducing interfacial tension and facilitating a finer, more homogeneous, blend dispersion.

Compatibilization of blends of polypropylene (PP) and LCPs processed using extrusion and injection-moulding techniques has been attempted with maleic anhydride-functionalized polypropylene[7,8] and ethylene-based terpolymers[8], with significant improvements in tensile strength and modulus observed. Our own previous work on PP/LCP polyblend fibres[9–11] showed that, under optimum processing and drawing conditions, improvements in initial fibre modulus may be observed upon addition of LCP to PP fibres, but the overall tensile strength of the polyblend fibres was generally less than that of pure PP fibres. The sole exception to the latter observation was in polyblend fibres incorporating Rodrun LC3000, a poly(ethylene terephthalate)/*p*-hydroxybenzoic acid (PET/PHB)copolymer, whose flexible structure was more compatible with PP than were those of the wholly aromatic Vectra LCPs also assessed. Owing to the greater compatibility and interfacial adhesion, the PP/Rodrun LC3000 fibres exhibited a 5% increase in tenacity over conventional PP fibres[11]. We now report our own findings on the use of compatibilizers based upon acrylic acid-functionalized polypropylene in the production of PP/LCP polyblend fibres.

EXPERIMENTAL

Materials

The thermotropic LCP used exclusively was Rodrun LC3000 (**1**), supplied by Unitika. It is a copolymer of



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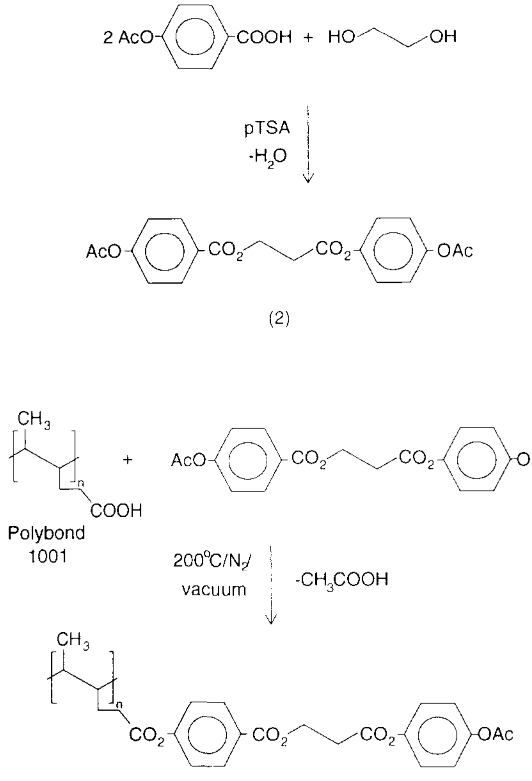

Scheme 1 Synthesis of functional compatibilizer FC1

poly(ethylene terephthalate) (PET) and *p*-hydroxybenzoic acid (PHB), with a melting temperature of 220°C. The matrix polypropylene used was Statoil 151, supplied by Statoil Ltd, which has a melt flow index (*MFI*) of 14. Polybond 1001 (PP-AA), a polypropylene functionalized with 6% w/w acrylic acid, was supplied by BP Chemicals Ltd.

Synthesis of functional compatibilizer

The functional compatibilizer (denoted FC1) was synthesized by grafting 4,4′-ethylenedioxy di-4-acetoxybenzoate (**2**), which has a similar structure to the repeat unit of Rodrun LC3000, onto PP-AA via a melt condensation procedure, as illustrated in *Scheme 1*.

Synthesis of **2**. *p*-Acetoxybenzoic acid (16 g, 0.088 mol) (synthesized according to a literature procedure[12]), ethylene glycol (2.7 g, 0.044 mol) and *p*-toluenesulfonic acid (0.02 g) were refluxed in anhydrous toluene (50 ml) in a flask fitted with a Dean–Stark trap and condenser under N_2 for a period of 12 h until the theoretical water of reaction was collected. Upon completion, excess solvent was removed by rotary evaporation to give a white solid, which was subsequently recrystallized from methanol and dried *in vacuo* at 60°C. A white microcrystalline product was obtained, pure by t.l.c., and whose structure was confirmed by ^{1}H n.m.r. Yield = 30.5 g (79%). M.p. = 183–185°C.

Synthesis of FC1. PP-AA (10 g, 0.007 mol acrylic acid) and **2** (2.7 g, 0.007 mol) were placed in a flask equipped with N_2/vacuum inlet, overhead stirrer and cold trap (0°C). The system was purged with N_2 and heated to a temperature of 200°C whereupon a melt formed and the stirrer was switched on. The system was held at this temperature, under a continuous flow of N_2 for 1 h. A vacuum was then applied to the system for a further hour, with the acetic acid produced collected in the cold trap. Upon completion, the system was cooled to room temperature, and the product, a cream-coloured homogeneous solid, collected. I.r. (thin film): 1601, 1510 cm^{-1} (*p*-subst. arom. C=C str.).

Prior to blending with PP and LCP pellets, FC1 was extruded as a monofilament in a simple rod-spinning apparatus, equipped with a 0.5 mm die, at 200°C, with the extrudate being quenched in air. The filament was then finely chopped in order to enable more efficient dry blending.

Melt extrusion and hot drawing

Melt extrusion was carried out using a 25 mm single-screw Labspin Extruder (Extrusion Systems Ltd) with a 2.5 cm^3 metering pump. The die head was equipped with a trifilament (three 0.5 mm diameter holes) spinneret.

The PP, LCP and PP-AA pellets were pre-dried in a vacuum oven at 100°C for 12 h prior to use. The PP/LCP and PP/LCP compatibilizer (PP-AA or FC1) were premixed in the ratios 100/10 and 100/10/2.5 w/w respectively, these being the previously determined optimum LCP content ratios for LCP fibril formation and hence reinforcement[9]. The temperature profile employed was 200/240/240/240/240/240°C, representing three extruder barrel zones, metering pump and two die head zones. The pump speed used was 3 rpm, corresponding to an extrusion rate of 12.2 m min^{-1}, with take-up speed 80 m min^{-1}.

Hot drawing was carried out on a small-scale apparatus consisting of two pairs of advancing rollers and hot plate. A two-stage drawing process was employed for all samples, in the manner previously determined for obtaining optimum final fibre properties for PP/LCP polyblend fibres[10]. This procedure consists of partially drawing the fibre at 120°C, prior to the fibre being drawn to its maximum extent at 160°C. A one-stage procedure was employed in initial studies, for comparative purposes. This involved drawing the fibre to its maximum extent at 150°C.

Tensile testing

Tensile properties were measured using a Nene tensile tester. The tests were carried out at 20°C and 65% relative humidity with gauge length of 20 mm and extension rate of 20 mm min^{-1}. Fibre thickness was measured in tex (equivalent to the mass in grams of 1000 m of fibre). The draw ratios of the fibre samples were calculated from the ratios of their tex values, since the draw ratio could not accurately be obtained from roller speeds during hot drawing owing to slippage and fibre shrinkage. The units used for fibre tenacity are newtons per tex (N tex^{-1}). Tests were carried out five times for each sample, with standard deviation in the range 2–4%.

Hot-stage microscopy

Microscopy of samples was carried out on an Olympus BH2 polarizing microscope equipped with a Linkam PR600 hot-stage apparatus and Yashica 135 mm camera. Samples were prepared by placing a small length of fibre between two glass coverslips and heating to 180°C, whereupon the PP melted and the LCP morphology could be observed.

Differential thermal analysis

Differential thermal analysis of the fibre samples was carried out on a Mettler FP90 instrument, linked to a PC equipped with Mettler data-processing software. Samples were run over the temperature range 40–200°C, at a heating rate of 20°C min^{-1}.

The crystallinities of each fibre sample were calculated using the following formula:

$$X_c(\%) = \frac{\Delta H_S}{\Delta H_{PP}} \times \frac{1}{(1-x)} \times 100$$

where X_c is the crystallinity of the fibre sample, ΔH_S is the measured heat of fusion of sample, $\Delta H_{PP} = 209\,\text{J g}^{-1}$ is the heat of fusion of 100% crystalline isotactic polypropylene and $x = 0.1$ is the weight fraction of LCP in blend.

Thermal stability

The stability of fibres at elevated temperatures is an important factor in their overall physical properties. In order to assess the thermal stability of the fibres produced in this study, samples of accurately measured length were subjected to heat treatment in a controlled environment at temperatures of 130°C (duration 10 min and 5 h) and 150°C (duration 10 min). After treatment, longitudinal shrinkage, tensile strength and crystallinity of the fibre samples were assessed.

RESULTS AND DISCUSSION

Synthesis of functional compatibilizer

The melt grafting procedure employed in the synthesis was successful, with the presence of the functional moiety confirmed by the i.r. spectral data. Similar data have been cited as evidence of successful grafting of *p*-hydroxybenzoic acid oligomers to carboxy-functionalized acrylic polymers[13]. It was initially thought that, owing to the two acetoxy groups present on each functional molecule, the occurrence of crosslinking would be a possibility. However, during initial extrusion of the functional compatibilizer in the rod-spinning apparatus, no significant increases in melt viscosity, indicative of crosslinking and gelation, were observed in comparison with standard PP-AA. The low concentration of functional groups (6%) would tend to facilitate site isolation, which would lessen the effect of any crosslinking that had occurred during melt grafting.

Melt extrusion

The extrusion process was carried out at 240°C, primarily because PP-AA is reported to decompose at temperatures significantly in excess of 230°C, a factor that may also be important for the stability of the functional compatibilizer. Moreover, the LCP could also be processed at 240°C owing to its melt temperature of 220°C. The *MFI* of the PP used (14) rendered it more suitable for spinning at 240°C than the tape-grade PP (*MFI* 3) used previously[9–11], owing to its lower melt viscosity.

No specific difficulties arose during extrusion, and indeed drawdown ratios of 6.5 were able to be attained. In previous work with PP/Rodrun LC3000 polyblend fibres[11], the drawdown ratio was limited to 4 owing to problems with melt fracture. This observation may be explained since polypropylene of a different melt viscosity was used. It has been established that the viscosity ratio of the PP and LCP components of the blend is of great importance to the LCP morphology within the fibres and consequently to fibre processability during extrusion[14].

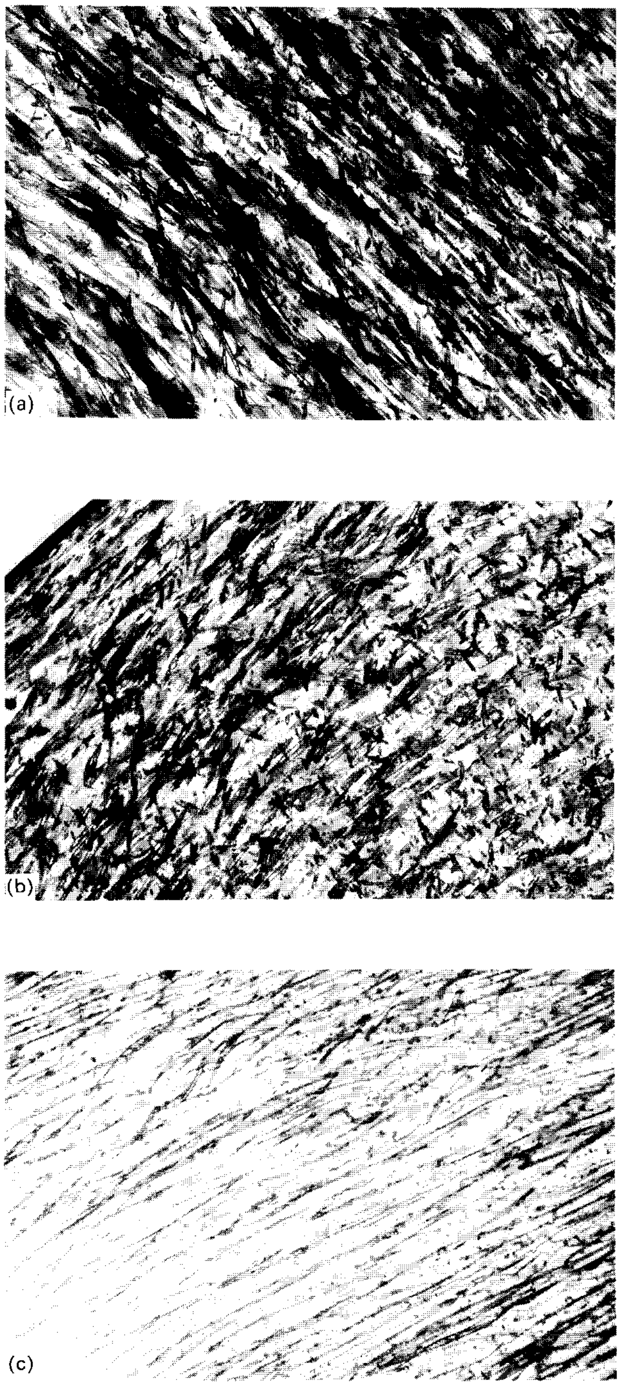

Figure 1 Hot-stage photomicrographs (original magnification ×100) of as-spun fibre samples: (a) PP/LCP (100/10); (b) PP/LCP/FC1 (100/10/2.5); and (c) PP/LCP/PP-AA (100/10/2.5)

As-spun fibres

The effect of compatibilization upon LCP morphology within the as-spun polyblend fibres is clearly illustrated by the hot-stage photomicrographs, shown in *Figure 1*.

Table 1 Tensile properties of one-stage drawn fibres

Sample	Thickness (tex)	Draw ratio	Extension (%)	Tenacity (N tex^{-1})
PP	6.48	11.59	22.8	0.643
PP/LCP	6.52	11.52	21.5	0.584
PP/LCP/FC1	6.43	11.68	16.8	0.713

Table 2 Tensile properties of two-stage drawn fibres

Sample	Thickness (tex)	Draw ratio	Extension (%)	Tenacity (N tex^{-1})
PP	4.76	18.06	12.9	0.776
PP/LCP	5.01	15.00	13.2	0.672
PP/LCP/FC1	5.20	14.45	14.4	0.662

The polyblend fibre incorporating the functional compatibilizer, FC1, possesses a more widely dispersed LCP fibril structure, indicative of a reduction in interfacial tension between the PP and LCP blend components. The fibre compatibilized with PP-AA has a much more oriented LCP structure, with the LCP fibrils having noticeably higher aspect ratios than the other two samples.

Drawn fibres

Tables 1 and *2* show the tensile testing results obtained for one-stage and two-stage drawn fibre samples from initial fibre extrusion experiments with standard PP, PP/LCP and PP/LCP/FC1 samples. The compatibilized fibre exhibits the highest tenacity of the one-stage drawn samples, but the lowest of the two-stage drawn. Most interestingly, a fall in fibre tenacity is observed with the two-stage drawn compatibilized fibre sample compared to the one-stage drawn sample, which is without precedent in previous work upon PP and PP/LCP fibres[9–11]. This can be explained with reference to the rationale behind the two-stage drawing process itself[10], namely that LCP fibril rupture during the drawing process may be minimized by first partially drawing the PP matrix, in order that the LCP fibrils have enhanced mobility during the final drawing stage. This mobility is crucially dependent upon the lack of adhesion between the PP and LCP phases. The increase in interfacial adhesion promoted by the compatibilizer would therefore be expected to have a detrimental effect upon fibres drawn using a two-stage process. This is further supported by hot-stage photomicrographic evidence. Although very little change in LCP structure is observed between the one-stage drawn samples shown in *Figure 2*, the LCP fibrils are pronouncedly smaller in the two-stage drawn fibres incorporating FC1 in comparison with the standard PP/LCP polyblend fibre, as illustrated in *Figure 3*. This is a clear indication that LCP fibril rupture is occurring to a greater extent during the two-stage drawing process for the compatibilizer sample, as a direct consequence of the increase in adhesion between PP and LCP phases.

Table 3 shows the tensile testing results obtained from further studies into production of PP/LCP fibres using PP-AA as compatibilizer. In this instance only a two-stage drawing process was assessed. The main feature of the results is that there appears to be little difference in tensile strength between the samples, with no pronounced decrease observed for the compatibilized sample. Indeed, there appears to be a small increase in fibre tenacity. The LCP structure within the PP/LCP/PP-AA sample also appears to differ little from that of the standard PP/LCP fibre. These observations would seem to indicate a different type of compatibilization occurring with PP-AA, as opposed to FC1. Studies by Xanthos *et al.*[15] on blends of PP-AA with PET established that the presence of the acrylic acid groups caused a fourfold decrease in interfacial tension compared to standard PP. This was attributed to enhanced specific interactions, as opposed to true covalent reactions, between the polar components of the blend. Porter[16] has reviewed transesterification-type reactions and their effect upon compatibility in polymer blends, including those containing LCPs. It is conceivable that such reactions could take place between the acrylic acid moieties present on PP-AA and the ester linkages in the LCP during melt processing. The compatibilization effect observed, therefore, appears to be an interaction between the polar acrylic acid groups and the LCP itself, which decreases the interfacial tension in the blend, as indicated by the marked difference in LCP fibril structure in the as-spun sample. These interactions do not appear to have such a detrimental effect upon fibre properties during two-stage drawing, which indicates that the increase in interfacial adhesion observed with FC1 is not observed to such a great extent in this case.

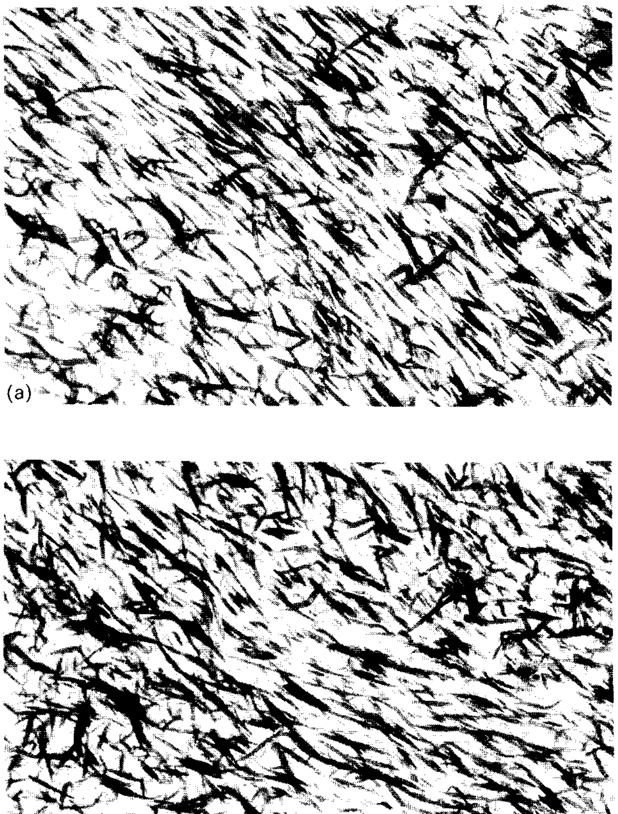

Figure 2 Hot-stage photomicrographs (original magnification ×100) of one-stage drawn fibre samples: (a) PP/LCP (100/10); and (b) PP/LCP/FC1 (100/10/2.5)

Table 3 Tensile properties of two-stage drawn fibres

Sample	Thickness (tex)	Draw ratio	Extension (%)	Tenacity (N tex^{-1})
PP	2.56	24.12	14.9	0.856
PP/LCP	5.81	12.92	15.9	0.838
PP/LCP/PP-AA	3.37	12.42	21.2	0.873

Table 4 Crystallinity data for fibre samples

Sample	Crystallinity (%) As-spun	Crystallinity (%) Two-stage drawn
PP	40.1	61.8
PP/LCP	42.6	64.3
PP/LCP/FC1	43.4	61.8
PP/LCP/PP-AA	61.7	70.7

The fibre crystallinity data shown in *Table 4* indicate that the presence of PP-AA in the PP/LCP fibres causes a pronounced increase in crystallinity, with 20% and 10% increases observed over all other samples, for the as-spun and two-stage drawn fibres respectively. Again, this result can be explained by the blend interactions caused by the acrylic acid groups present on PP-AA. Studies on the thermal properties of PP-AA/PET blends have shown that the PP-AA inhibited crystallization of the PET blend component[15]. While no observation regarding the crystallinity of the Rodrun PET/PHB LCP can be made from the thermal measurements carried out in this study, it is clear that the crystallinity of the polypropylene component is markedly affected by the presence of PP-AA. No such increase in crystallinity was observed for the fibres containing FC1 over conventional PP and PP/LCP fibres, again underlining the difference between the compatibilizing effects of PP-AA and FC1.

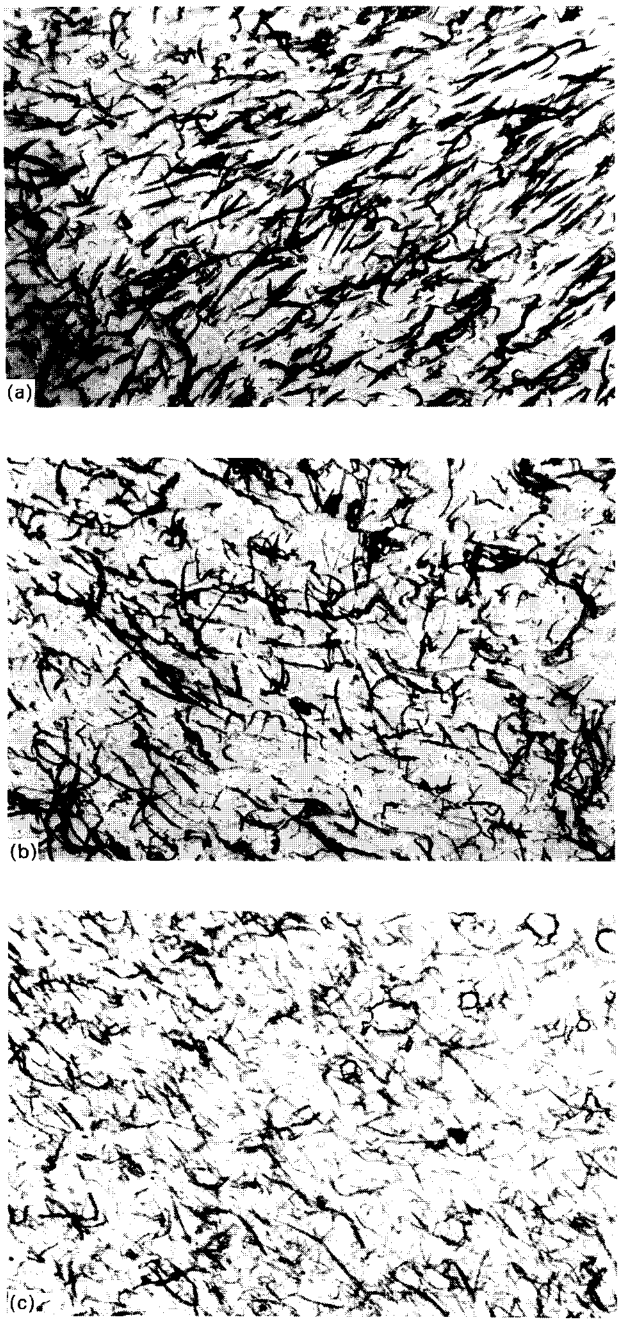

Figure 3 Hot-stage photomicrographs (original magnification ×100) of two-stage drawn fibre samples: (a) PP/LCP (100/10); (b) PP/LCP/FC1 (100/10/2.5); and (c) PP/LCP/PP-AA (100/10/2.5)

Thermal stability

The overall fibre shrinkage, changes in fibre tenacity and crystallinity upon heat treatment are illustrated graphically in *Figures 4*, *5* and *6*. The most important observation that can be made from the results is that the fibre containing the functional compatibilizer, FC1, displays extremely favourable thermal stability in

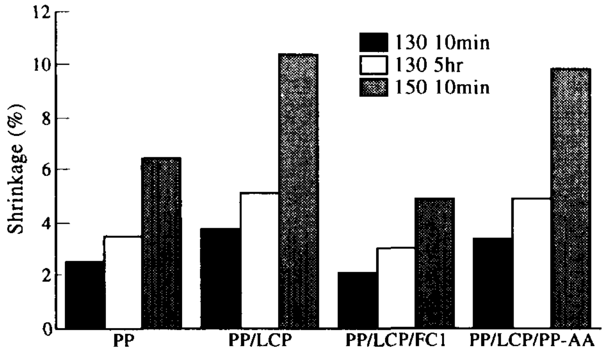

Figure 4 Effect of heat treatment upon fibre shrinkage

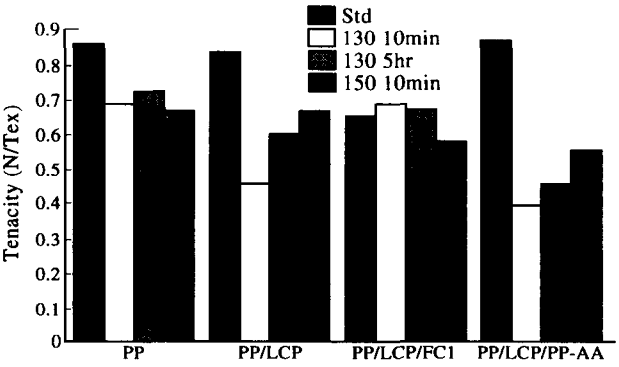

Figure 5 Effect of heat treatment upon fibre tenacity

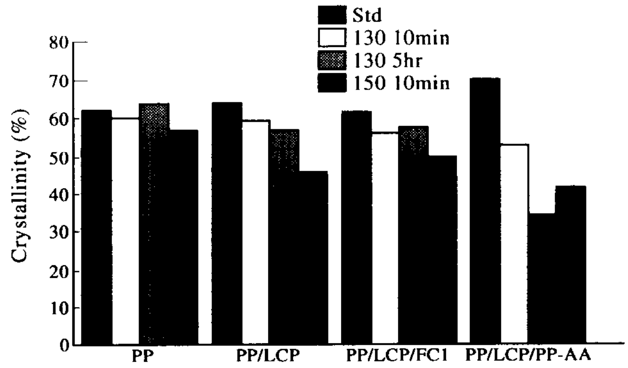

Figure 6 Effect of heat treatment upon fibre crystallinity

comparison with the other PP/LCP polyblend fibres, and also with pure PP fibre. In terms of shrinkage, the fibre containing FC1 exhibits the lowest shrinkage of all the samples, including the pure PP. The improved adhesion between the PP and LCP phases accounts for the improvement observed over the PP/LCP and PP/LCP/PP-AA fibres, whereas the improvement over PP is most probably due to the LCP fibrils acting as a filler, inhibiting PP matrix relaxation due to the enhanced miscibility between the PP and LCP phases. The greater shrinkage observed for the standard PP/LCP fibre over PP fibre is most probably attributable to poor interfacial adhesion and miscibility; therefore voids could be formed within the PP matrix, causing increased shrinkage.

Fibre tenacity (*Figure 5*) was generally observed to fall upon heat treatment, with the PP/LCP and PP/LCP/PP-AA fibres showing the greatest drops in tenacity. The tenacity of the fibre incorporating FC1 showed the least change, which again reflects improvements in blend adhesion and miscibility. The overall trend observed with fibre crystallinity (*Figure 6*) seems to be a slight decrease upon heat treatment, which is proportional to the severity of the treatment. The fibre containing PP-AA as compatibilizer exhibits the largest overall decrease upon heat treatment. This suggests that the previously discussed blend interactions responsible for the increase in crystallinity observed for this fibre are susceptible to thermal dissociation, accounting for the losses in fibre tenacity and crystallinity, and increase in shrinkage upon heat treatment, in comparison with the fibre containing FC1.

CONCLUSIONS

The incorporation of a compatibilizer containing functional groups of a similar structure to the reinforcing bulk LCP in PP/LCP polyblend fibres has a clear effect upon the LCP morphology within the fibres, and consequently on the fibre properties. The increase in interfacial adhesion caused by the compatibilizer means that a two-stage drawing process is not the most favourable for obtaining optimum fibre tenacity, when compatibilizer is present in the blend.

Polypropylene functionalized with acrylic acid, PP-AA, also proved to have a pronounced compatibilization effect upon PP/LCP fibres. Significant increases in fibre crystallinity and LCP orientation within the fibres were observed, with no adverse effect upon fibre tenacity during two-stage drawing. This is attributable to the occurrence of specific polar interactions between the blend phases, as opposed to the interfacial reaction observed with the functional compatibilizer.

The functional compatibilizer significantly improves the thermal stability of PP/LCP polyblend fibres, owing to enhanced phase miscibility and adhesion, endowing them with thermal characteristics similar to, or better than, those of pure PP fibre.

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