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Polymer 40 (1999) 701–716

polymer

# Influence of a reactive terpolymer on the properties of in situ composites based on polyamides and thermotropic liquid crystalline polyesters

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Received 16 December 1997; revised 7 February 1998; accepted 20 March 1998

**Abstract**

Small amounts of a reactive terpolymer added to a binary blend of polyamides and thermotropic liquid crystalline polyesters prior to injection moulding yielded in situ composites with significantly higher modulus and strength along the machine/reinforcement direction and substantially higher strength and toughness along the transverse direction of injection moulded parts. These were attributed to enhanced fibrillation of the liquid crystalline polymer (with fibril formation observed along the core regions of injection moulded parts also) when injection moulded in the presence of the terpolymer and improved interfacial adhesion characteristics between the components of the in situ composite. Finally, in situ composites injection moulded in the presence of the terpolymer displayed smoother surfaces. 

*Keywords: In situ*; composites; Polymer blends; Compatibilization

## 1. Background

Thermotropic liquid crystalline polymers (TLCPs) tend to form fibrillar morphologies in polymer processing operations that incorporate elongational flow fields. Hence, their applicability as reinforcements in polymeric composites has been explored since the mid to late eighties by Kiss [1], Blizard and Baird [2], Weiss and co-workers [3], and Isayev and Modic [4]. Such composites are often referred to as in situ composites. The technology and properties of in situ composites have been reviewed recently [5,6].

A good portion of the published literature on in situ composites involves melt-blending of thermoplastic matrices and TLCPs in an injection moulder [1,7–20]. In situ composites generated under injection moulding conditions reveal highly oriented skin regions with well developed TLCP fibrils, and less oriented core regions dominated by undeformed TLCP droplets. It has been experimentally shown that the orientation of the TLCP phase along the skin region of an injection moulded in situ composite is significantly higher than that of the core region, with the Herman's orientation function (measured using WAXS) measured to be 0.8 along the skin region and 0.65 along the core region [15]. Therefore, the reinforcing potential of TLCPs is not fully exploited under injection moulding conditions. Also, because TLCP molecules are easily oriented along the flow direction, thermoplastic matrices are reinforced only along this direction. This results in practically no reinforcement along the transverse direction of injection moulded parts, with the strength and toughness along this direction being strongly dependent on interfacial adhesion characteristics between the TLCP fibrils and the matrix.

Almost all combinations of thermoplastics and TLCPs are immiscible and incompatible. Due to resulting poor interfacial adhesion between the phases, the mechanical properties (especially strength and toughness along the transverse direction of injection moulded parts) tend to be very low in blends of thermoplastics and TLCPs. However, partial miscibility in certain combinations of thermoplastics and TLCPs have led to better than expected tensile and flexural properties, with more uniform and smaller TLCP fibril diameters [11,13,14]. Partial miscibility between TLCPs and thermoplastics has also led to better dispersion of the TLCP phase within the in situ composite [21,22].

Compatibilization of in situ composites have also been considered to enhance both the reinforcing potential of TLCPs, as well as to increase interfacial adhesion between

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0032-3861/98/$ - see front matter 
*PII* S0032-3861(98)00257-2

the phases [17–19,23–30]. Maleic anhydride grafted polypropylene (MAGPP) was used to compatibilize in situ composites based on polypropylene reinforced with various TLCPs under injection moulding conditions [17–19,23]. Small amounts of MAGPP provided in situ composite samples with better tensile properties and toughness. MAGPP was thought to lower the interfacial tension between the phases which leads to more efficient droplet deformation. Thus, the finer droplets generated along the screw of the injection moulder resulted in TLCP fibrils of smaller diameters. MAGPP also served to enhance interfacial adhesion between the phases, which in turn resulted in higher strength values along the transverse direction of injection moulded samples [17–19]. In samples with relatively high loadings of MAGPP, the dispersed TLCP droplets were too small to fibrillate subsequently during the mould filling step. Therefore, optimization of the compatibilizer amount is critical to the overall performance of the in situ composite [19].

Thus, while addition of TLCPs to thermoplastics results in a significant enhancement in modulus, the strength values are at best only slightly superior to those of the thermoplastic. Injection moulded parts reveal especially poor strength values along the transverse direction, presumably due to weak interfacial adhesion between the matrix and the reinforcing fibrils. Therefore, the purpose of this work is to extend previous efforts to enhance the reinforcement provided by TLCPs under injection moulding conditions and to improve interfacial adhesion characteristics between the TLCP fibrils and the matrix polymer to systems other than those that are based on polypropylene. The specific objectives of this work are to evaluate the effectiveness of both a modified injection nozzle and a terpolymer with reactive functionalities on the properties of injection moulded in situ composites based on nylons reinforced with liquid crystalline polyesters. This work also addresses the mechanism and morphology development associated with the enhancements achieved in the reinforcement provided by TLCPs via injection moulding in the presence of the terpolymer.

## 2. Experimental methods

### 2.1. Materials

Nylon-11 (Rilsan B; grade BESVO TL) was obtained from Elf Atochem North America, Inc. Nylon-11 displays a glass transition temperature at approximately 55°C, and it melts at 185°C. The nylon 6 used in this work was obtained from Akzo. Nylon 6 displays a glass transition temperature of approximately 55°C and a melting point of 215°C. One of the TLCPs employed in this work was a hydroquinone-based polyester (HX8000) from DuPont. The structure of this material is proprietary. As-received HX8000 pellets display a calorimetric glass transition temperature of approximately 110°C and a melting point of approximately 277°C. The other TLCP used in this work was LC3000, obtained from Unitika of Japan. LC3000 is a copolyester based on hydroxybenzoic acid (HBA) and poly (ethylene terephthalate) [PET], with the composition being HBA/PET 60/40 mole%. The reactive terpolymer used is a commercial polymer based on ethylene-acrylic ester-maleic anhydride obtained from Elf Atochem North America, Inc. (Lotader AX8900). The terpolymer melts at approximately 100°C. The amount of terpolymer present in the composite is always indicated as a weight fraction (%) of the overall weight of the thermoplastic/TLCP blend without the terpolymer.

### 2.2. Processing of in situ composites: injection moulding

The injection moulder employed was an Arburg Allrounder (model 221-55-250) with an end-gated 76 by 76 mm rectangular mould (1.8 mm thickness). The mould was equipped with a film gate that created two-dimensional rectilinear flow throughout the mould cavity. For in situ composites with HX8000 as the reinforcing TLCP, the injection moulder barrel temperatures were set at 210°C in the first zone, 285°C in the second zone, and 265°C in the third zone, and the nozzle was set at 250°C. For in situ composites based on LC3000, the second zone was set to 275°C with all other zone temperatures corresponding to those set for HX8000-based in situ composites. An injection speed of approximately 9.5 $cm^3 sec^{-1}$ was used always. The injection and holding pressures were observed to be approximately 7 and 4 MPa, respectively.

An extended nozzle on the injection moulder was employed to generate most of the in situ composites, while the standard nozzle was used as a control to demonstrate the effectiveness of the extended nozzle. The extended nozzle had three Kenics mixing elements embedded within the pipe section leading to the nozzle end-cap [31]. The surface of the extended nozzle pipe section was set at 240°C in the injection moulding of all in situ composites. However, due to viscous heating effects, the extrudate from the injection moulder was typically a few (4–8°C) degrees hotter than the nozzle set-point.

### 2.3. Morphological observations

The size and size-distribution of the reinforcing TLCP fibrils within the injection moulded in situ composites were examined by observing their cross-sections using a Stereoscan S200 scanning electron microscope, which employed an accelerating voltage of 15 kV. Samples were freeze-fractured immediately after immersion in liquid nitrogen for 5 min. The fractured surfaces were coated with a layer of gold using a SPI sputter coater prior to microscopic examination. The gold coating was applied to enhance phase contrast between the reinforcing TLCP fibrils and the matrix.

### 2.4. Mechanical testing methods

The tensile properties of injection moulded plaques were measured using an Instron mechanical tester (model-4204). Thin strips cut from the moulded plaques were tested using a 5-kN load cell, with the sample grips 1.2 in. apart. An extensiometer (Instron model 2630-25) was employed to measure the strain. The applied load was recorded as a function of strain using a crosshead speed of 1.27 mm/min, and the tensile modulus and strength were determined according to ASTM D 638-87b. The tensile toughness of all specimens was estimated as the area under the corresponding stress–strain curve. All mechanical properties reported represent the average of at least six measurements, with standard deviations always indicated (in figures and tables).

### 2.5. Atomic force microscopy (AFM)

A Digital Instruments Nanoscope IIIa scanning probe microscope was used to examine the surface roughness characteristics of the in situ composites. The AFM cantilever was operated in the tapping mode at its resonant frequency. A two-dimensional surface area of $50 \times 50$ micron$^2$ was scanned by the cantilever, and the three-dimensional surface area detected by the probe was recorded. The ratio of the three-dimensional surface area detected that is in excess of the two-dimensional surface area to that of the two-dimensional surface area is referred to as the surface area differential and is an estimate of the surface roughness.

### 2.6. Dynamic mechanical measurements

The dynamic mechanical properties of both nylon-11 and HX8000 melts as well as the in situ composite melts were investigated using a Rheometrics Mechanical Spectrometer (RMS 800) in the torsional mode using parallel plate (25 mm diameter) geometry. All dynamic frequency sweeps were carried out at a plate gap of 1 mm and a strain of 5% under a nitrogen atmosphere. The solid state dynamic mechanical properties of the in situ composite samples were measured using a Seiko (DMS 200) dynamic mechanical analyzer in the tensile mode at a heating rate of 1°C/min, from 25 to 175°C in a nitrogen atmosphere.

## 3. Results and discussion

### 3.1. Mechanical properties—influence of the reactive terpolymer

Prior to examining the mechanical properties of in situ composites injection moulded in the presence of the terpolymer, the influence of an extended nozzle alone on the tensile properties of in situ composites was investigated. After the effects of the extended nozzle are considered, the influence of the reactive terpolymer on the properties of in situ composites based on nylons and thermotropic liquid crystalline polyesters will be discussed. An extended nozzle on the injection moulder was employed to generate in situ composites, and the properties of composites thereof were compared to those produced using a standard nozzle arrangement. The extended nozzle had three Kenics mixing elements embedded within the pipe section leading to the nozzle endcap. This section was attached to the original nozzle on the injection moulder, with a separate heater and thermocouple controlling the temperature of this extended nozzle section. The extended nozzle section was set at 240°C for all in situ composite processing.

The tensile properties (machine/flow direction modulus and strength) of injection moulded in situ composites generated with and without the aid of the static mixer nozzle are shown in Table 1. For the nylon-11/HX8000 (65/35 wt%) in situ composite, an approximately 19% increase in tensile modulus and an approximately 27% increase in tensile strength were observed as a result of the static mixer nozzle. The above results indicate that the static mixer nozzle served to enhance the reinforcing capability of HX8000 under the given injection moulding conditions. These results were consistent with those obtained for in situ composites based on poly (ether imide) reinforced with a non-crystallizable liquid crystalline polyester (DuPont TLCP, HX1000) [32]. Also, the tensile properties along the transverse direction of the above in situ composites were observed to be insensitive to the application of the static mixer nozzle during the injection moulding process.

Scanning electron microscopy was used to examine the influence of the static mixer nozzle on the morphology of the injection moulded in situ composites. Fig. 1 shows micrographs of the nylon-11/HX8000 in situ composite injection moulded without (a) and with (b) the static mixer nozzle. These micrographs display well developed HX8000 fibrils embedded within the nylon-11 matrix for both cases. However, the HX8000 fibrils within the composite generated using the static mixer nozzle appear to be of significantly smaller diameters, with the average diameter decreasing from approximately 4.5–5.0 microns to approximately 3.0–3.5 microns. Also, a more uniform distribution of fibril diameters is evident in composites generated using the static mixer nozzle. Smaller fibril diameters could be an

Table 1
Machine direction tensile properties of nylon-11/HX8000 (65/35 wt%) in situ composite injection moulded without and with the static mixer nozzle: tensile modulus (GPa) and tensile strength (MPa). Numbers in parentheses indicate standard deviations based on at least six measurements

| Sample (machine direction properties) | Tensile modulus (GPa) | Tensile strength (MPa) |
|---|---|---|
| Nylon 11/HX8000 65/35 wt% (standard nozzle) | 2.95 (0.13) | 42.50 (1.99) |
| Nylon 11/HX8000 65/35 wt% (static mixer nozzle) | 3.51 (0.12) | 53.98 (2.32) |

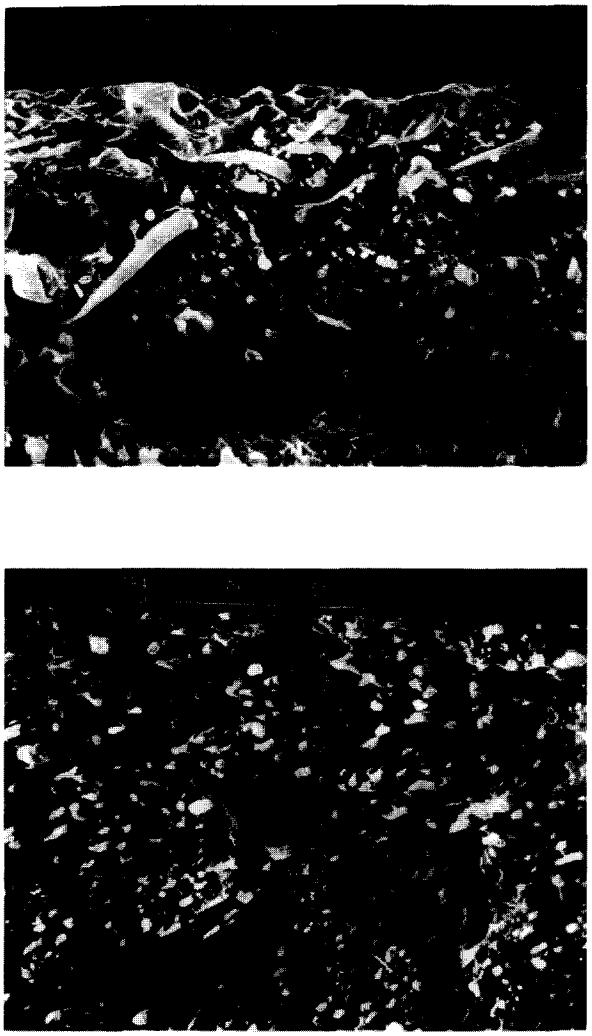


Fig. 1. Scanning electron micrographs of nylon-11/HX8000 (65/35 wt%) in situ composite injection moulded without (a) and with (b) the static mixer nozzle. The machine direction of the injection moulded composite is normal to the plane of the micrograph.

indirect indication of higher aspect ratio TLCP fibrils, which in turn can be responsible for the enhanced tensile properties measured for in situ composites generated using the static mixer nozzle.

Dynamic mechanical measurements were performed on the composite samples at temperatures just high enough to melt HX8000 (290°C). Fig. 2 shows these results plotted as the magnitude of the complex viscosity ($|\eta^*|$) versus frequency for the nylon-11/HX8000 composite generated with and without the static mixer nozzle. The $|\eta^*|$ of the sample generated using the static mixer nozzle is significantly higher than that generated under standard conditions, across the range of frequencies examined. This result is consistent with those of fibre filled systems wherein polymers with higher aspect ratio and similar volume fraction reinforcement display higher melt viscosities [33]. This result combined with the morphological results clearly suggests that injection moulded in situ composites generated using the static mixer nozzle possess TLCP fibrils of higher aspect ratios, and this is manifested in the improved tensile properties measured for these samples. As a result, all subsequent in situ composites were injection moulded using the static mixer nozzle. The discussion that follows will focus on the tensile properties of in situ composites that were injection moulded in the presence of the reactive terpolymer, and the influence of the terpolymer alone will be elucidated as all subsequent injection moulding experiments are carried out using the extended nozzle.

The tensile properties (modulus, strength, and toughness) of injection moulded in situ composites based on nylon-11 and HX8000 (65/35 wt%) are shown in Table 2 (A: machine direction properties; B: transverse direction properties) and are also plotted as a function of terpolymer amount present (Fig. 3: tensile modulus; Fig. 4: tensile strength; Fig. 5: tensile toughness). The properties of pure nylon-11 are also included for comparison purposes. Addition of 35 wt% HX8000 to nylon-11 leads to a significant increase in machine direction tensile modulus (three and a half times) and a sizeable increase in the machine direction tensile strength. This is a manifestation of the reinforcing potential of HX8000. However, the tensile properties along the transverse direction of the in situ composite do not display any improvements compared to nylon-11. In fact, the tensile strength along the transverse direction of the in situ composite is less than half that of pure nylon-11. This kind of anisotropy in the mechanical properties of in situ composites is consistent with previously reported results [13–19]. This is attributed to the rigid backbone structures of TLCPs and their ease of orientability, which force the TLCP chain segments to align preferentially along the flow or machine direction. Therefore, TLCP fibrils generated during mould filling tend to reinforce thermoplastics significantly along the flow/machine direction only. Lack of adhesion between the TLCP fibrils and the matrix is presumably responsible for the poor strength measured along the transverse direction of injection moulded in situ composites.

Fig. 3 shows the tensile modulus and Fig. 4 shows the tensile strength of nylon-11/HX8000 in situ composite as a function of terpolymer amount present. A systematic increase in the machine direction modulus and strength are observed with addition of small quantities of the terpolymer. Samples with 4 wt% terpolymer display the highest machine direction modulus and strength values; these in situ composites display an approximately 27% improvement in machine direction tensile modulus, and a 19% improvement in machine direction tensile strength relative to those processed without the terpolymer. The tensile toughness (Fig. 5) along the machine direction of the nylon-11/HX8000 in situ composite with the terpolymer added does not reveal any improvements relative to those without the terpolymer. In summary, the above results indicate that small amounts of the terpolymer served to enhance the reinforcement provided by HX8000 when melt-blended with nylon-11 in an injection moulder. Such an effect has

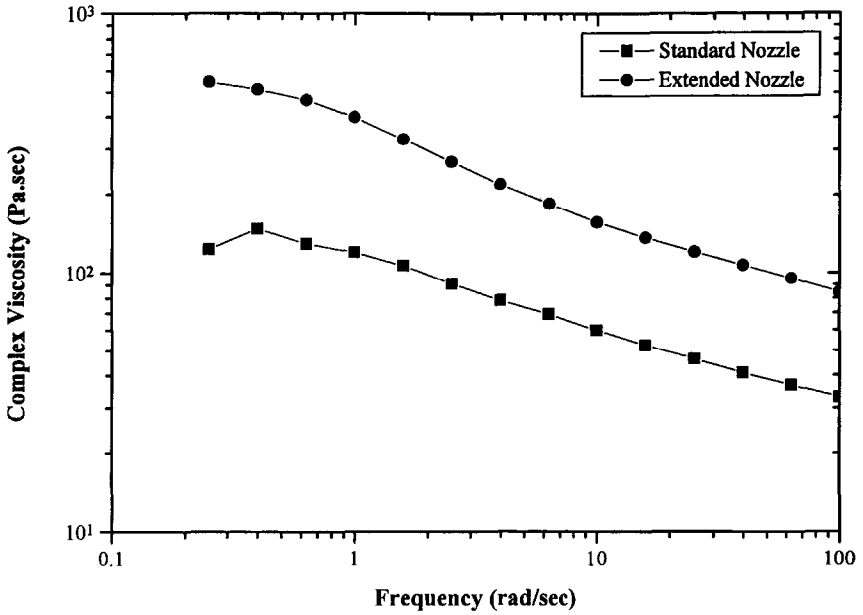


Fig. 2. Dynamic mechanical properties of nylon-11/HX8000 (65/35 wt%) in situ composite injection moulded without and with the static mixer nozzle, plotted as complex viscosity ($|\eta^*|$, Pa·sec) versus angular frequency (rad/sec) at 290°C.

usually been attributed to enhanced fibrillation, with TLCP fibrils of smaller diameters observed in polypropylene-based composites injection moulded in the presence of MAGPP [16–19]. This in turn translates to higher effective aspect ratios of the reinforcing fibrils within the composite.

At very high concentrations of the terpolymer (10 wt%), a dramatic decrease in modulus and a slight decrease in strength is observed along the machine direction of injection moulded in situ composite samples. This is consistent with previously reported results for in situ composites with excessive amounts of similar compatibilizing agents, wherein TLCP fibrillation was inhibited, and coalescence of the TLCP droplets was observed [19,25]. It has also been suggested that too much compatibility between the phases can be detrimental to TLCP fibril formation, as deformation of the very fine droplets formed is not easily achieved [4,34,35]. The decrease in modulus at high terpolymer concentrations can also be attributed to the fact that the composite now contains a significant amount of the terpolymer which has inherently poor tensile properties (the terpolymer has a reported flexural modulus of approximately 0.12 GPa and a tensile strength of approximately 10 MPa [36]).

The tensile modulus along the transverse direction of injection moulded nylon-11/HX8000 in situ composite is observed to be largely independent of terpolymer amount present, with only the sample with 4 wt% terpolymer displaying a small improvement. However, both tensile strength and tensile toughness along the transverse direction of the in situ composite are observed to increase systematically with the amount of terpolymer present. The sample with 4 wt% terpolymer reveals the highest tensile strength,

Table 2
Tensile properties of nylon-11/HX8000 (65/35 wt%) in situ composite injection moulded with varying amounts of Lotader terpolymer: tensile modulus (GPa), tensile strength (MPa), and tensile toughness (MPa). (A) machine direction properties; (B) transverse direction properties. The tensile properties of pure nylon-11 are also included for comparison purposes. Numbers in parenthesis indicate standard deviations based on at least six measurements

| Sample | Tensile modulus (GPa) | Tensile strength (MPa) | Tensile toughness (MPa) |
|---|---|---|---|
| (A) Machine direction properties | | | |
| Pure Nylon-11 | 0.89 (0.07) | 31.54 (1.58) | – |
| Nylon-11/HX8000 65/35 wt% (0 wt% terpolymer) | 3.51 (0.12) | 53.98 (2.32) | 0.63 (0.05) |
| Nylon-11/HX8000 65/35 wt% (1 wt% terpolymer) | 3.60 (0.23) | 59.91 (3.11) | 0.68 (0.03) |
| Nylon-11/HX8000 65/35 wt% (4 wt% terpolymer) | 4.45 (0.36) | 63.97 (2.05) | 0.62 (0.05) |
| Nylon-11/HX8000 65/35 wt% (10 wt% terpolymer) | 3.03 (0.19) | 56.78 (1.35) | 0.84 (0.09) |
| (B) Transverse direction properties | | | |
| Pure Nylon-11 | 0.89 (0.07) | 31.54 (1.58) | – |
| Nylon-11/HX8000 65/35 wt% (0 wt% terpolymer) | 1.03 (0.05) | 14.52 (0.76) | 0.39 (0.03) |
| Nylon-11/HX8000 65/35 wt% (1 wt% terpolymer) | 1.01 (0.02) | 26.76 (2.34) | 0.98 (0.22) |
| Nylon-11/HX8000 65/35 wt% (4 wt% terpolymer) | 1.21 (0.12) | 29.23 (5.18) | 0.87 (0.21) |
| Nylon-11/HX8000 65/35 wt% (10 wt% terpolymer) | 0.93 (0.04) | 25.73 (1.48) | 1.62 (0.43) |

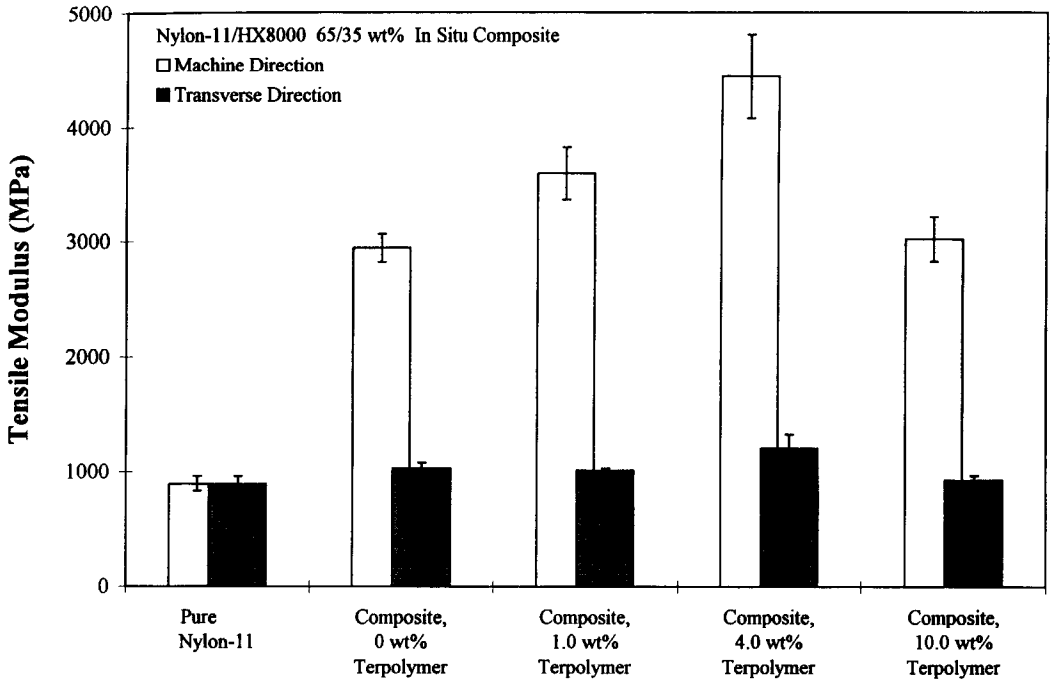


Fig. 3. Tensile modulus (MPa) of pure nylon-11 and nylon-11/HX8000 (65/35 wt%) in situ composites injection moulded with varying amounts of terpolymer. Open bars represent machine direction modulus values and filled bars represent transverse direction modulus values.

while the tensile toughness continues to increase at terpolymer amounts greater than 4 wt%. Thus, the sample with 4 wt% terpolymer reveals an approximately 102% improvement in transverse direction tensile strength, and an approximately 123% improvement in transverse direction tensile toughness relative to those without the terpolymer. The transverse direction properties of injection moulded in situ composites are largely governed by interfacial adhesion between the TLCP fibrils and the thermoplastic matrix. Therefore, the significant improvements observed in the transverse direction properties indicates that the terpolymer serves to enhance interfacial adhesion between the HX8000 fibrils and nylon-11.

Such an increase in the overall reinforcement provided by

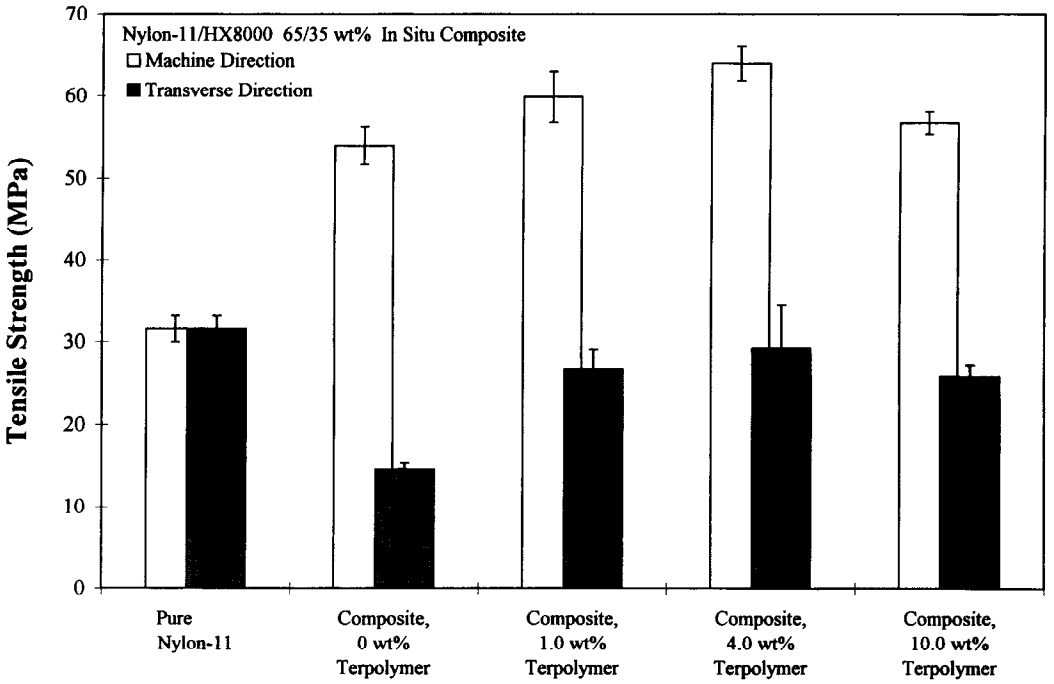


Fig. 4. Tensile strength (MPa) of pure nylon-11 and nylon-11/HX8000 (65/35 wt%) in situ composites injection moulded with varying amounts of terpolymer. Open bars represent machine direction strength values and filled bars represent transverse direction strength values.

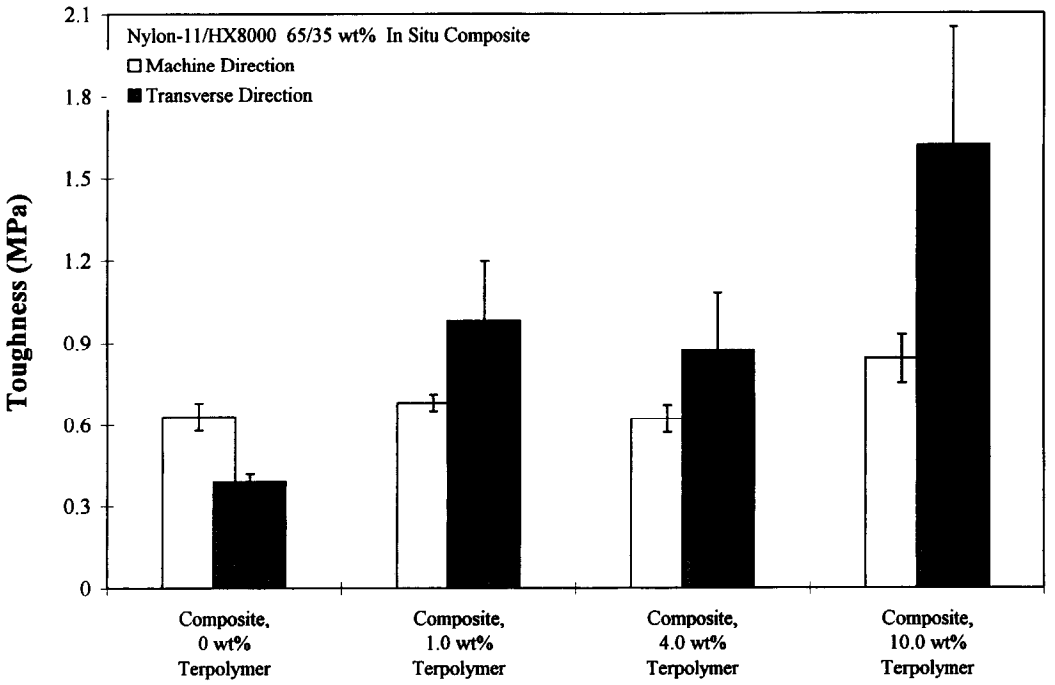


Fig. 5. Tensile toughness (MPa) of nylon-11/HX8000 (65/35 wt%) in situ composites injection moulded with varying amounts of terpolymer. Open bars represent machine direction toughness values and filled bars represent transverse direction toughness values.

the TLCP in the presence of the terpolymer can lead to significant cost-savings as lower amounts of TLCP are required to achieve the same level of properties. For example, an application warranting a tensile modulus of approximately 3.5 GPa will now require only 25 wt% HX8000 as opposed to 35 wt% HX8000 via conventional means (without any terpolymer). This 10% savings in material costs can lead to significant economical advantages when considered on a bulk production scale, especially since TLCPs are relatively expensive materials.

Because the terpolymer appears to be very effective for in situ composites based on nylon-11 and HX8000, its effectiveness on other combinations of polyamides and liquid crystalline polyesters was evaluated. More specifically, in situ composites based on nylon 6/HX8000 (60/40 wt%), and nylon 6/LC3000 (60/40 wt%) were also injection moulded with and without the terpolymer and their tensile properties were measured. Table 3 shows the tensile properties of the nylon 6/HX8000 (60/40 wt%) in situ composite without any terpolymer and with 5 wt% terpolymer added to the mixture. Small amounts of the terpolymer added to the nylon 6/HX8000 (60/40 wt%) in situ composite results in a significant increase in machine direction tensile modulus (~22%), and machine direction tensile strength (~35%). This is a manifestation of the improved reinforcement provided by HX8000 when injection moulded in the presence of the terpolymer. Table 3 also indicates that small amounts of the terpolymer added to the nylon 6/HX8000 (60/40 wt%) in situ composite results in significant increases in transverse direction tensile strength (~105%) and transverse direction tensile toughness (~46%). This is a manifestation of improved interfacial adhesion between the HX8000 fibrils and nylon 6. These results are consistent with the results described for the nylon-11/HX8000 (65/35 wt%) in situ composite.

Table 4 shows the tensile properties of the nylon 6/LC3000 (60/40 wt%) in situ composite without any terpolymer and with 5 wt% terpolymer added to the mixture.

Table 3
Tensile properties of nylon 6/HX8000 (60/40 wt%) in situ composite injection moulded without and with 5 wt% Lotader terpolymer: tensile modulus (GPa), tensile strength (MPa), and tensile toughness (MPa). (A) Machine direction properties; (B) transverse direction properties. Numbers in parenthesis indicate standard deviations based on at least six measurements

| Sample | Tensile modulus (GPa) | Tensile strength (MPa) | Tensile toughness (MPa) |
|---|---|---|---|
| (A) Machine direction properties | | | |
| Nylon 6/HX8000 60/40 wt% (0 wt% terpolymer) | 4.70 (0.24) | 63.60 (1.61) | 0.97 (0.10) |
| Nylon 6/HX8000 60/40 wt% (5 wt% terpolymer0 | 5.74 (0.36) | 85.67 (2.24) | 1.13 (0.12) |
| (B) Transverse direction properties | | | |
| Nylon 6/HX8000 60/40 wt% (0 wt% terpolymer) | 2.23 (0.14) | 14.75 (0.84) | 0.26 (0.05) |
| Nylon 6/HX8000 60/40 wt% (5 wt% terpolymer) | 2.05 (0.27) | 30.24 (2.18) | 0.38 (0.05) |

Small amounts of the terpolymer added to the nylon 6/LC3000 (60/40 wt%) in situ composite results in a significant increase in machine direction tensile modulus (~31%), and machine direction tensile strength (~58%). This is a manifestation of the improved reinforcement provided by LC3000 when injection moulded in the presence of the terpolymer. Table 4 also indicates that small amounts of the terpolymer added to the Nylon 6/LC3000 (60/40 wt%) in situ composite results in significant increases in transverse direction tensile strength (~32%) and transverse direction tensile toughness (~24%). This is a manifestation of the improved interfacial adhesion between the LC3000 fibrils and nylon 6. These results are consistent with the results described for the nylon-11/HX8000 (65/35 wt%) and nylon 6/HX8000 (60/40 wt%) in situ composites. These results basically reveal the potential of the terpolymer in enhancing the reinforcement provided by TLCPs for a wide variety of in situ composites based on polyamides reinforced with thermotropic liquid crystalline polyesters.

Having demonstrated the effectiveness of the terpolymer in enhancing the performance of various in situ composites, the sections that follow will focus more on the underlying mechanisms. The in situ composite based on nylon-11 and HX8000 will be used as an example to demonstrate the influence of the terpolymer on the morphology development and related properties of in situ composites under injection moulding conditions.

### 3.2. Morphological examinations

Scanning electron microscopy was used to examine the morphology of the nylon-11/HX8000 in situ composite and the influence of the terpolymer on the geometry and size distribution of the HX8000 phase. Injection moulded in situ composites are known to reveal skin-core morphologies that are induced by the mould filling flow kinematics. Hence, separate morphological examinations were carried out along both the skin and core regions to fully elucidate the influence of the terpolymer on the morphology of in situ composites.

Figs. 6 and 7 contain scanning electron micrographs along the skin and core portions, respectively, of injection moulded nylon-11/HX8000 composite samples, respectively, as a function of terpolymer amount added ((a): 0 wt% terpolymer; (b): 1 wt% terpolymer; (c): 4 wt% terpolymer). The skin portions (Fig. 6) of the samples reveal well developed HX8000 fibrils embedded within the nylon-11 matrix. Samples with 1 and 4 wt% terpolymer reveal distinctly smaller fibril diameters relative to those injection moulded without the terpolymer. This may be an indication of higher aspect ratio TLCP fibrils along the skin regions of composites injection moulded with small amounts of the terpolymer relative to those without the terpolymer. Fig. 8 shows the size distribution of HX8000 fibrils along the skin regions plotted as an approximate number of fibrils of a certain diameter versus diameter (the size distribution of the TLCP phase was determined by physically measuring the diameter of 80 different fibrils and/or droplets from two micrographs taken at two different locations of the same sample; 40 fibrils/droplets from each SEM micrograph were considered for the above analysis). This plot clearly shows that addition of the terpolymer results in HX8000 fibrils of lower diameters with a narrower size distribution. The average diameter of HX8000 fibrils is estimated to decrease from approximately 3 microns in composite samples generated without the aid of the terpolymer to approximately 2 microns in composites generated in the presence of small amounts of the terpolymer.

The TLCP phase appears to be present as large, undeformed droplets along the core regions of the nylon-11/HX8000 in situ composite (Fig. 7(a)). This is consistent with previous observations, in that minimal fibrillation of the TLCP phase is evident along the core regions of injection moulded in situ composites, as the extensional stresses present along the core regions are very low compared to those along the skin regions. In situ composites with 1 wt% terpolymer reveal HX8000 droplets of significantly smaller diameters, with the diameters decreasing from approximately 6 microns to less than 2 microns (Fig. 7(b); also note that the magnification on Fig. 7(a) is 409, while those of Fig. 7(b) and (c) are $> 800$). This result is consistent with the morphological examinations along the skin regions of the same in situ composite, with addition of the terpolymer providing smaller TLCP phase domains. These undeformed TLCP droplets present along the core regions do not really contribute to the overall reinforcement of the composite in any way.

Table 4
Tensile properties of nylon 6/LC3000 (60/40 wt%) in situ composite injection moulded without and with 5 wt% Lotader terpolymer: tensile modulus (GPa), tensile strength (MPa), and tensile toughness (MPa). (A) Machine direction properties; (B) transverse direction properties. Numbers in parenthesis indicate standard deviations based on at least six measurements

| Sample | Tensile modulus (GPa) | Tensile strength (MPa) | Tensile toughness (MPa) |
|---|---|---|---|
| (A) Machine direction properties | | | |
| Nylon 6/LC3000 60/40 wt% (0 wt% terpolymer) | 2.83 (0.17) | 29.41 (2.12) | 0.32 (0.06) |
| Nylon 6/LC3000 60/40 wt% (5 wt% terpolymer) | 3.71 (0.12) | 46.41 (2.07) | 0.62 (0.11) |
| (B) Transverse direction properties | | | |
| Nylon 6/LC3000 60/40 wt% (0 wt% terpolymer | 1.97 (0.13) | 22.95 (3.57) | 0.79 (0.23) |
| Nylon 6/LC3000 60/40 wt% (5 wt% terpolymer) | 1.83 (0.12) | 30.31 (2.21) | 0.98 (0.18) |

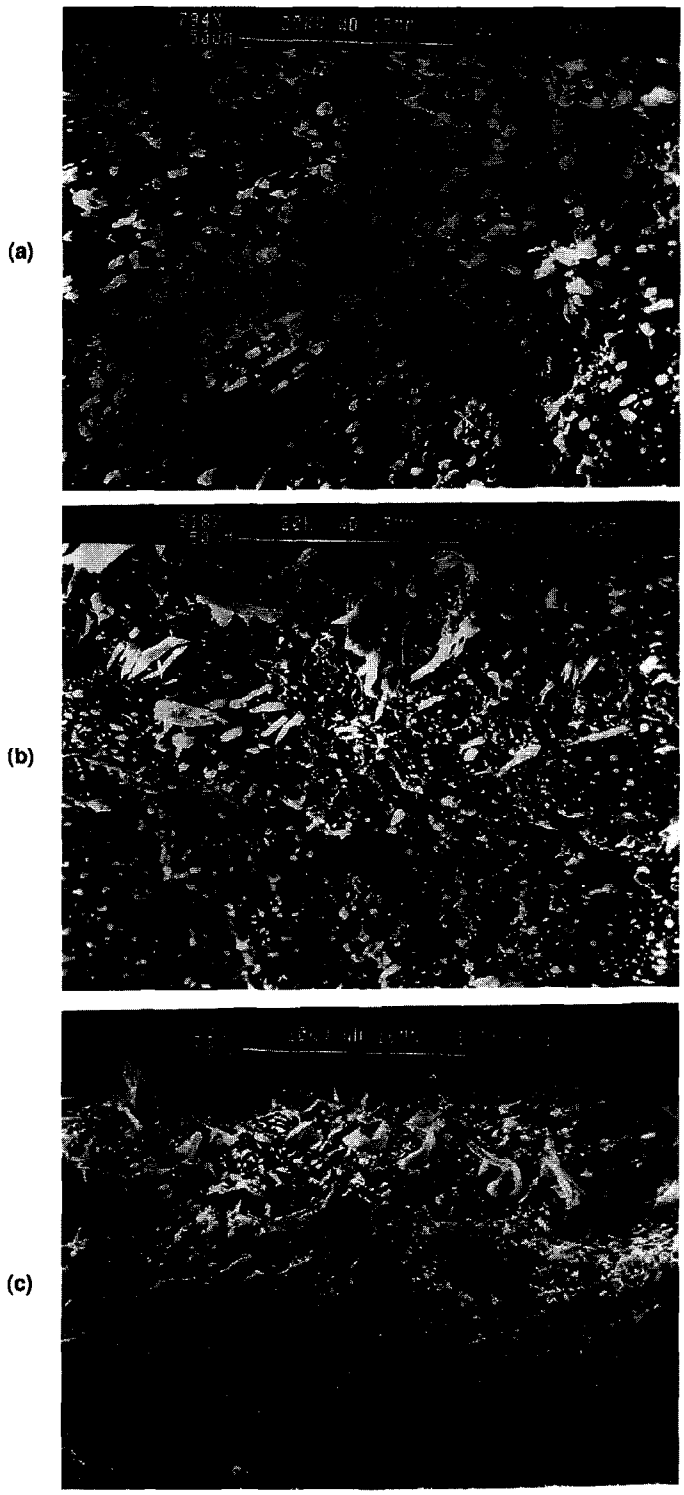


Fig. 6. Scanning electron micrographs showing the **skin** regions of nylon-11/HX8000 (65/35 wt%) in situ composite injection moulded with (a) 0 wt% terpolymer, (b) 1 wt% terpolymer, and (c) 4 wt% terpolymer. The machine direction of the composite is normal to the plane of the micrograph.

Nevertheless, a morphological transformation is observed along the core region of the nylon-11/HX8000 in situ composite with 4 wt% terpolymer; the core region displays well developed HX8000 fibrils as opposed to undeformed droplets. These fibrils along the core regions will provide considerable reinforcement to the matrix, nylon-11. Fig. 9 shows the size distribution of the HX8000 phase along the core regions plotted as an approximate number of fibrils of a certain diameter versus diameter. Consistent with observations along the skin regions, this plot clearly shows that

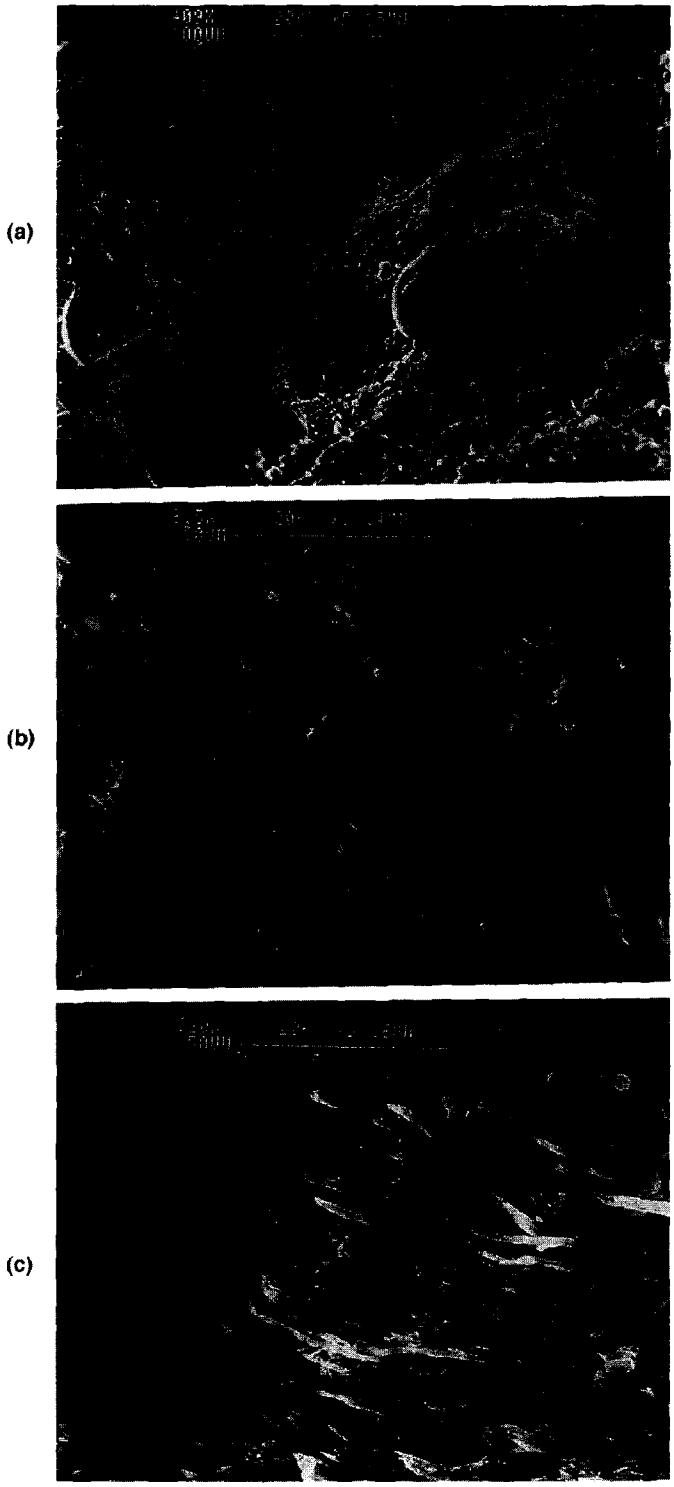


Fig. 7. Scanning electron micrographs showing the **core** regions of nylon-11/HX8000 (65/35 wt%) in situ composite injection moulded with (a) 0 wt% terpolymer, (b) 1 wt% terpolymer, and (c) 4 wt% terpolymer. The machine direction of the composite is normal to the plane of the micrograph. Also note that the magnification of (b) and (c) is approximately twice that of (a).

addition of small amounts of the terpolymer results in HX8000 phase domains of smaller diameters with a narrower size distribution along the core regions.

The morphological examinations clearly reveal the principal effects that are responsible for the significant improvements in tensile properties observed along the machine direction of injection moulded nylon-11/HX8000 in situ composites when small amounts of the terpolymer are added. Addition of the terpolymer appears to enhance the reinforcement provided by HX8000 under injection

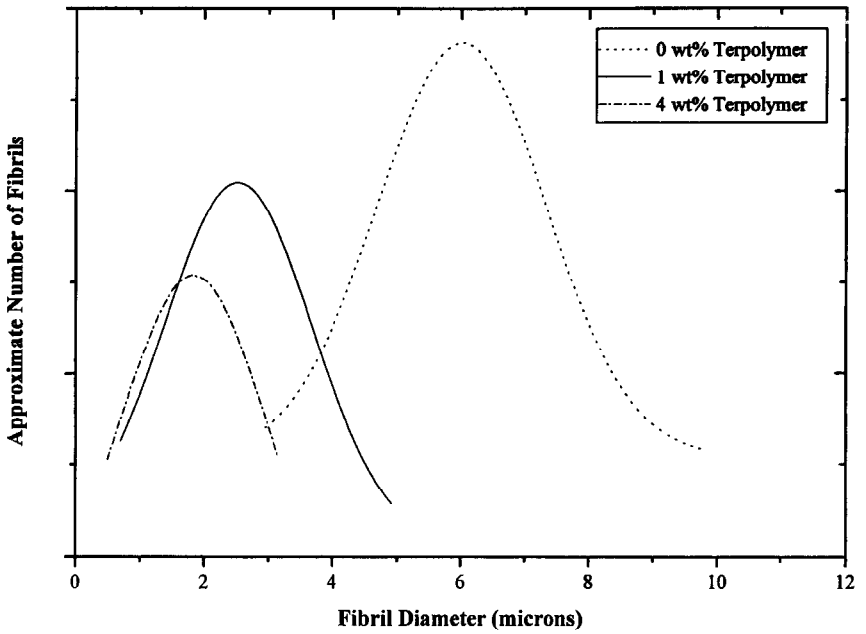


Fig. 8. TLCP phase size distribution along the skin regions of nylon-11/HX8000 (65/35 wt%) in situ composite injection moulded with 0, 1 and 4 wt% terpolymer, plotted as an approximate number of fibrils versus fibril diameter. These curves are based on the micrographs shown in Fig. 6.

moulding conditions, which is evident in the potentially higher aspect ratio fibrils present along the skin regions and the formation of well developed HX8000 fibrils (as opposed to undeformed spherical droplets) along the core regions.

### 3.3. Miscibility characteristics

The significant improvements achieved in the transverse direction tensile strength and tensile toughness for the in situ composite could be a direct result of enhanced adhesion between nylon-11 and the HX8000 fibrils. This indicates that there could be some interactions such as hydrogen bonding between the two polymers. In order to determine if such interactions induced at least partial miscibility between nylon-11 and HX8000, solid state dynamic mechanical measurements were made on in situ composite samples generated with and without small amounts of the terpolymer. Fig. 10 shows the dynamic mechanical loss factor (tan $\delta$) plotted as a function of temperature for both

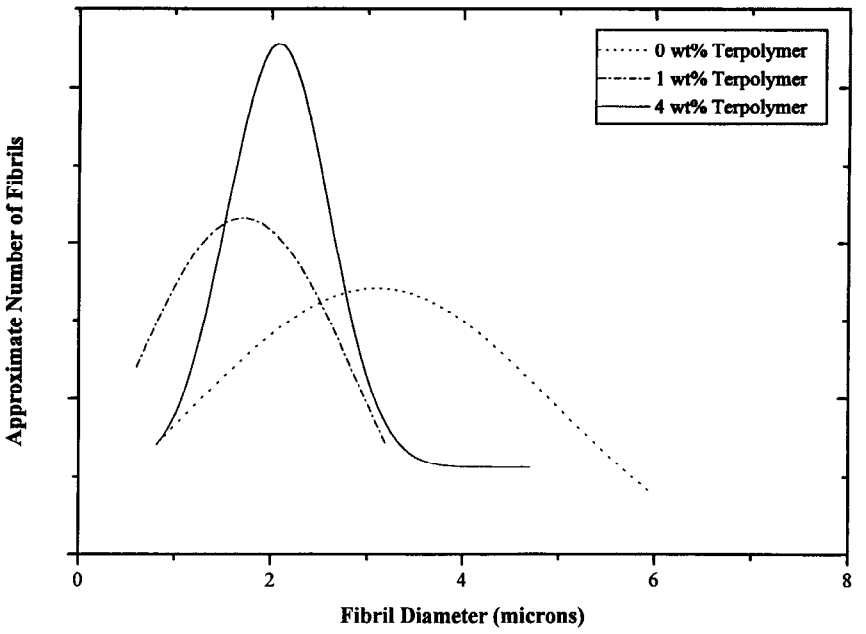


Fig. 9. TLCP phase size distribution along the core regions of nylon-11/HX8000 (65/35 wt%) in situ composite injection moulded with 0, 1 and 4 wt% terpolymer, plotted as an approximate number of fibrils versus fibril diameter. These curves are based on the micrographs shown in Fig. 7.

samples. These data reveal two peaks; the low temperature peak is the glass transition of the nylon-11 phase, and the high temperature peak corresponds to the glass transition of the HX8000 phase. Both glass–rubber relaxation peaks do not reveal any shifts in temperature or magnitude, indicating that addition of the terpolymer did not affect the miscibility between the two phases in any way.

### 3.4. Surface roughness via atomic force microscopy

Atomic Force Microscopy (AFM) was used to probe the surfaces of the in situ composite samples generated with and without the terpolymer. The surface area differential (which is an estimate of the surface roughness) of a nylon-11/HX8000 (65/35 wt%) in situ composite is shown in Table 5. A surface area differential of 0% indicates a perfectly smooth surface. It is evident that the in situ composite with 4 wt% terpolymer has a significantly smoother surface, with an approximately 38% lowering of the surface roughness evident. Smoother surfaces in PP/TLCP composites have been observed previously when the injection moulding was carried out in the presence of small amounts of MAGPP [17]. However, this is the first report that quantifies the surface roughness of such in situ composites via any means. Surface smoothness can be correlated with the size of the TLCP fibrils that are protruding out of the surface, with lower aspect ratio (more fibril ends) fibrils yielding a rougher surface. Thus, the surface analysis results are consistent with the fibril sizes determined via morphological examinations as in situ composites generated in the presence of the terpolymer display smaller TLCP fibril diameters (possibly higher aspect ratios).

### 3.5. Discussion on TLCP fibril formation

The ultimate morphology of injection moulded in situ composites develops primarily in two stages. They are initial shearing along the screw of the injection moulder barrel (and extended nozzle section) followed by a combination of shear and extensional forces imposed during mould-filling. The initial dispersion of the minor component of the blend within the matrix phase occurs in the screw of the injection moulder. In the case of nylons reinforced with LC polyesters, the nylons melt initially and encapsulate the unmelted TLCP pellets, which in turn forms the dispersed phase. Melting of the TLCP and subsequent shearing by the screw in the injection moulder leads to breakup and dispersion of the TLCP phase into droplets, with higher shear rates providing a blend with a more uniform distribution of dispersed phase particle sizes. For Newtonian fluids, Taylor proposed that the breakup of the dispersed droplets in simple shear flow can be described by a balance between shear and interfacial forces [37,38]. This can be expressed in terms of the *Capillary number* ($C_a$):

$$C_a = \frac{\eta_m a \gamma}{\sigma} \tag{1}$$

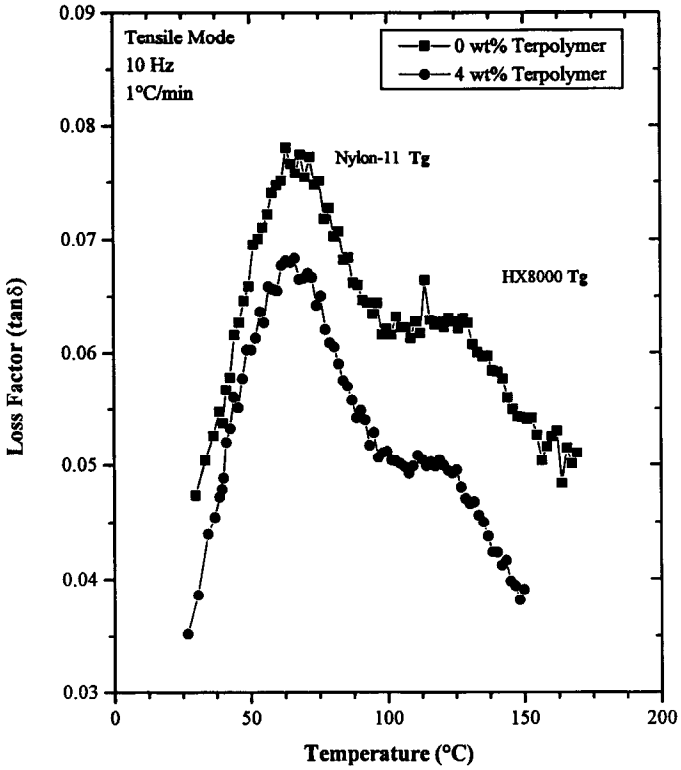


Fig. 10. Solid state dynamic mechanical properties of nylon-11/HX8000 (65/35 wt%) in situ composite injection moulded with 0 and 4 wt% terpolymer, plotted as loss factor (tan δ) versus temperature. The test was performed at a heating rate of 1°C/min and at a frequency of 10 Hz.

Table 5
Surface analysis results of nylon-11/HX8000 (65/35 wt%) in situ composite injection moulded without and with 4 wt% Lotader terpolymer: 2-d surface area scanned (micron$^2$); 3-d surface area detected (micron$^2$); surface roughness = [3-d surface area − 2-d surface area]/[2-d surface area] (%)

| Sample | 2-d Area (micron$^2$) | 3-d Area (micron$^2$) | Surface roughness |
|---|---|---|---|
| Nylon-11/HX8000 composite (0 wt% terpolymer) | 2500 | 2545.6 | 1.82% |
| Nylon-11/HX8000 composite (4 wt% terpolymer) | 2500 | 2528.4 | 1.14% |

where, $\eta_m$ is the matrix viscosity, $a$ is the diameter of the dispersed phase droplet, $\gamma$ is the shear rate, and $\sigma$ is the interfacial tension. The *viscosity ratio* ($k = \eta_d/\eta_m$), which is defined as the ratio of the dispersed phase viscosity to that of the matrix phase is another important parameter that controls drop breakup and morphology development in multiphase systems. Drop breakup in shear flow is predicted to occur more readily at viscosity ratios less than or very nearly equal to one. Taylor's work has been the basis of most subsequent studies on morphology development in immiscible polymer blends.

In order to estimate the approximate viscosity ratio in the blending of nylon-11 and HX8000, dynamic mechanical tests were performed on the individual polymers at 285°C. Fig. 11 shows the dynamic frequency sweeps of the polymers, plotted as $|\eta^*|$ versus dynamic angular frequency. These data clearly indicate that the reinforcing TLCP, HX8000, is less viscous than nylon-11 across the range of frequencies examined, which is favorable for breakup and dispersion of the TLCP phase along the screw of the injection moulder barrel (assuming that the Cox-Merz rule applies, i.e., $|\eta^*(\omega)| \approx \eta(\gamma)$ is true for nylon-11 and HX8000).

In order to qualify the effect of the terpolymer on breakup of the dispersed phase droplets along the screw of the injection moulder, the blend melt was collected as it exited the nozzle. This provides an opportunity to examine the morphology that developed prior to the mould filling step. The scanning electron micrographs of the extrudate from the nozzle of the injection moulder are shown in Fig. 12 for the blends without (a) and with (b) the terpolymer. These are quite different from those of the composite samples discussed earlier, in that minimal fibrillation of the TLCP phase is evident at this stage. This is consistent with the general belief that the vast majority of the TLCP fibril formation occurs as a result of extensional forces imposed during the mould filling step [15,16]. These micrographs also reveal a significant reduction in the size of the dispersed TLCP phase in the blend with small amounts of the terpolymer. This can be partially attributed to a lowering of the interfacial tension between nylon-11 and HX8000 by the terpolymer, which basically decreases the critical Capillary number and hence the shear stresses that are required for drop breakup (from Taylor's theory; see Eq. (1)).

While Taylor's theory was qualitatively successful in predicting the size of the dispersed phase for Newtonian systems under shear flow, it underestimates the same for viscoelastic fluids. This has been attributed to a competing effect between drop breakup and coalescence which occurs at moderate to high levels of the minor component [39–41]. Stabilization against coalescence is another important factor in obtaining a fine and uniform dispersion in viscoelastic fluid mixtures. In fact, it has been shown that block and/or graft copolymers used to compatibilize multiphase blends do serve to minimize coalescence via stabilization of the dispersed phase droplet [41–43]. Therefore, smaller

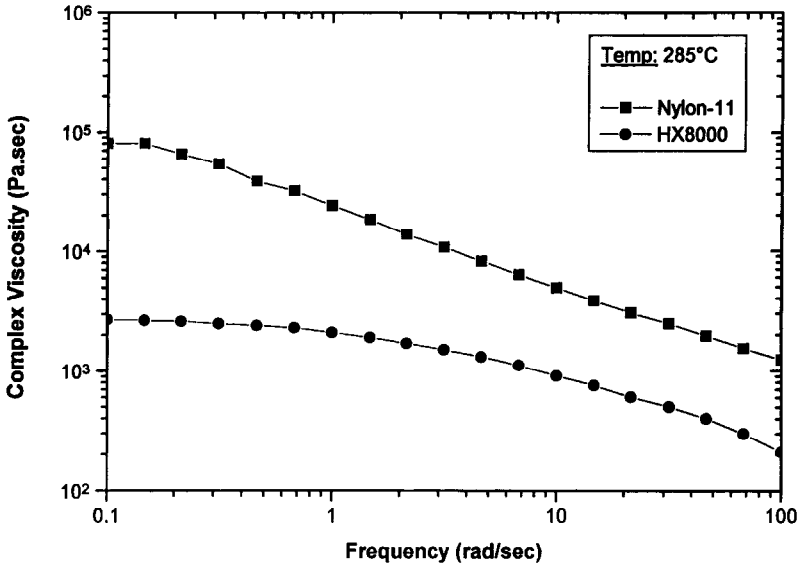


Fig. 11. Dynamic mechanical properties of nylon-11 and HX8000 at 285°C, plotted as complex viscosity ($|\eta^*|$, Pa·sec) versus angular frequency (rad/sec).

HX8000 particles dispersed within nylon-11 in the presence of the terpolymer (Fig. 12) could also be due to a lower degree of TLCP agglomeration and coalescence during the mixing and dispersion process.

The size of the dispersed TLCP phase is lower in the presence of the terpolymer, and this can be attributed to a combination of lower interfacial tension and a lesser degree of coalescence. This explains the smaller TLCP fibril diameters observed along the skin regions of the injection moulded in situ composites (morphology results). This result is largely consistent with the large body of literature on compatibilization of multiphase polymer blends. However, while the objective of blend compatibilization has been to predominantly decrease the size of the dispersed phase, our goals are to enhance fibrillation of the dispersed phase, while preserving the fibrillar morphology. Hence, use of the word 'compatibilization' in the in situ composite formation process can be somewhat misleading. As a result, this terminology has been avoided for the most part during this discussion. However, results from investigations of the mechanism and morphology development during compatibilization can be applied to the in situ composite formation process.

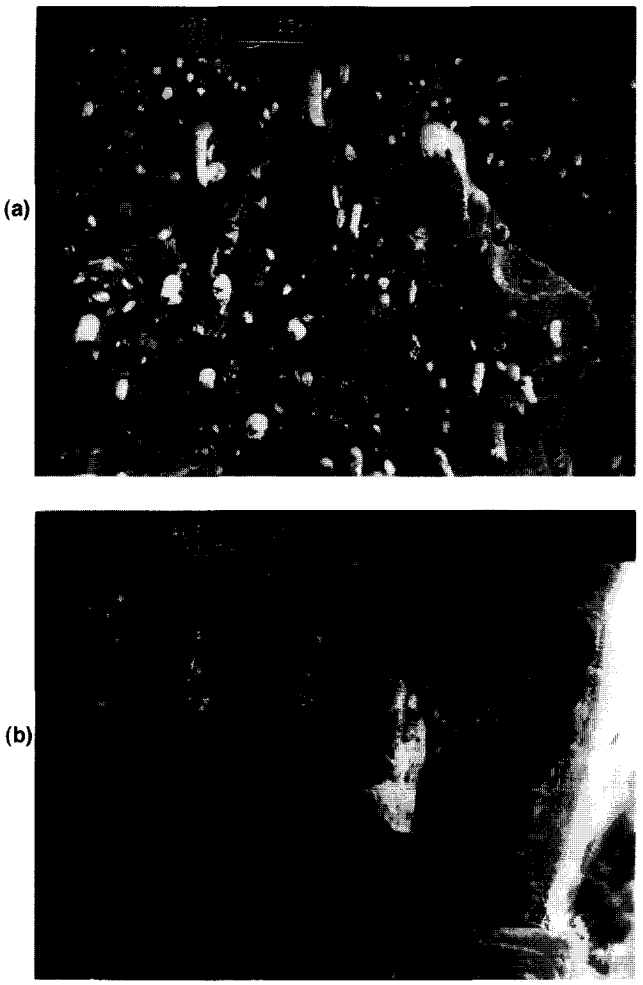


Fig. 12. Scanning electron micrographs showing the extrudate cross-section of nylon-11/HX8000 (65/35 wt%) in situ composite from the injection moulder (prior to the mould filling step) with the blend containing (a) 0 wt% terpolymer and (b) 4 wt% terpolymer.

Retention of the fibrillar (elongated) morphology during drop breakup in the processing of multiphase blends is easier for TLCPs relative to conventional thermoplastics. This is due to the long relaxation timescales of TLCPs and their relatively high solidification temperatures. For example, during the processing of in situ composites based on nylon-11 and HX8000, as the individual polymers are cooled from temperatures above their melting points (similar to the mould filling/composite formation step), HX8000 begins to solidify at approximately 250°C while nylon-11 begins to solidify closer to 180°C [viscosity data during cooling are presented in reference [44]].

Fibrillation of the TLCP phase along the core region of injection moulded specimens cannot be completely attributed to either lower interfacial tension or lesser coalescence. The elongational forces imposed by the advancing front during the mould filling step are largely conveyed to the matrix phase (nylons in our case). In order to fibrillate the dispersed phase, an efficient transfer of forces from the matrix to the dispersed phase is essential. It has been shown that under elongational flow conditions, the deformation of the dispersed phase will correspond to that of the matrix phase only when the viscosity ratio is less than or equal to one [45]. However, mould filling and subsequent cooling during the generation of in situ composites is a non-steady-state, non isothermal process that is completed in less than 10 sec. This means that the viscosity of the two phases (and hence the viscosity ratio) is changing rapidly with time as the TLCP solidifies prior to the matrix. Therefore, we propose that the improved adhesion between the TLCP and the matrix polymer in the blend with small amounts of the terpolymer can lead to a more efficient transfer of forces between the phases, which in turn promotes affine deformation of the TLCP droplets. Thus, the enhanced degrees of TLCP fibrillation can also be attributed to a lower degree of dissipation of forces at the interface of the bi-component blend. This illustrates the use of appropriate additives to enhance the reinforcement provided by TLCPs as is evident in more efficient fibril formation along both the skin and core regions of injection moulded in situ composites.

Also, addition of appropriate compatibilizing agents to conventional blends is known to delay the onset of capillary instability effects, which in turn breaks up an elongated drop into several smaller droplets. Such a phenomenon could also be occurring during the mould filling or composite formation step. Thus, enhanced fibrillation of the TLCP phase under injection moulding conditions can be attributed to a combination of improved adhesion between the phases (hence, better transfer of forces across the interface), lower degree of droplet coalescence, lower interfacial tension, and a lower degree of capillary instability effects.

## 4. Conclusions

It was shown that appropriate functional polymers can be used effectively to not only enhance the fibrillation and hence the reinforcement provided by TLCPs under injection moulding conditions, but also to improve the interfacial adhesion characteristics between the matrix and TLCP fibrils. A terpolymer based on ethylene-acrylic ester-maleic anhydride was proven to be very effective for in situ composites based on polyamides reinforced with liquid crystalline polyesters under injection moulding conditions, with the results being consistent with those obtained for polypropylene-based in situ composites via addition of maleic anhydride grafted polypropylene. Addition of the terpolymer served to enhance fibrillation of the TLCP phase, which not only led to higher aspect ratio fibrils along the skin regions of the injection moulded specimens, but also induced fibrillation of the TLCP droplets present along the core regions. This led to significantly higher modulus and strength values along the flow/machine direction of injection moulded in situ composites. These effects have been attributed to a combination of several phenomena. First of all, the terpolymer can lower the interfacial tension between the phases leading to lower shear stresses required for droplet deformation. Second, addition of the terpolymer can minimize coalescence and agglomeration of the TLCP droplets via stabilization of the dispersed phase droplet. The above phenomena are more prominent during the shear-dominated flow along the screw of the injection moulder barrel and could be directly responsible for the potentially higher aspect ratio fibrils along the skin regions. Finally, enhanced interfacial adhesion between the phases can promote affine deformation of the TLCP droplets during the mould-filling step via efficient transfer of forces between the matrix phase and the TLCP droplets, which in turn induces fibrillation of the TLCP phase along the core regions in addition to fibrillation along the skin portions of injection moulded specimens.

The vast improvements in the strength and toughness measured along the transverse direction of in situ composites generated in the presence of the terpolymer indicates an enhancement in interfacial adhesion between the TLCP and the matrix. This is possible if some degree of interactions (such as hydrogen bonding) existed between the different blocks of the copolymer and the blend components. However, any such interactions that are present do not appear to influence the miscibility characteristics of the multiphase blend in any way. Also, in situ composite samples generated in the presence of the terpolymer reveal significantly smoother surfaces compared to those injection moulded in the absence of the terpolymer; this is consistent with morphological results if higher aspect ratio fibrils are thought to yield smoother surfaces.

## Acknowledgements

The authors wish to acknowledge Foster-Miller for financial support. Nylon-11 and Lotader terpolymer were obtained through the courtesy of Jim Mason at Elf Atochem North America, Inc. The expertise of Stephen McCartney (Virginia Tech) for the AFM work is greatly appreciated. The assistance of Mike McLeod in the SEM examinations and Varun Ratta (Professor G. L. Wilkes's Polymer Characterization Laboratory, Virginia Tech) for the DMA data is also appreciated.

## References

[1] Kiss G. Polymer Engineering and Science 1987;27:410.
[2] Blizard KG, Baird DG. Polymer Engineering and Science 1987;27:653.
[3] Weiss RA, Huh W, Nicolais L. Polymer Engineering and Science 1987;27:673.
[4] Isayev AI, Modic M. Polymer Composites1987;8:158.
[5] Baird DG. Thermoplastic in-situ composites. In Salamone JC, editor. Polymeric materials encyclopedia, vol. 5. New York: CRC Press, 1996:3207.
[6] Handlos AA, Baird DG. Journal of Macromolecular Science—Macromol Chem Phys 1995;135:183.
[7] Seigmann A, Dagan A, Kenig S. Polymer 1985;26:1325.
[8] Zhuang P, Kyu T, White JL. Polymer Engineering and Science 1983;23:632.
[9] Seppala J, Heino M, Kapanen C. Journal of Applied Polymer Science 1988;28:1095.
[10] Chapleau N, Carrecu PJ, Peleteiro C, Lavoie PA, Malik TM. Polymer Engineering and Science 1876;1992:32.
[11] Bafna SS, Sun T, Baird DG. Polymer 1993;34:708.
[12] La Mantia FP, Cangialosi F, Pedretti U, Roggero A. European Polymer Journal 1993;29:671.
[13] Baird DG, Bafna SS, deSouza JP, Sun T. Polymer Composites 1993;14:214.
[14] Bafna SS, Sun T, de Souza JP, Baird DG. Polymer 1995;36:259.
[15] deSouza JP, Baird DG. Polymer 1985;1996:37.
[16] O'Donnell HJ, Baird DG. Polymer Engineering and Science 1996;36:963.
[17] Datta A, Chen HH, Baird DG. Polymer 1993;34:759.
[18] Datta A, Baird DG. Polymer 1995;36:505.
[19] O'Donnell HJ, Baird DG. Polymer 1995;36:3113.
[20] Blizard KG, Federici C, Federico O, Chapoy LL. Polymer Engineering and Science 1990;30:1442.
[21] Meretz S, Kwiatkowski M, Hinrichsen G. International Polymer Processing 1991;VI:239.
[22] Laivins GV. Macromolecules 1989;22:3974.
[23] Baird DG, Datta A. US Patent No. 5621041, 1997.
[24] Seo Y, Hong SM, Hwang SS, Park TS, Kim KU, Lee S, Lee J. Polymer 1995;36:515.
[25] Seo Y, Hong SM, Hwang SS, Park TS, Kim KU, Lee S, Lee J. Polymer 1995;36:525.
[26] Dutta D, Weiss RA, He J. Polymer 1996;37:429.
[27] Wei K, Hwang W, Tyan H. Polymer 1996;37:2087.
[28] Singer M, Simon GP, Varley R, Nobile MR. Polymer Engineering and Science 1996;36:1038.
[29] Miller MM, Cowie JMG, Brydon DL, Mather RR. Polymer 1997;38:1565.
[30] Seo Y. Journal of Applied Polymer Science 1997;21:359.
[31] Krishnaswamy RK, Baird DG, Bin Wadud SE. US Patent Application in Process, 1997.
[32] Krishnaswamy RK, Baird DG, Bin Wadud SE. Unpublished data.
[33] Laun HM. Colloid and Polymer Science 1984;262:257.
[34] Tsuruta A, Kawaguchi H, Ishikawa T. US Patent No. 5043400, 1991.
[35] Isayev A, Modic M. US Patent No. 4728698, 1988.
[36] Elf Atochem Lotader Product Literature, 1996.

[37] Taylor GI. Proceedings of the Royal Society of London 1932;A138:41.
[38] Taylor GI. Proceedings of the Royal Society of London 1932;A146:501.
[39] Huneault MA, Shi ZH, Utracki LA. Polymer Engineering and Science 1995;35:115.
[40] Roland CM, Bohm AGG. Journal of Polymer Science—Polymer Physics Edition 1984;28:2011.
[41] Sundararaj U, Macosko CW. Macromolecules 1995;28:2647.
[42] Majumdar B, Keskkula H, Paul DR. Polymer 1994;35:1386.
[43] Favis BD. Polymer 1994;35:1552.
[44] Krishnaswamy RK, Baird DG. Polymer Composites 1997;18:526.
[45] Delaby I, Ernst B, Muller R. Journal of Macromolecular Science Physics Edition 1996;B35:547.