

# Fibres from polypropylene and liquid crystal polymer blends using compatibilizing agents: 3. Assessment of graft side chain liquid crystalline compatibilizers based upon acrylic acid-functionalized polypropylene

M. M. Miller and J. M. G. Cowie\*

*Department of Chemistry, Heriot-Watt University, Edinburgh EH14 4AS, UK*

and D. L. Brydon and R. R. Mather

*The Scottish College of Textiles, Galashiels TD1 3HF, UK*

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Graft side-chain liquid crystalline functional copolymers based upon acrylic acid-functionalized polypropylene (PP-AA) were assessed as compatibilizers for polypropylene/liquid crystalline polymer (LCP) polyblend fibres. The compatibilization effect observed was found to be dependent upon the liquid crystalline phase temperature range of the compatibilizer, with the most favourable being in a liquid crystalline state during fibre melt extrusion and hot drawing, thus contributing a lubricating effect to the blend and giving enhanced physical properties as a result. © 1997 Elsevier Science Ltd. All rights reserved.

**(Keyword: polypropylene; liquid crystalline polymer; polyblend fibre)**

## INTRODUCTION

The technique of reinforcement of conventional thermoplastics with thermotropic liquid crystalline polymers (LCPs) via blending to obtain enhanced physical properties has been well documented in recent literature<sup>1–3</sup>. Due to the fundamental immiscibility of these types of polymer, it is generally accepted that, in order to attain optimum properties, a compatibilizer should be used. The compatibilizer is in the form of a functional graft or block copolymer consisting of segments which may interact with individual blend components<sup>4,5</sup>. The location of the compatibilizer at the phase interfaces reduces interfacial tension, resulting in improved blend component dispersion with adhesion between blend phases also increased.

In terms of polypropylene (PP) and LCP melt blends, compatibilization has been achieved using maleic anhydride-functionalized polypropylene<sup>6,7</sup> and ethylene-based terpolymers<sup>7</sup>, with significant improvements in the resulting physical properties observed. Previous work by ourselves utilized a functional graft copolymer based on acrylic acid-functionalized polypropylene (PP-AA) and PP-AA itself as compatibilizers for PP/LCP polyblend fibres<sup>8</sup>. PP-AA was found to enhance fibre crystallinity and orientation with an increase in fibre tenacity observed. The functional compatibilizer was found to have a detrimental effect upon fibre tenacity when a two-stage hot drawing procedure was used. The reduced fibre tenacity was

attributed to the rupture of the fibrillar reinforcing LCP phase during drawing owing to the enhanced interphase adhesion promoted by the compatibilizer. In order to alleviate this problem, a strategy was devised whereby the compatibilizer itself possessed liquid crystalline properties, ideally during the extrusion and hot-drawing of the blend fibre thus having a lubricating effect, but would still promote interphase adhesion and blend dispersion in the final fibre. To this end, a wide range of graft side-chain liquid crystalline polymers were synthesized based upon PP-AA<sup>9</sup>. We now report the use of two of these polymers as compatibilizers for PP/LCP polyblend fibres.

## EXPERIMENTAL

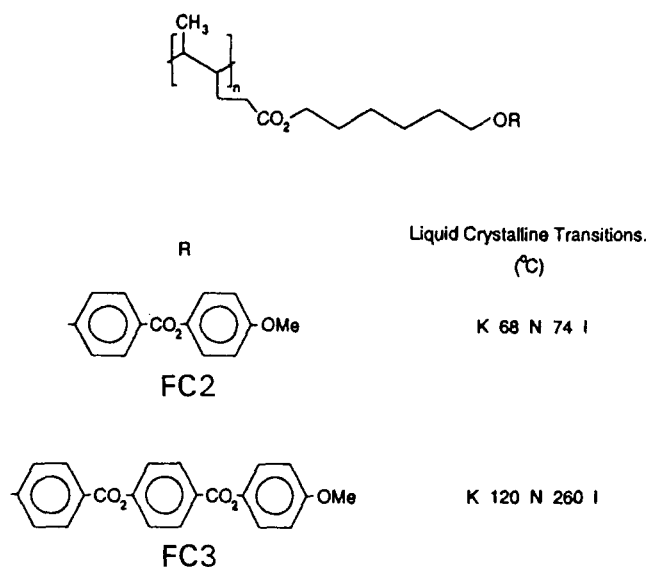
### *Materials*

The thermotropic LCP used exclusively was Rodrun LC3000, supplied by Unitika. It is a copolymer of polyethylene 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 compatibilizers*

The two liquid crystalline functional compatibilizers FC2 and FC3 were synthesized from PP-AA using a melt phase condensation procedure which has been outlined

\* To whom correspondence should be addressed



**Figure 1** Structure and liquid crystalline phase transitions of functional graft compatibilizers

previously<sup>8,9</sup>. The structure and liquid crystalline phase transitions of the two compatibilizers are outlined in *Figure 1*.

Prior to blending with PP and LCP pellets, both compatibilizers were 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 resulting filaments were 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<sup>3</sup> metering pump. The die head was equipped with a monofilament ( $d = 0.5$  mm holes) spinneret as used in previous work<sup>10–12</sup>.

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 (FC2 or FC3) were pre-mixed 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<sup>9</sup>. 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 2 rpm<sup>-1</sup>, corresponding to an extrusion rate of 8.1 mm min<sup>-1</sup>, with take-up speed 60 m min<sup>-1</sup>.

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<sup>10</sup>. 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, 65% relative humidity with gauge length of 20 mm and extension rate of 20 mm min<sup>-1</sup>. 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 due to slippage and fibre shrinkage. The units used for fibre tenacity are Newton tex<sup>-1</sup> (N tex<sup>-1</sup>). Tests were carried out five times for each sample, with observed standard deviation being less than 5%.

#### *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 cover slips and heating to 180°C, whereupon the PP melted and the LCP morphology could be observed.

## RESULTS AND DISCUSSION

### *Synthesis of functional compatibilizer*

The synthesis of the graft functional compatibilizers was successfully accomplished, with grafting confirmed by the observance of nematic liquid crystalline phases for the functional polymers FC2 and FC3, since the ungrafted functional molecules did not display similar properties<sup>9</sup>. The low concentration of acyclic acid graft sites (6% w/w) present in PP-AA meant that the liquid crystalline phases were observed as microdomains dispersed throughout the PP matrix, although this was not anticipated to influence the potential compatibilization effect greatly due to the effectiveness of the previously assessed functional compatibilizer<sup>8</sup>.

### *Melt extrusion*

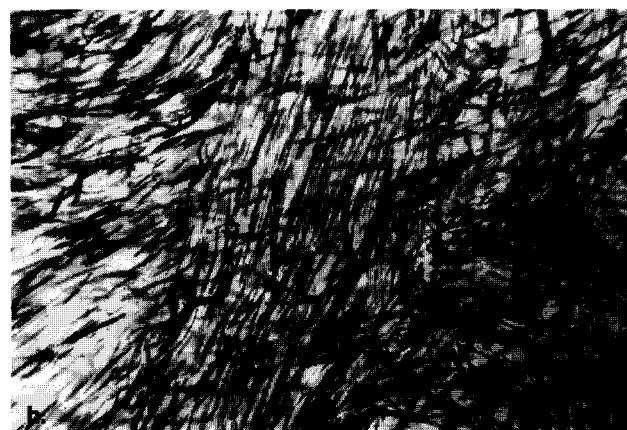
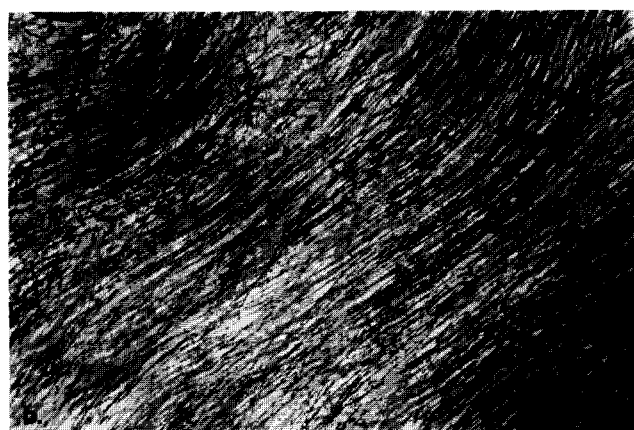
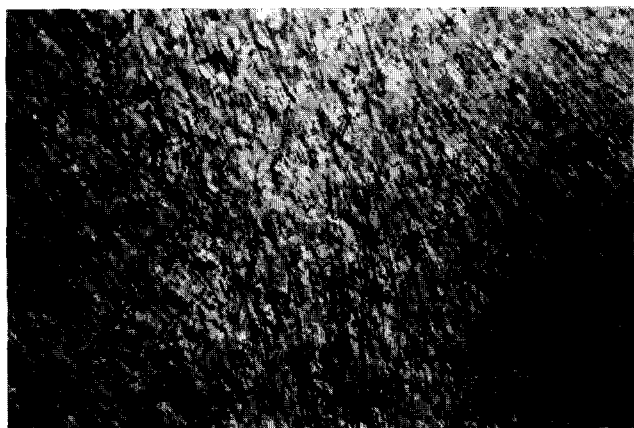
As in previous work<sup>8</sup>, the extrusion process was carried out at 240°C, in order to alleviate the risk of thermal decomposition of the compatibilizer. The extrusion and take-up speeds used were reduced slightly from those previously employed with a trifilament spinneret<sup>8</sup>, although draw-down ratios in excess of 6.5 were still able to be attained with no significant problems, as observed previously<sup>8</sup>.

### *As-spun fibres*

The morphology of the as-spun PP/LCP and PP/LCP/FC3 fibres is illustrated in the photomicrographs shown in *Figure 2*. It can be clearly seen that the fibre incorporating the compatibilizer exhibits greatly increased LCP fibril aspect ratio, orientation and dispersion over the non-compatibilized fibre. This suggests that the compatibilizer is endowing the blend with a lubricating and orienting effect during the melt extrusion process, and also promoting a reduction in interfacial tension, these effects being commonly associated with compatibilization.

### *Drawn fibres*

The tensile testing results obtained for all the drawn fibre samples are summarised in *Table 1*. The main features of the data are that the uncompatibilized PP/Rodrun LCP fibre displays a 5.5% increase in tenacity



**Figure 2** Hot-stage photomicrographs of as-spun fibre samples ( $\times 100$  magnification): (a) PP/LCP (100/10); (b) PP/LCP/FC3 (100/10/2.5)

**Figure 3** Hot-stage photomicrographs of two-stage drawn fibre samples ( $\times 200$  magnification): (a) PP/LCP (100/10); (b) PP/LCP/FC3 (100/10/2.5)

**Table 1** Tensile properties of two-stage drawn fibres

Sample	Fibre thickness (Tex)	Draw ratio	Extension (%)	Tenacity (N/Tex)	Modulus (N/Tex)
PP	0.98	10.39	17.05	0.94	8.53
PP/LCP	0.80	10.46	19.62	0.99	5.56
PP/LCP/FC2	1.71	9.78	27.99	0.86	4.31
PP/LCP/FC3	0.76	12.09	19.95	1.00	6.27

over pure PP fibre. This is identical to the results obtained by Qin *et al.*<sup>12</sup> for monofilament PP/LCP fibres. The magnitude of the tenacity obtained in this work, however is slightly less, owing to the higher MFI of the sample of polypropylene being used (MFI 14 as opposed to 3) and a lower processing temperature (240°C as opposed to 280°C).

There is a slight increase in tenacity observed for the sample containing FC3 compatibilizer over standard PP/LCP fibre, as well as a significant increase in modulus. In contrast, the fibre tenacity and modulus exhibited by the PP/LCP fibre containing polymer FC2 are clearly lower than that of the standard PP/LCP fibre, with a significant reduction in modulus observed along with an increase in extension, suggesting a breakdown of the fibre microstructure during the drawing process. These trends must be a direct consequence of the liquid crystalline properties of the compatibilizers themselves. Since polymer FC3 is in a liquid crystalline state during both melt

processing and hot drawing, it may have a lubricating effect, as well as promoting interfacial adhesion, and will thus alleviate the loss in tenacity observed previously for compatibilizer FC1<sup>8</sup>. A similar loss in tenacity (and also in modulus) is clearly being observed in the case of polymer FC2, which is not in a liquid crystalline state during processing and drawing, and does not therefore appear to have a similar lubricating effect.

The hot-stage photomicroscopy results further support these observations. It can be seen clearly from the photomicrographs of the two-stage drawn samples shown in Figure 3, that the sample containing polymer FC3 has a longer, more well preserved and oriented fibril structure than the uncompatibilized sample, which would appear to be directly related to the increases in tenacity and modulus observed for the sample containing polymer FC3. Photographic evidence of the morphology of the fibre containing FC2 is not available, but independent observation of the morphology has

confirmed the breakdown of the LCP fibril structure, resulting in comparatively poor fibre physical properties.

## CONCLUSIONS

Liquid crystalline graft polymers based upon PP-AA have been shown to be effective compatibilizers for PP/LCP blend fibres, with LCP morphology within the fibres, and final fibre physical properties profoundly influenced by compatibilization. Increases in LCP fibril length, orientation and dispersion were observed, along with a significant increase in modulus and a very small tenacity increase in the case of compatibilizer FC3. The effectiveness of the compatibilizer is highly dependent upon the temperature range over which liquid crystalline behaviour is observed, with the most favourable compatibilizer displaying a nematic mesophase between 120 and 260°C, encompassing the temperatures utilized in melt extrusion and hot drawing procedures. In contrast, a compatibilizer whose liquid crystallinity falls outwith these temperatures was found to have a detrimental effect upon final fibre properties, similar to that observed previously with a non-liquid crystalline functional compatibilizer.

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