#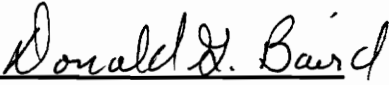 Processing and Properties of Composites based on High Density PolyEthylene and Thermotropic Liquid Crystalline Polymers.

by

Marjan Wesselingh

Thesis submitted to the Faculty of

The Virginia Polytechnic Institute and State University

in partial fulfillment of the requirements of the degree of

MASTERS OF SCIENCE

in Chemical Engineering

APPROVED:

Donald G. Baird
Dr. Donald G. Baird, Chairman

Ronald G. Kander
Dr. Ronald G. Kander

George B. Wills
Dr. George B. Wills

January, 1995

Blacksburg, Virginia

C. 2

LD
5655
V855
1995
W477
C. 2

Processing and Properties of Composites based on High Density PolyEthylene and Thermotropic Liquid Crystalline Polymers.
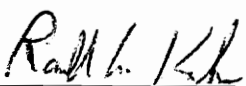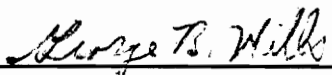
by Marjan Wesselingh

Donald G. Baird, Chairman

Department of Chemical Engineering

(ABSTRACT)

This research was concerned with the processing and properties of composites of high density polyethylene (HDPE) and thermotropic liquid crystalline polymers (TLCPs). Strands of HDPE reinforced with TLCPs were generated using a novel dual extruder mixing technique. It was shown that the strength and modulus of the strands improved with increased strand drawing. Post-processing of the blended strands was done by means of compression and injection molding. It was observed that when the fiber aspect ratio dropped, the composite mechanical properties decreased. When pregenerated fibrils were maintained during injection molding at temperatures above the matrix melting point, but below the TLCP melting point, microcomposites were obtained. Microcomposites generated at the lowest temperatures had higher tensile properties than found for in situ composites and similar to glass reinforced HDPE. At 170°C the pregenerated fibers were no longer deformed during injection molding and high aspect ratio fibrils were maintained. The fiber orientation and addition of a compatibilizer were also studied. This study shows it is possible to extrusion blend HDPE with TLCPs and by optimizing the post-processing conditions, to obtain microcomposites with better properties than in situ composites.

Acknowledgements

Table of Contents

List of Figures

vi

List of Tables

1. Introduction

For the development of new materials, two important variables must be optimized: cost and performance. Although thermotropic liquid crystalline polymers (TLCPs) are considered to be expensive materials, they are easily processable and can show excellent properties. Blending TLCPs with thermoplastics not only lowers the material cost, but can also improve the orientation within the TLCP phase and thus enhance the reinforcing ability of the TLCP. In this chapter, it is first explained why and how TLCPs can be blended with thermoplastics. Then the most recent developments in the field are reported in the literature review (section 1.2), as well as some considerations important for processing polyethylene. The objectives of this research are given in section 1.3.

1.1   Introduction to blends of TLCPs and thermoplastics

Thermotropic liquid crystalline polymers (TLCPs) are composed of highly symmetric aromatic constituents that are sufficiently rigid to provide high strength yet flexible enough to allow for melt processing. The molecular structure of two such TLCPs is given in Figure 1.1.

Vectra A
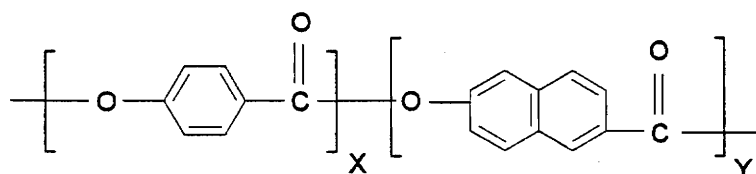
Vectra B
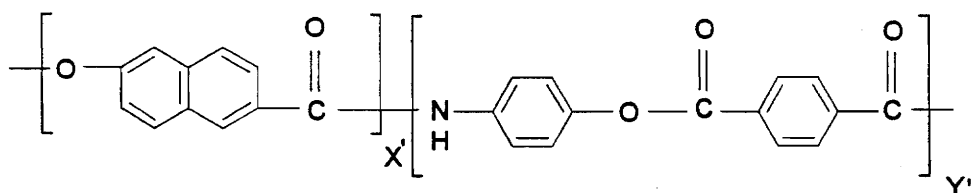
Figure 1.1   Molecular structure of two commercial TLCPs: Vectra A and Vectra B
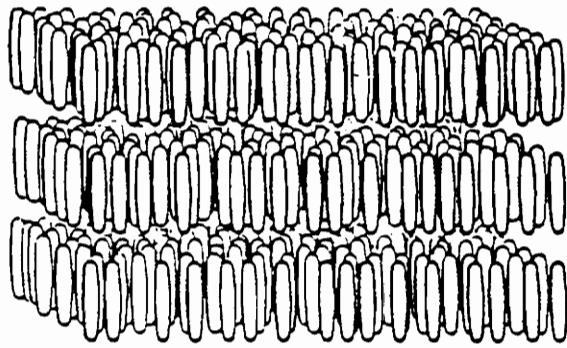
A) SMECTIC
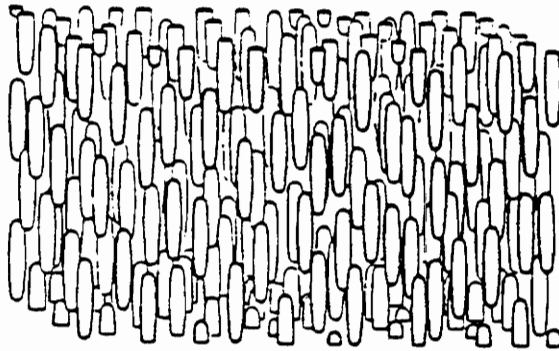
B) NEMATIC
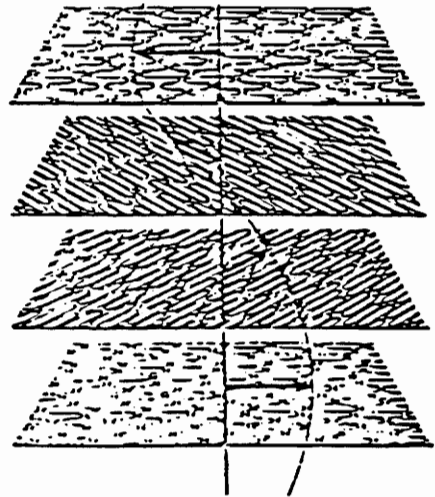
C) CHOLESTERIC

Figure 1.2   Mesogenic phases as found in LCPs. In the nematic mesophase the rods are
oriented along one preferred axis only [1]

The aromatic groups provide stiffness in the chain backbone that can result in an ordering of molecular rods in the material, known as the nematic mesophase (Figure 1.2 [1]). In the nematic phase, the orientation of the rods is only along one preferred axis, which results in anisotropy.

Northolt and Sikkema [2] describe several structural models for LCPs, as shown in Figure 1.3. The material will exhibit high stiffness and strength along the rod direction, when all rods are aligned, but also have overlapping tails or connections. When a TLCP is stretched in an elongational flow field, the rods are highly oriented but will remain in a random tail end distribution, resulting in very strong fibers.

Several factors favor blending of TLCPs with thermoplastics. Although pure TLCPs can be directly molded into parts, the manufacturing of parts is affected by the high TLCP cost and the limited TLCP properties developed in the polymer flow. It is often difficult to generate a primarily extensional flow field necessary for the development of the strong fibers during a molding process. The latter is important to obtain optimum orientation within the TLCP phase, to create long fibrillar structures and orientation of these fibers. The cost of neat TLCPs forms a major limitation for competitiveness in the engineering materials market. Blending TLCPs with a thermoplastic matrix can remedy these problems in two ways: the cheaper matrix reduces the overall cost, and flow characteristics can be influenced during the blending process.
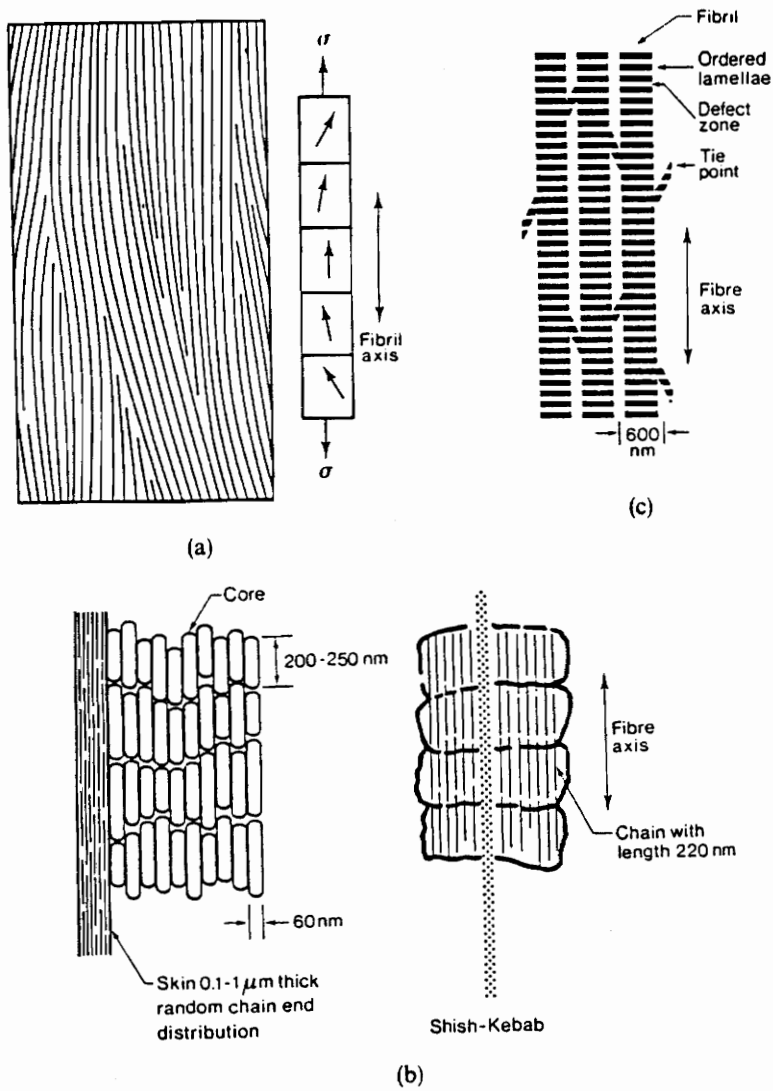
Figure 1.3   Models for the structure of aromatic polyamide fibers, according to (a) Northolt, (b) Morgan, and (c) Panar [2]

TLCP / thermoplastic blends are referred to as in situ composites, when the reinforcing fibers are formed during the final shaping process. However, it is also possible to reprocess in situ blends without changing the fibrillar TLCP structure. The resulting material is called a microcomposite, because micron-size fibrils are maintained in the final shaping process. In either case, it is important to obtain long and thin fibers, with good properties and large surface area. Recent developments in how these TLCP fibers can be obtained and used more effectively are discussed in the next section.

1.2   Literature Review

In a recent review, Handlos and Baird [3] discussed many aspects of how in situ composites are generated. They showed that a fibrillar morphology is required to reinforce thermoplastics with TLCPs, which can be achieved in extensional flow fields such as those found in processes like injection molding and fiber spinning. However, additional drawing provides better orientation of TLCP fibrils and results in the best properties. The aim of this section is to review the status of current research in the field of TLCP reinforced thermoplastics. The following paragraphs will cover some recent literature on how reinforcing TLCP fibrils can be generated and oriented, followed by a discussion on how to use fibrils in post-processing techniques, and how to improve their reinforcing ability. Finally, some remarks will be made on using high density polyethylene as a matrix polymer to blend with TLCPs.

1.2.1   Morphology development in TLCP-thermoplastic blends

It is generally accepted that the reinforcing potential of fibers in a matrix increases with the fiber aspect ratio. The Tsai-Halpin theory (equation 1) predicts the blend modulus ($E_{composite}$) as a function of the volume fractions, V, of the matrix (HDPE) and fibers

(TLCP), their respective moduli (E_{HDPE} and E_{TLCP}) and the fiber aspect ratio, ξ [4]:

$$E_{composite} = \frac{E_{HDPE}\,(\,E_{TLCP} + \xi\,(\,V_{HDPE}\,E_{HDPE} + V_{TLCP}\,E_{TLCP}\,))}{V_{HDPE}\,E_{TLCP} + V_{TLCP}\,E_{HDPE} + \xi\,E_{HDPE}} \qquad (1)$$

ξ is defined as twice the length/diameter ratio of the fibers. This means that for low aspect ratios the stiffness of matrix and fibers is dominated by the modulus of the major component:

$$\frac{1}{E_{composite}} = \frac{V_{TLCP}}{E_{TLCP}} + \frac{V_{HDPE}}{E_{HDPE}} \qquad (2)$$

Equation 2 is referred to as the lower bound of a composite modulus. However, at high aspect ratios (above hundred), the moduli of fibers and matrix appear to be additive, resulting in higher strength:

$$E_{composite} = V_{TLCP}\,E_{TLCP} + V_{HDPE}\,E_{HDPE} \qquad (3)$$

Equation 3 is known as the 'Rule of Mixtures', or the upper bound of a composite modulus. The validity of this model is studied in many recent publications [3-12]. The moduli of blends all increased with draw ratio, implying that the aspect ratio of fibers indeed increased upon drawing. The tensile strength of infinitely long fiber reinforced composites can be predicted according to Piggott [23]:

$$\sigma_{composite} = V_{TLCP}\,\sigma_{TLCP} + V_{HDPE}\,\sigma_{TLCP}\,\frac{E_{HDPE}}{E_{TLCP}} \qquad (4)$$

where σ is the strength of each constituent.

Earlier research assumed that most of the property enhancement from increased draw was due to the finer fibrillation and the resulting effective use of TLCP reinforcement. Most of

these studies assume that the TLCP modulus itself remains constant during blending, whereas the composite modulus only increases with fiber aspect ratio and composition. However, recent efforts [6-8] indicate that the modulus of the TLCP phase itself is highly dependent on the phase morphology. Thus, the TLCP modulus, as used in equations 1-3, can no longer be assumed constant.

Northolt and Sikkema [2] and Lin and Yee [6,7] have developed a model to predict this LCP modulus increase as a function of orientation within the LCP phase, as shown in Figure 1.4. The Lin and Yee model [6] directly relates the TLCP fiber modulus (E_f) to the average orientation of the polymer chains given by $<\sin^2\Theta>$:

$$\frac{1}{E_f} = \frac{1}{E_c} + \frac{<\sin^2\theta>}{2G} \tag{5}$$

where E_c is a polymer chain modulus and G a shear modulus. Lin and Yee [6,7] report about moduli for Vectra A fibrils ranging from 2.2 to 75 GPa, and predict a modulus for Vectra B of 110 GPa. Robertson et al.[8] report that such a high modulus could indeed be obtained in highly drawn PP - TLCP blends. Although this theory does predict a maximum achievable modulus for a certain polymer chain, this still complicates the Tsai-Halpin theory (equation 1), because that maximum level is not reached in most blends. It is thus still difficult to predict what modulus can be reached in a particular TLCP fiber. Thus the validity of the Tsai-Halpin theory is highly dependent on the assumed orientation, or modulus, within the TLCP phase.
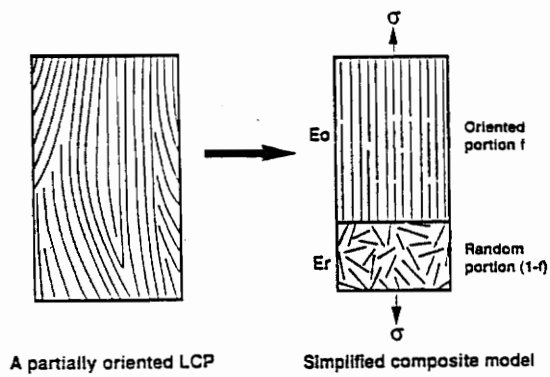
Figure 1.4   Lin and Yee composite model of an oriented LCP [6]

Since a high orientation level is important for tensile properties, it is imperative to understand under what circumstances this orientation can best be achieved. As mentioned before, an extensional flow field is very important to improve orientation. Another aspect for orientation development is that the shear viscosity of a dispersed phase has to be lower than the matrix viscosity in order to favor elongation of dispersed droplets [9-16]. Because of their low melt viscosity, TLCPs are very suitable to form elongated fibers when blended with more viscous thermoplastics.

The blend composition also influences morphological development. For TLCP concentrations below 10%, droplets do not get a chance to coalesce into fibers [17]. However, for higher TLCP concentrations, often a phase change from fibers into lamella-like structures occurs [16]. At very high TLCP concentrations, the major and minor phase can even be reversed, so that the thermoplastic is dispersed in the TLCP matrix. This results in a lower orientation of the TLCP phase at higher concentrations, which is reflected in a leveling of properties, as shown in Figure 1.5.
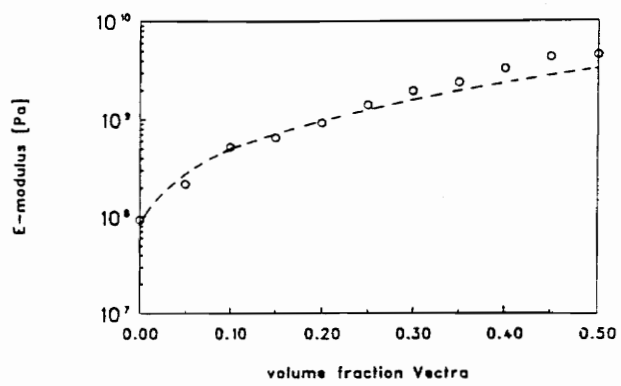
Figure 1.5   Leveling of the tensile modulus with TLCP concentration as predicted (---)
by Verhoogt et al.[16]

Polymer compatibility also affects morphological development in blends. It appears that for two incompatible phases, a fibrillar morphology is more likely to form than a structure with ribbons, platelets or lamellae [9,14]. This effect can easily be related to the surface tension between the two phases [18], since a high surface tension (as for incompatible polymers) results in a lowering of surface area by drop formation. These drops will form fibers when subjected to an extensional flow. When the surface tension is low (as for compatibilized systems and polymers that contain similar polar groups), the energy released upon a decrease in surface area is much smaller, and therefore planar structures with high surface area are likely to be found in these systems. However, the possible property increase from TLCP orientation in fibers of more incompatible systems can be outweighed by a decrease in phase adhesion [16], which will be discussed in section 1.2.5.

Besides the need for a low viscosity ratio and phase incompatibility, an extensional flow field is also necessary for the formation of sufficiently long fibers for in situ composites. Shear flow, as found in extruder channels, is not sufficient to generate high aspect ratio fibrils [2]. This is an important process design factor, because the fibers of in situ composites are formed in the last shaping process.

If the product has to be an injection molded part, an extruded sheet or blown film, maximum fibril elongation can not be obtained during the process [4,12,19,20]. For a fiber drawing or spinning process, however, it is possible to stretch the extrudate extensively upon exiting the die, resulting in fibril formation (Figure 1.6 [21]). Using a spinning or drawing process, we can obtain highly reinforced strands. The need to create in situ composites in highly extensional flow fields to obtain optimum TLCP fiber reinforcement, limits the use of these composites. It may therefore be useful to first generate long fibers in one process, and then maintain these fibers in a following shaping process. The retention of fibrils through the final processing step creates microcomposites. Processes like these will be discussed in section 1.2.4.
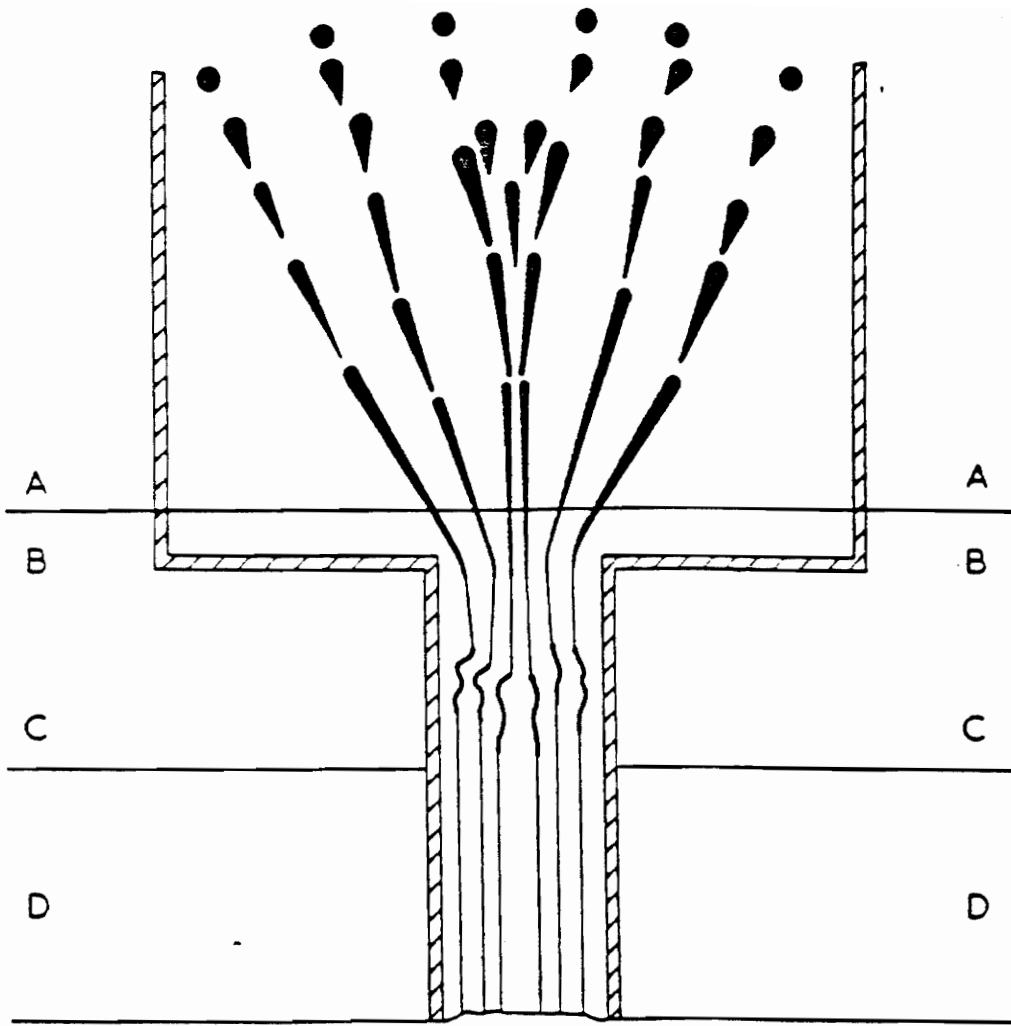
Figure 1.6   Representation of the fibrillation process in convergent flow [21]

1.2.2 Fiber orientation

The enhanced reinforcement in TLCP / thermoplastic blends is the result of the formation of fibers in the composite. It is important to understand how to optimize the reinforcing potential of the fibers, once they are generated. So, the question arises, how to translate the high properties of strands into the production of more useful parts and items. In the ideal case, strand properties should be maintained, when fibers remain long and are aligned uniaxially. However, unidirectional fiber alignment is only feasible in compression molding applications. Also, when the fibers are all aligned in one direction, the properties in the transverse direction will significantly differ from those along the machine direction; a problem known as anisotropy.

When the fibers can be randomly distributed, e.g. in a lamination process, the properties will be isotropic. For a two dimensional random fiber orientation, Piggott [23] derived the following equation from composite theory to predict the composite modulus:

$$E_{composite} = \frac{3}{8} E_P + \frac{5}{8} E_T$$

(6)

where E_p and E_T are the rule of mixtures and the series model modulus prediction respectively, as found in equations (2) and (3). Sabol [5] reported that it was possible to produce randomly oriented PP/TLCP laminates with modulus values approaching the theoretical prediction.
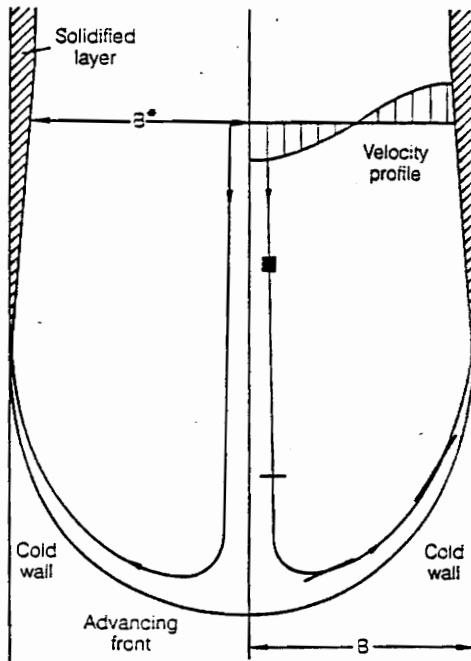
Figure 1.7   Tadmors Fountain Flow mechanism [22]

In injection molding applications, however, the fiber distribution is never random. The orientation distribution is always strongly related to the location in an injection molded part. The fiber orientation in injection molding applications is often related to the fountain flow mechanism, as shown in Figure 1.7 [22]. When the mold is filled, the flow advances from the core. The fluid is then stretched at the front and laid up on the wall, where it is rapidly solidified in a highly oriented state [24]. Thus, the orientation in the core remains random and properties are isotropic. However, in the skin, the fibers are highly aligned in the flow direction, resulting in an oriented layer with different characteristics, as found in various fiber filled systems [22,25-27]. MacDonald [28] presents how these oriented structures can be used in a hierarchical model, as shown in Figures 1.8 and 1.9.

Molecular Morphoplogy

Crystallinity (5-10nm)

Below Tm   Above Tm

Chain conformation (0.5nm)

Crystallites

Molecular motions transitions, Tg etc

Melting behaviour →

Stiffness/temperature characteristics

Flow properties

Micromorphology

−1-10μm−   Optical appearance

Mouldings, extrusions (>mm)

Domains   Disclinations

Layer 100μm

Skin 40%
Core 20%
Skin 40%

Direction of flow

Macromorphology

Anisotropy, mechanical properties

Figure 1.8   Hierarchy of structure in LCPs [28]

1. Introduction

17

It is difficult to relate the mechanical blend properties to the skin-core structure, because the orientation in the layers differs, and the thickness of the layers changes with the processing conditions (e.g. melt temperature, injection speed, mold thickness and mold temperature [22]). The random core orientation results in lower, but isotropic properties, whereas alignment in the skin imposes anisotropy, with improved tensile properties in the orientation direction. However, as long as the layer thickness and orientation remain unknown, the final properties can not be predicted. Therefore, it is important to keep injection molding parameters, and thus fiber orientation, uniform when comparing properties of molded composites.

A last remark is made about influencing the fiber orientation through the use of prepregs. In this case, continuous fibers can be ordered in knit and woven structures, thus spreading the reinforcing potential effectively in two directions. Although these techniques show great promise for influencing properties in desired material directions [8], they are labor intensive and a lot of research is yet to be conducted to find effective uses for TLCP blends to create composites by these techniques.
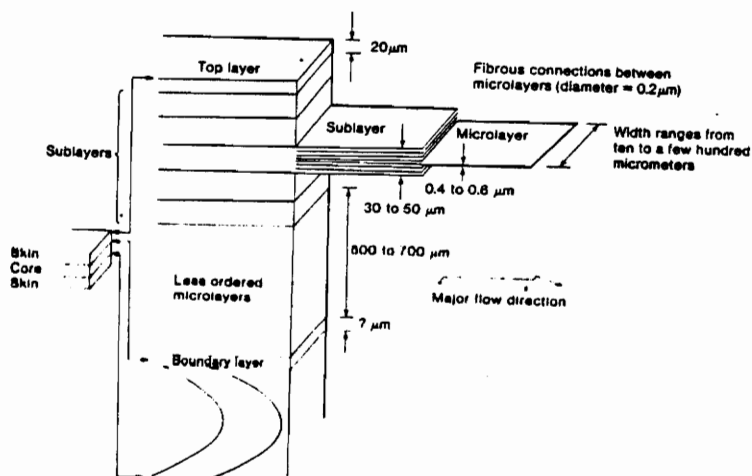
Figure 1.9   Schematic illustration of proposed hierarchical model in LCP injection-molded bars [28]

1.2.3 Matrix Dependence

In the previous section, the influence of the structure of the TLCP phase on blend properties was discussed. Because blend properties are most dependent on the strongest phase, the TLCP morphology in reinforced thermoplastics is believed to be the most important. Changes in the morphology of the thermoplastic matrix are believed to have little influence on the blend properties. Nonetheless, some recent research has focused on the thermoplastic matrix morphology. Bertilsson et al.[25] report that a possible explanation for low predictions of the Tsai-Halpin equation for carbon fiber filled polyethylene could be the change in matrix structure and crystallinity upon addition of the fibers. Mehta and Deopura [29] report that the crystallization of PET decreases by the addition of TLCP to the matrix. Yet, Seppala et al. [30] report that the matrix crystallinity for three thermoplastic / TLCP blends increases upon addition of TLCP, with the most significant increase for PET. Clearly, the effect of crystallinity of the matrix on blend properties is not yet well understood.

It can be seen why literature has given little attention to the matrix properties. For example, if a thermoplastic with a 1 GPa modulus is blended with only 10% of a 100 GPa TLCP, the rule of mixtures (equation 3) predicts a blend modulus of 10.9 GPa. If the matrix stiffness would even be 50% higher, the blend modulus would still remain at 11.4 GPa; only a minor improvement.

However, from a processing point of view, the matrix behavior is very important. The viscosity ratio and compatibility influence blend morphology formation as was briefly discussed in section 1.2.2. In the next section, the melting temperature of the matrix will be considered an important factor for post-processing of blends.

1.2.4   Post-processing methods for pre-blended composites.

There are three principle methods to obtain blends of TLCPs and thermoplastics in a final useful shape. First, the TLCP can be dry-blended (e.g. tumbled) with the matrix and directly be melt-processed into a final product. Second, it is possible to pre-blend the TLCP and matrix in a melt process, and then remelt the whole blend during post-processing. In both of these methods, in situ composites are obtained, because the reinforcing fibers are formed in the final shaping process. Section 1.2.1 already covered how in situ composites are obtained and how properties are developed. However, in the third case, it is possible to only remelt the lower melting matrix of certain pre-blended TLCP - thermoplastic mixtures. This allows the TLCP fibers to stay intact, resulting in a microcomposite, laminate or prepreg. Although preservation of the initial fiber structure has very distinct advantages, relatively little research has been dedicated to this type of post-processing [8,13,20,31-35]. This section will discuss some of the recent efforts to obtain composites at low processing temperatures.

TLCP fibers were embedded in a thermoplastic matrix in studies by Robertson [8] and Brady [35]. It was found that the fibers impose a substantial property improvement in the orientation directions only. Brady concludes from SEM micrographs that poor fiber transverse properties - rather than fiber/matrix adhesion - appear to limit the transverse properties. He also reports that the processing temperature for making Vectran composites (commercial Vectra A fibers, with the same structure as given in Figure 1.1) should be kept under 275°C, so that the crystal size in the annealed fibers is not changed. The achieved reinforcement in prepregs from blended PP/TLCP strands, laminated well below the TLCP melting point, reported by Robertson [8] is very large, but the anisotropy limits possible applications.

Sabol [5] found that the length of strands used to produce laminates was critical for their

reinforcement. He succeeded in producing isotropic laminates, but showed that the composite theory prediction (equation 6) could not yet be achieved even by molding randomly oriented strands of 30 mm. length. In laminated films, Grevecoeur [13] and Isayev [20] found that the anisotropy becomes more balanced upon layering films in different directions before molding. However, the properties of the films were much lower than of strands. This can be explained by the limited draw imposed during the film casting process and the resulting low fiber aspect ratio.

Handlos et al. [31-34] have made substantial progress in obtaining microcomposites from pre-blended polypropylene (PP) / TLCP strands. They found that the actual reinforcement in the composite is highly dependent on the processing temperature at which the final product is created, even when this is well below the TLCP melting point. In injection molding [31], only at very low temperatures (190°C) the TLCP fibers did not deform, resulting in better composite properties. Also, a dependence of properties on initial strand draw ratio was reported, with the use of higher drawn strands with finer fibrils resulting in better reinforced injection molded microcomposites. They also produced reinforced extruded films and blown bottles this way.

Obtaining composites at temperatures below the TLCP melting point has not been given much attention yet. One reason for this may be that it is difficult to obtain blends with a much lower melting matrix in the first place. However, substantial progress has been made by Sukhadia et al. [11] to overcome the processing temperature difference by the use of a novel dual extruder technique. Now the challenge is to use this temperature difference to obtain better reinforced composites.

1.2.5 Compatibilization

The addition of a compatibilizer to polymer blends can have two major effects. First, by increasing affinity between the phases (or reducing the surface tension), the compatibilizer can change the morphology of the blend. Thus the addition of a third phase with affinity for both other phases usually results in a finer dispersed blend structure, as discussed in section 1.2.1 and often mentioned in the literature [16,18,36-39]. Second, compatibilizers have also been found to increase adhesion between two phases, thus improving mechanical properties of the blend. Compatibilizers are usually copolymers, with one constituent resembling one phase of the blend, and the other constituent resembling the other phase. This allows the compatibilizer to mix with both phases (changing the morphology) and form links between the phases (adhesion).

The combined functionality of compatibilizers in the formation and adhesion of phases of in situ blends complicates the prediction of property enhancement by compatibilizer addition. For in situ blends, different effects have been reported, ranging from virtually no effect at all [5] to a more than 50% increase of modulus and tensile strength [26]. The nature of the blend constituents and the compatibilizer concentration appear to be a major factor in the effectiveness of improving dispersion and adhesion. Examples of compatibilizers include maleic anhydride and acrylic acid grafted polyolefins [37], as well as liquid crystalline polymers with groups resembling the matrix in their backbone [38]. Lee [38] reported chemical interaction between two different TLCP phases as confirmed by DSC and NMR. Because TLCPs containing PET groups are known to show better compatibility with PET [18], this could ultimately result in improved blend properties. However, O'Donnell [26] reports that for PP/TLCP blends, no chemical interaction between the maleic anhydride grafted PP compatibilizer and the TLCP exists. A mechanism like hydrogen bonding could explain improved compatibility in this case.

For compatibilizers in solid filled thermoplastics, such as glass filled composites and microcomposites, the dispersion of phases no longer plays a role, and improved properties could only result from improved adhesion between the phases. Constable [40] reports significant property enhancement for maleated PP added to glass-filled PP. Improvements in tensile and flexural strength were reported, as well as a higher Izod impact resistance and heat deflection temperature. However, the same type of adhesion to glass may not be applicable to TLCP fibers. Carfagna [41] reports that practically no mechanical friction and chemical interaction exist between a TLCP filament and a PC matrix. Chemical and thermodynamic theories on polymer blends can provide some understanding of the mechanisms of compatibilization [42], but have so far not predicted effective compatibilization of systems with polyolefins and TLCPs.

1.2.6 Polyethylene as a matrix for TLCP blends

Polyethylene is a linear polyolefin with the following molecular structure: $-(-CH_2-CH_2-)-_n$. High density polyethylene has a density just below that of water, typically ranging from .94-.97 g/cm^3, and a melting point around 135°C. Applications include films, wraps, bags, household containers, pipes, gasoline tanks, bottles and toys [43]. Reinforcement of this type of plastic, could find many practical applications, for the resins' neat modulus is typically only 1 GPa. This is already done in glass and mica filled polyethylene. From a theoretical viewpoint, the above literature review revealed a number of reasons why polyethylene could be a suitable candidate for blending with TLCPs. Because of the low melting point of HDPE, it will be possible to post-process HDPE/TLCP blends at temperatures well below the higher TLCP melting range. Also, the nonpolarity of HDPE will allow little compatibility with the more polar TLCPs, which should result in distinct fibrillar structures in blends when generated in an extensional flow field. However, not much research has been conducted on HDPE/TLCP blends. Harada et al. [44,45] published a brief study on blends of HDPE and Vectra A. They found that the blend strength (tensile and flexural), and Izod impact strength improved significantly only at very high TLCP concentrations, as shown in Figure 1.10. At low TLCP concentrations, the tensile strength of the blend was even lower than the neat HDPE matrix. Harrisson et al. [46-49] published an ongoing series on PE/TLCP blends for thin film applications. For PE/Vectra blends [46], the reinforcement obtained was limited by the obtained fiber aspect ratio of only 6. The low melting experimental TLCP used in later studies [47-49] allowed them to extrude the blends at 215°C, and the addition of mixer elements did result in a film modulus enhancement. However, the blends with the experimental TLCP do lack the advantage of being able to post-process the material at temperatures well below the TLCP melting range.
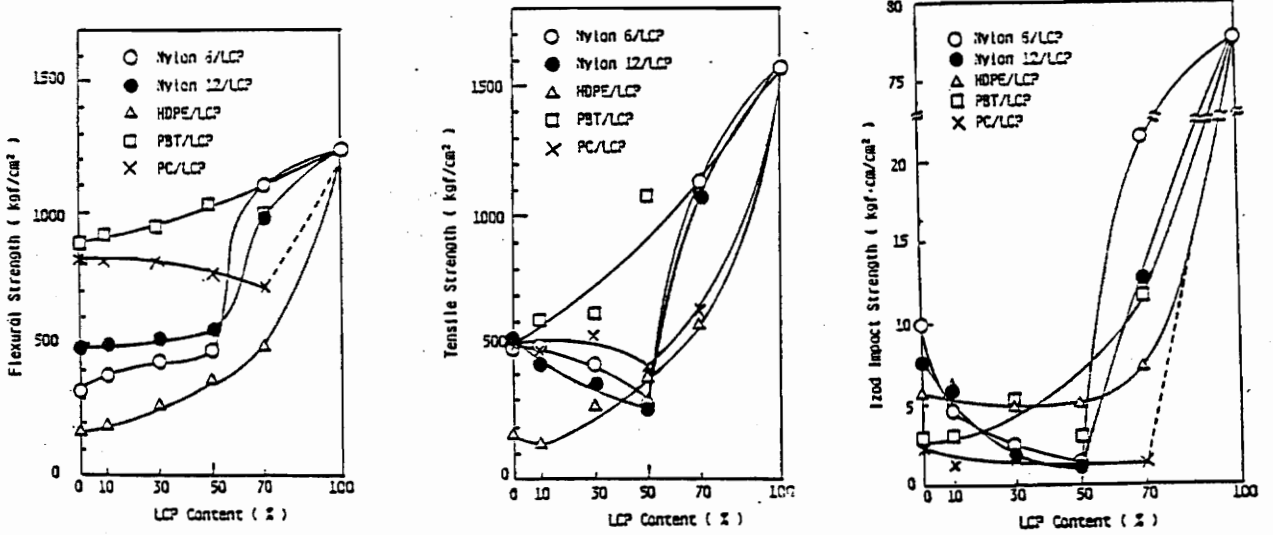
Figure 1.10   Flexural (a), Tensile (b), and Izod impact strength (c) of HDPE/Vectra A
and other blends as a function of TLCP content, as found by Harada et
al.[45]

The lack of overlap in recommended processing temperatures (180-220°C for HDPE and 290-300°C for TLCPs like Vectra A and B) imposes problems. The HDPE will have to be heated to a higher temperature somewhere during the blending process. Degradation, which can be expected under such circumstances, has been studied by Dontula et al.[50]. They found that at barrel temperatures below 300°C, the HDPE viscosity increased, indicating crosslinking. At temperatures above 300°C, the viscosity decreased though, indicating chain scission. Therefore, the exact extent of degradation is difficult to measure from viscosity data, because the two chain alterations compete. Because degradation increases with shear rate and residence time, these two factors have to be minimized during the high temperature blending. The dual extruder process developed by Sukhadia et al. [11] provides an excellent solution for this problem. Since the matrix can be plasticized at much lower temperatures in a second extruder, it is only allowed to reside at high temperatures in the mixing region. Meanwhile, the nature of the static mixers used in this process allows very little shear during the mixing.

The structure of polyethylene also appears to be suitable for blending with TLCPs. Getlichermann and David [51] report that even polymers like styrene-butadiene and styrene-isoprene form long filaments in a PE matrix, provided the viscosity ratio is low enough. In a very different study by Motamedi et al. [52] it is reported that only on layers of PE, a Vectra TLCP and a fluorinated copolymer, facilitated growth of oriented crystals was possible. Although the materials are not blended in this study, it suggests that PE and Vectra A must possess similar structures to facilitate this growth of crystals.

The crystallinity in PE, was found to be influenced by fillers. Hatakeyama [53] reported that fibers accelerated the nucleation process and retarded the crystal growth of PE. This is comparable to crystallization in other thermoplastics, as was discussed in section 1.2.3.

1.3   Research Objectives

In order to develop new, strong, lightweight materials, different blends of TLCPs and thermoplastics can be evaluated. The above literature review reveals that the majority of research on TLCP blends has concentrated on in situ composites. Little work has been published on obtaining composites from pregenerated fibers while not deforming the fibrils during processing. Only microcomposites of PP and TLCPs have been reported. It is therefore of interest to obtain microcomposites of TLCPs and other thermoplastics in order to see if properties can be further improved.

The use of HDPE as the matrix for blends with TLCPs has several advantages over other thermoplastics. First, the processing temperature ranges of HDPE and most TLCPs do not overlap. Therefore, a dual extrusion process where the matrix can be extruded at a lower temperature than the TLCP can minimize matrix degradation and improve fiber generation. Second, HDPE is a nonpolar polymer, which has little affinity for more polar TLCPs. This could affect the morphology of blends, because high surface tension between phases decreases dispersion. Compatibilization and the associated increased adhesion between phases could affect a blend of two disliking phases positively. Third, the HDPE matrix can be post-processed at much lower temperatures than most other thermoplastics. Pregenerated TLCP fibers are more likely to remain solid during lower post-processing temperatures, which should translate into better final product properties. Fourth, premixing of incompatible polymers should increase interfacial area, which could result in better properties for the pre-blended microcomposites over in situ injection molded parts. Finally, HDPE is a material with widespread use and its price is attractive to produce stronger materials with HDPE.

Thus, the objectives of this research project are given below.
1.   Generate blends of TLCPs and HDPE in single and dual extrusion processes and

determine the effect of the blending method on strand properties.

2. Determine if drawing improves strand properties.

3. Establish properties of microcomposites after different post-processing methods. Determine the effect of the type of process (compression molding, film extrusion and injection molding), the post-processing temperature and the addition of a compatibilizer.

4. Determine whether HDPE/TLCP microcomposites have better properties than in situ blends, and compare these properties to those of glass filled HDPE.

1.4   References

[1]   Chung,T.S., Polym.Eng.Sci., 29(1989)10, 625

[2]   Northolt,M.G., Sikkema,D.J., in 'Liquid Crystal Polymers: From Structures to Applications' (Ed. A.A.Collyer), Elsevier, London, 1992, p.309

[3]   Handlos,A.A., Baird,D.G., J.Macromol.Sci.-Revs.Macromol.Chem., submitted

[4]   Engberg,K., et al., Polym.Eng.Sci., 34 (1994) 17, 1336-1345

[5]   Sabol,E.A., Baird,D.G., Polym.Comp., submitted

[6]   Lin,Q., Yee,A.F., Polymer, 35 (1994) 16, 3463-3469

[7]   Lin,Q., Yee,A.F., Polym.Comp., 15 (1994) 2, 156-162

[8]   Robertson,C., DeSouza,J.P., Baird,D.G., SPE Antec '95, submitted

[9]   Qin,Y., et al., Polymer 34 (1993) 17, 3597-3604

[10]   Heino,M.T., Seppala,J.V., J.Appl.Pol.Sci. 44 (1992) 2185-2195

[11]   Sukhadia,A.M., Datta,A., Baird,D.G., Int.Polym.Proc., VII (1992) 3, 218-228

[12]   La Mantia,F.P., et al., Eur.Pol.J. 29 (1993) 5, 671-677

[13]   Crevecoeur,G., Groeninckx,G., in 'Integration of Polymer Science and Technology', Lemstra,P.J., Kleintjes,L.A. (ed.), 5th Rolduc polymer meeting

[14]   Gonzalez-Nunez,R., Favis,B.D., Carreau,P.J., Polym.Eng.Sci. 33 (1993) 13, 851-859

[15]   Bretas,R.E.S., Collias,D., Baird,D.G., Polym.Eng.Sci. 34 (1994) 19, 1492-1496

[16]   Verhoogt,H., et al., Polym.Eng.Sci. 33 (1993) 12, 754-763

[17]   Sabol,E.A., Baird,D.G., Int.Polym.Proc., submitted

[18]   Meretz,S., Kwiatkowski,M., Hinrichsen,G., Int.Polym.Proc., VI (1991) 3, 239-246

[19]   Shi,F., Polym.-Plast.Technol.Eng.,33(1994)4, 445-455

[20]   Isayev,A.I., et al., Polym.Comp., 15 (1994) 4, 254-260

[21]   Tsebrenko,M.V., Polymer 17(1976)831

[22]   Bailey,R., Rzepka,B., Intern.Polym.Proc., VI (1991) 1, 35-41

[23]   Piggott,M.R., 'Load bearing fibre composites', Pergamon Press, Oxford (1980)

[24]   Baird,D.G., Collias,D.I., 'Introduction to Polymer Processing: Principles and Design', Hanser Publishers, 1995

[25]   Bertilson,H., et al., Polym.Comp., 13(1992)2, 121-132

[26]   Stokes,V.K., et al., SPE Antec '94, 2294-2299

[27]   Hudson,S.D., et al., Polym.Eng.Sci., 34 (1994) 17, 1327-1335

[28]   MacDonald,W.A., in 'Liquid Crystal Polymers: From Structures to Applications' (Ed. A.A.Collyer), Elsevier, London, 1992, p.407-446

[29]   Mehta,S., Deopura,B.L., Polym.Eng.Sci., 33(1993)14, 931-936

[30]   Seppala,J., Heino,M., Kapanen,C., J.Appl.Polym.Sci. 44 (1992) 1051-1060

[31]   Handlos,A.A., Baird,D.G., Int.Polym.Proc., submitted

[32]   Handlos,A.A., Baird,D.G., Polym.Comp., submitted

[33]   Handlos,A.A., Baird,D.G., Polym.Comp., submitted

[34]   Handlos,A.A., Sabol,E.A., Baird,D.G., SPE Antec '94, 1594-1598

[35]   Brady,L.R., Porter,R.S., J.Thermoplastic Comp.Mat., 3 (1990) 252-261

[36]   O'Donnell,H.J., Baird,D.G., Polymer, submitted

[37]   Chen,C.C., White,J.L., Polym.Eng.Sci., 33 (1993) 14, 923-930

[38]   Lee,W., Dibenedetto,A.T., Polym.Eng.Sci., 32 (1992) 6, 400-408

[39]   Datta,A., Chen,H.H., Baird,D.G., Polymer 34 (1993) 4, 759-766

[40]   Constable,R.C., SPE Antec '94, 127-130

[41]   Carfagna,C., et al., Polym.Comp., 13 (1992) 3, 169-173

[42]   Utracki,L.A., 'Polymer alloys and blends; thermodynamics and rheology', Hanser
         publishers, 1989

[43]   Juran, R.(ed.),Modern Plastics Encyclopedia, 66 (1989) 11, 75

[44]   Harada,T., et al., The Fifth Annual Meeting, PPS, April 11-14, 1989, Kyoto, Japan

[45]   Harada,T., et al., SPE Antec '92, 376-381

[46]   Lickhus,A.M., Harrison,I.R., SPE Antec '92, 2257-2259

[47]   Hsu,T.C., Harrison,I.R., SPE Antec '93, 1183-1185

[48]   Hsu,T.C., Meechumnarn,K., Harrison,I.R., SPE Antec '94, 2433-2435

[49]   Hsu,T.C., Lickhus,A.M., Harrison,I.R., Polym.Eng.Sci., 33(1993)13, 860-863

[50]   Dontula,N., Campbell,G.A., Connelly,R., Polym.Eng.Sci., 33 (1993) 5, 271-278

[51]   Getlichermann,M., David,C., Polymer, 35 (1994) 12, 2542-2548

[52]   Motamedi,F., et al., J.Polym.Sci., Pol.Phys.Ed., 32 (1994) 453-457

[53]   Hatakeyama,T., Kitano,T., Klason,C., Intern.Polym.Proc., III (1988)4, 230-233

2. Materials and methods

The following chapter describes the materials and methods that were used during this research project. Although the experiments and polymers are also briefly covered in Chapter 3, the next paragraphs will give a broader description and some background of why certain choices in experimentation were made.

2.1 Materials

High density polyethylene (HDPE) is a polymer with characteristics useful for blending with TLCPs. As concluded in Chapter 1, reinforcement would provide a stronger material for the already widespread applications of HDPE. But the uniqueness as opposed to other thermoplastics to make TLCP blends with, lies in the low melting temperature of HDPE. HDPE melts around 135°C, compared to 170°C for PP, and above 280°C for most commercial TLCPs. The glass transition temperature of HDPE is also significantly lower than for other thermoplastics: -120°C for HDPE versus -15°C for PP and 70°C for PET [1]. This means that at room temperature, HDPE will behave as a viscoelastic, rubber-like material, with a low stiffness. Several types of polyethylene exist (LDPE, LLDPE, HDPE), and many different grades are found for each type. For an initial trial, blends of LDPE and a TLCP were made in a single screw extruder and then injection molded. For this blend, the matrix modulus of .1 GPa was improved to .8 GPa. Although this is a significant improvement, the composite modulus is still below that of HDPE and PP. Therefore, the choice for HDPE with a matrix modulus of approximately 1 GPa was made.

HDPE is typically characterized by a Melt Flow Index (MFI); a single point viscosity. Because of the importance of the viscosity ratio between the matrix and the dispersed

phase in morphology development, a number of different MFI polyethylenes were tested. The choice for a polyethylene with a viscosity that is higher than the melt viscosity of TLCPs was made: a film grade HDPE, LM6187, donated by Quantum Chemicals. It has a MFI of 1.15 and a 1% secant modulus of 1 GPa [2]. For extrusion, this appeared to be a good choice, but for injection molding this resin did show very viscous behavior and some slip-stick effects were observed.

The TLCPs used were Vectra A910 and Vectra B950; two aromatic copolymers made by Hoechst-Celanese. Vectra A is a random copolyester of 73 mol% hydrobenzoic acid and 27 mol% 2-hydroxy 6-naphthoic acid, and has a melting range of 279-308°C. Vectra B is a copolyesteramide of 60 mol% 2-hydroxy 6-naphthoic acid, 20 mol% terephthalic acid and 20 mol% 4 hydroxy acetanalide and has a melting range of 259-290°C [3] and a T_g of 110 °C [4]. Their structures were given in Figure 1.1. The choice of these resins was influenced by the fact that comparisons with published research results on PP/Vectra blends could be made [5]. Also, Vectra B has shown adhesion to maleic anhydride grafted polyolefins [6], which could provide better blend properties.

A maleic anhydride grafted polyethylene (MAPE) from BP was used. The function of copolymers of polyolefins and more polar molecules like maleic anhydride or acrylic acid is twofold. The affinity of these copolymers to both the nonpolar matrix and a more dispersed phase improves dispersion and mixing between the phases by lowering surface tension and increasing surface area [6]. Copolymers have also been found to promote adhesion. Acrylic acid modified polyethylene was found to be unsuitable for blending at high temperatures, because of thermal instability, that did not occur as severely with maleic anhydride grafted polyethylene. The MAPE of choice was an experimental resin donated by BP: PolyBond 3009. It melts at 127°C, has a MFI of 5 and a secant modulus of .8 GPa [7].

For comparison with the TLCP fiber filled HDPE, a 20 wt% glass filled HDPE, RTP703, was purchased from RTP Company. It has a tensile modulus of 3.4 GPa when tested according to ASTM D-790 [8].

2.2   Extrusion blending

In situ composite strands were made by extrusion blending. Initially, a single extruder with several exit flow configurations was compared to a dual extruder system. The die setup at the extruder exit was altered to study the importance for the processability and performance of the blends. In order to obtain mixing in the single extruder, it was equipped with a long capillary die (increasing shear), or with 18 Kenics static mixer elements. The static mixers split the flow over and over, thus increasing the surface area between two phases. Next, blends were generated in a dual extruder mixing system, (shown in Figure 2.1) that was developed in our labs and described by Sabol [9]. The polymer streams from two single screw Killion KL-100 extruders were introduced into each other. The TLCP melt stream temperature at the end of the first extruder was maintained at 320°C and was led through a Zenith HD-556 metering pump to obtain regular and predictable flow rates. Meanwhile, the matrix stream was heated from an extruder temperature of 250°C to meet the TLCP flow at 300°C. Blends with Vectra A were made using a simple T-joint where the streams met, followed by pipes containing 18 Kenics static mixers of 1.27 cm diameter. Blends with Vectra B were made using a distribution head [9], and were further mixed in three Kenics and four 2.54 cm diameter Koch static mixer elements. It was shown by Sabol [5] that Koch mixer elements were more efficient in mixing, than Kenics elements, so that less elements could be used, resulting in a shorter residence time. The mixing sections were maintained at a temperature around 300°C and drawing of the extrudate appeared to be most stable at an exit temperature of 305°C. A die with a 3 mm hole (both in length and diameter) provided flow of extrudate into a vertical drawing chimney.
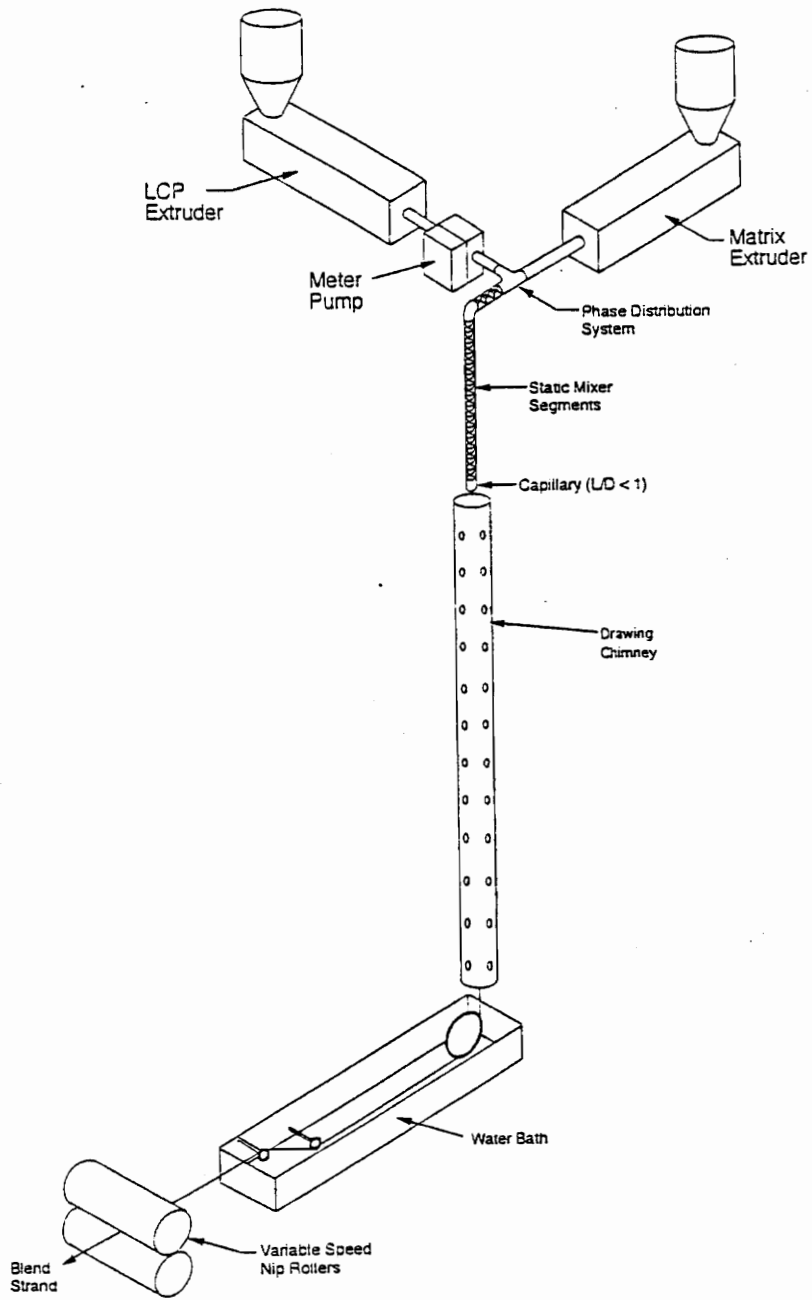
Figure 2.1   Dual extruder system, as described by Sabol [9]

2. Materials and Methods   36

It was observed that the short die initiated a substantial swell of the extrudate. When the extrudate was allowed to flow freely into air by cutting it off at the die exit, the diameter of the outflowing polymer easily doubled over the die diameter. However, when the extrudate was allowed to flow down, the gravity force would extend the material, and swell was no longer observed, as shown in Figure 2.2. However, it can be seen that in this case part of the gravity or drawing force is used to eliminate the swell. Therefore, it could be useful to increase the die channel length in order to decrease the die swell and improve the efficiency of drawing.

The stabilized air in the chimney provided a gradual cooling of the extrudate. When polymer was cooled quickly after exiting, the density difference between the molten and solidified polymer would create a sudden shrinkage of material, resulting in voids. The chimney provided air stability, resulting in a more stable flow with less voids. The strands were then quenched in a water bath and drawn by a nip-roll or fiber take-up device.

2.3 Post-processing methods: compression molding, sheet extrusion and injection molding.

The blended strands were further processed by means of three methods: compression molding, sheet extrusion and injection molding.

First, strands were pressed into plaques at a temperature lower than the TLCP melting point, but above the HDPE melting point. The pregenerated fibers were aligned and heated to 150°C and then quickly cooled in a Carver laboratory press (model 2696) under an initial pressure of 30 MPa. Although it was difficult to align highly drawn strands uniaxially, this appeared to be very important for accurate results. When poorly aligned fibers were molded and tested for tensile properties, failure would always occur near
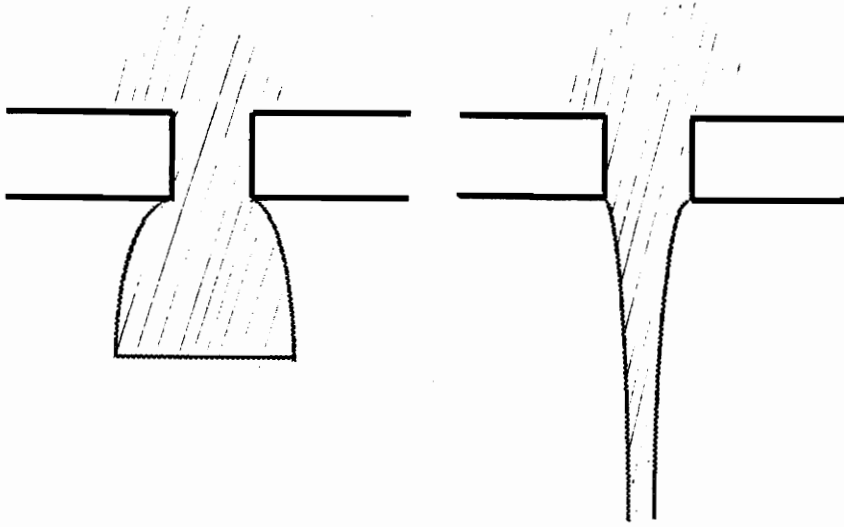
Figure 2.2   Die swell, as observed when extrudate flows freely (a) and when pulled
              down by gravity or a take-up device (b)

imperfections. Although care was taken to align fibers well, some influence of imperfect orientation could not be eliminated.

Strands were pelletized with a Killion cutter into pellets of approximately 3 mm length. The pellets were then used for sheet extrusion and injection molding. Initially, blends of 20 and 40 wt% TLCP had been made in the dual extruder process. Due to the fibrillar TLCP structure, surrounded by the soft HDPE matrix, strands could only be pelletized when the TLCP concentration was low. For higher concentration TLCP blends, no single cutting device, including scissors and a cutting board, could cut the TLCP fibers effectively. At 40% TLCP, the matrix would be peeled from the TLCP fibers, but long fibers would remain, resulting in large clots of continuous fibrillar material instead of pellets.

Sheet extrusion of pelletized strands was performed with a 10 cm wide coathanger sheet die. At temperatures above the TLCP melting point (290°C), the continuous pregenerated fibers were mostly deformed into droplets, as shown in Figure 2.3, which also resulted in low tensile properties. However, sheet extrusion at low temperatures resulted in very irregular sheets. Because the sheet extrusion process required considerable amounts of material and resulted in poorly reproducible results, further post-processing was focussed on injection molding.

Injection molding of pelletized strands was performed in an Arburg Allrounder injection molder (model 221-55-250). The end-gate mold with T-distribution manifold produced plaques of 75x80x1.5 mm. The first zone barrel temperatures of the injection molder were maintained at 105 and 165°C, but the last zone temperatures were varied from 170 to 290 °C. Also, some of the pelletized strands were diluted with pure matrix HDPE and/or MAPE to study the compatibilizing effect. However, 20 wt.% TLCP blends diluted with 50% polyethylene, only contain 10% TLCP in the final product, which is clearly reflected in much lower reinforcement.
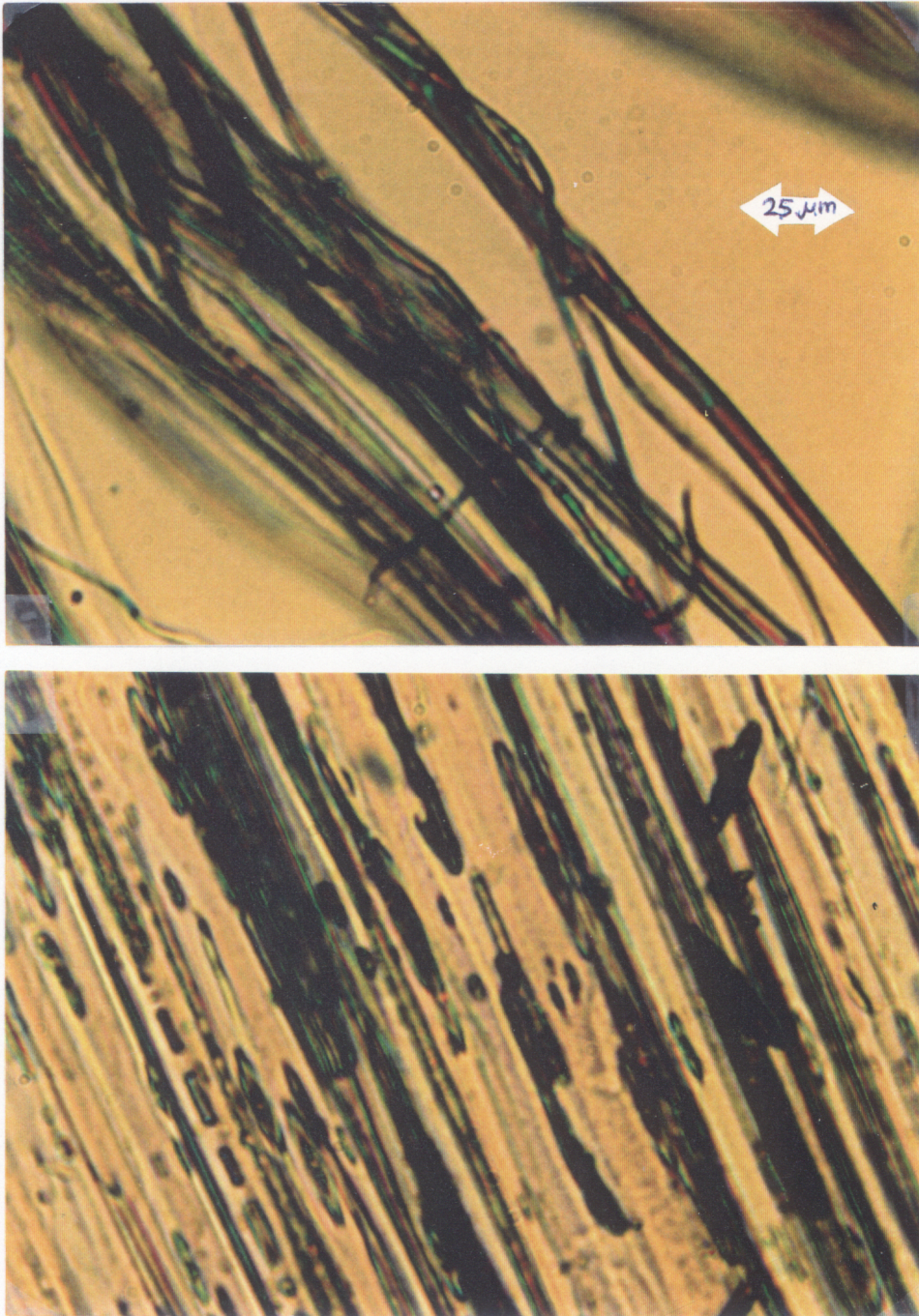
Figure 2.3   Optical Micrographs of HDPE/ 20% Vectra A blends:

(a) strands show full continuous fibers

(b) sheet extruded at 290°C shows droplets and short fibers

2.4 Characterization: tensile testing, morphology and rheology.

The Young's modulus and tensile strength of strands were obtained from force measurements on 148 mm long samples during stretching with a crosshead speed of 1.27 mm/min in an Instron 4204 mechanical testing apparatus (ASTM D3376-75). In order to prevent strand breakage in the grips, strands were held in place with the aid of a piece of masking tape. Plaques were first cut into 9 mm wide bars and then tested with a strain gage attached (ASTM D638-87b). For samples that would not break (pure HDPE and most 10% TLCP composites), the yield strength was calculated.

The overall morphology of samples was looked at through a Zeiss polarizing light microscope. Samples were cut with a razor blade, covered with immersion oil and photographed at low magnifications. More detailed pictures of the shape and size of phases were obtained by fracturing samples in liquid nitrogen, sputtering them with gold, and observing them in a Cambridge Stereoscan S200 scanning electron microscope with an accelerating voltage of 15 kV.

Dynamic mechanical testing was performed on resins to establish their flow behavior prior to and after blending. Frequency sweeps at a strain of 10% and at several temperatures were made with a Rheometrics RMS 800 Spectrometer equipped with parallel plates of 12.7 mm diameter and gap height 1.5 mm. The complex viscosities of matrix materials were determined at temperatures ranging from 190 to 290°C over frequencies of .1 to 100 s^{-1}.

2.5   References

[1]   v.d.Vegt, A.K., 'Polymeren, van keten tot kunststof', Delftse Uitgevers
        Maatschappij, 1991

[2]   Quantum product lit., 'Petrothene High Density Polyethylene for Blown and Cast
        Film'

[3]   Meretz,S., Kwiatkowski,M., Hinrichsen,G., Int.Polym.Proc., VI(1991)3, 239-246

[4]   Sabol,E.A., Baird,D.G., Polymer Composites, submitted

[5]   Sabol,E.A., Baird,D.G., Int.Polym.Proc., submitted

[6]   O'Donnell,H.J., Baird,D.G., Polymer, submitted

[7]   BP Product Bulletin, 3/93, Polybond Chemically Modified Polyolefins

[8]   RTP Co., RTP 700 series product information

[9]   Sabol,E.A., M.S. thesis, Virginia Polytechnic Institute and State University, May
        1994

3. Injection molding of composites based on high density polyethylene and thermotropic liquid crystalline polymers

The following chapter consists of a manuscript that will be submitted to Polymer Composites for publication.

3.0 Abstract

Strands of high density polyethylene (HDPE) reinforced with thermotropic liquid crystalline polymers (TLCPs) were generated using a novel dual extruder mixing technique. The strands displayed continuous, fine TLCP fibrils dispersed in the matrix. At 20 wt% TLCP reinforcement, the highest drawn strands reached tensile strengths over 100 MPa and moduli up to 10 GPa. The strands were pelletized and injection molded at temperatures above the melting point of the matrix but below that of the TLCP. At higher injection molding temperatures, the pregenerated fibers were deformed and the tensile moduli were reduced below 2 GPa, which is near the lower bound prediction. However, when the high aspect ratio fibrils were maintained in compression molded plaques and low temperature injection molded microcomposites, the moduli remained at 7 and 3 GPa respectively. At low injection molding temperatures, the fibers stayed rigid and distinct, whereas at higher temperatures large agglomerates were formed. The strength and stiffness of injection molded plaques of these composites increased in both the machine and transverse direction. The addition of maleic anhydride grafted polyethylene did not lead to any significant improvement in properties. For in situ blends, where the mixing and fiber formation occurred in the injection molding process, the machine direction tensile

properties were 50% lower than those of pregenerated TLCP fiber composites produced in injection molding at temperatures significantly below the melting point of the TLCP.

3.1   Introduction

There is a need to develop cheaper, stronger, lightweight materials. Thermotropic liquid crystalline polymers (TLCPs) have shown great promise as engineering thermoplastics, but their cost and the mechanical anisotropy exhibited in injection molded parts are major roadblocks for their widespread use. However, the use of TLCPs for reinforcement of thermoplastics represents a way of reducing the overall material cost. Much of the current research is centered on how to optimize properties of TLCP / thermoplastic blends [1]. Research studies show that the TLCP usually forms a fibrillar morphology when blended with a thermoplastic, such as PP, PET, PPS and PC, and subjected to an extensional flow [1-4]. Because the reinforcing fibers are formed in these blends during processing, they are often referred to as in situ composites. However, blends containing pregenerated TLCP fibers can also be processed in a manner similar to that of glass filled systems, when the matrix has a lower melting range than the TLCP [5,6] This form of composites is referred to as microcomposites, because of the small size reinforcing fibrils [5,6]. Property improvement can be obtained by increasing the fiber aspect ratio, orientation and adhesion [7-9]. A study by Handlos and Baird [5] shows that in a system of PP and TLCPs, the formation of fibrils in reinforced strands and conservation of the TLCP fibril aspect ratio in injection molded composites are critical steps for the generation of acceptable tensile properties. It was also observed that the mechanical anisotropy of injection molded microcomposite plaques was significantly reduced relative to that of the in situ composite systems [5]. Thus, reinforced composites can be made from TLCPs and thermoplastics, but the fiber formation and conservation are critical to produce useful and strong materials.

High density polyethylene (HDPE) is a low melting polymer with widespread use in bags, films, bottles, blown tanks, pipes, etc. [10]. Filling HDPE with glass fiber can improve the mechanical properties and reduce the creeping tendency, while the material cost remains low. However, glass fiber is brittle and heavy, makes the composite difficult to process at high concentration levels and is very abrasive to processing equipment. Furthermore, the glass fiber aspect ratio is reduced significantly during processing and recycling. Composites reinforced with TLCPs may not suffer from these limitations and are, therefore, of interest in the development of new materials.

Blends of polyethylene and TLCPs have only been reported briefly in literature. Hsu et al. [11] used an experimental low melting TLCP in a 5% blend but found that in film blowing the low fiber aspect ratio of 6 only resulted in a 28% increase in modulus, whereas a 300% increase was expected. Harada et al.[12] reported tensile strengths, flexural strengths and Izod impact strengths of HDPE blended with 0-100% Vectra A950. However, the addition of 10% TLCP lowered the tensile strength only to be improved at higher TLCP concentrations. Because HDPE has applications such as in extruded pipes and blow molded tanks where additional strength and stiffness are required, it is desired to determine whether TLCPs can be used to improve these properties.

The formation of in situ composites based on HDPE and TLCPs is not readily possible in processes such as extrusion and blow molding because of the lack of sufficient extensional stresses and the high melt temperatures required to process commercial TLCPs. The purpose of this work is to determine whether it is possible to pregenerate TLCP reinforcing fibrils in a strand extrusion process and then to process pelletized strands at temperatures below the melting point of the TLCP but above that of the matrix to form composite materials with enhanced properties.

3.2   Experimental

3.2.1   Materials

Two TLCPs were used in this study: Vectra A910 and Vectra B950, which are two aromatic copolymers produced by Hoechst-Celanese. Vectra A is a random copolyester of 73 mol% hydrobenzoic acid and 27 mol% 2-hydroxy 6-naphthoic acid and has a melting range of 279-308°C [13]. Vectra B is a copolyesteramide consisting of 60 mol%2-hydroxy 6-naphthoic acid, 20 mol% terephthalic acid and 20 mol% 4-hydroxy acetanalide and has a melting range of 259-290°C [13] and a glass transition temperature of 110 °C [9].

High density polyethylene (HDPE) was used as the matrix in this study. A film grade HDPE, LM6187, was donated by Quantum Chemicals. It has a melt flow index (MFI) of 1.15 [14]. A maleic anhydride grafted polyethylene (MAPE) provided by BP was used to promote adhesion. This resin, PolyBond 3009, melts at 127°C and has a MFI of 5 [15]. MAPE was added to the blends by dry blending it with the HDPE prior to processing. Glass reinforced HDPE was used to provide a comparison to properties of composites based on pelletized drawn strands. The 20 wt% glass filled HDPE, RTP703, was purchased from the RTP Company (Winona, MN).

3.2.2   Extrusion blending

In situ composite strands were in most cases generated in the dual extruder mixing system that was developed in our laboratories and described by Sabol [9]. The dual extruder system consisted of two single screw extruders (Killion model KL-100, diameter 24.5 mm with L/D=24) in which the matrix material and TLCP were plasticated separately. The

TLCP melt stream temperature at the end of the first extruder was maintained at 320°C and was led through a Zenith HD-556 metering pump to obtain regular and predictable flow rates for 20 wt% TLCP blends. Meanwhile, the matrix stream was heated from 250°C at the extruder exit to 300°C at the point where the TLCP was emersed in the matrix. The melt streams were joined by means of a distribution head [16]. The two streams were subsequently further blended in three 1.27 cm diameter Kenics and four 2.54 cm diameter Koch static mixer elements. In the static mixer sections, the stream was repeatedly split to obtain mixing and was maintained at a temperature of 300°C. Drawing of the extrudate appeared to be most stable at a die temperature of 305°C. A strand die with a 3 mm hole provided flow of the extrudate into a vertical drawing chimney. The strands were drawn and then quenched in a water bath and collected through a nip-roll or fiber take-up device.

3.2.2 Post-processing methods: compression and injection molding.

The strands were further processed to form composite materials by means of two methods. First, strands were pressed into plaques at a temperature lower than the TLCP melting point, but above the HDPE melting point. The pregenerated fibers were aligned in a mold and heated to 150°C and then quickly cooled in a Carver laboratory press (model 2696) under an initial pressure of 30 MPa. Second, strands were pelletized into pellets of approximately 3 mm in length. Injection molding of pelletized strands was performed in an Arburg Allrounder injection molder (model 221-55-250). An end-gated mold with a T-distribution manifold was used to produce plaques of 75x80x1.5 mm. Temperatures of the first barrel zones of the injection molder were maintained at 105 and 165°C, but the last zone temperatures were varied from 170 to 290 °C. In situ blends were produced by direct injection molding of dry blended pellets. Some microcomposites were produced with the addition of HDPE and MAPE to the pelletized strands before molding to study whether phase adhesion could be improved.

3.2.3 Mechanical, morphological and rheological properties

The Young's Modulus and tensile strength of individual strands were measured using an Instron 4204 mechanical testing machine. An initial gap length of 148 mm and a crosshead speed of 1.27 mm/min were used, as described in ASTM standard D3376-75. A major and minor strand diameter were measured to calculate the elliptical cross section of strands. The tensile properties of composite samples were measured according to ASTM standard D638-87b. Plaques were cut into 9 mm wide bars and sanded to eliminate the cutting marks. In addition to the Instron 4204 testing machine, a strain gage (Instron model 2630-25) was used to measure the strain during testing. For samples that would not break (pure HDPE and most 10% TLCP composites), the yield strength was measured.

The overall morphology of samples was observed using a Zeiss polarizing light microscope. Samples were cut with a razor blade, covered with immersion oil and photographed with low magnifications. More detailed pictures of the shape and size of phases were obtained by fracturing samples in liquid nitrogen, sputtering them with gold, and observing them in a Cambridge Stereoscan S200 scanning electron microscope with an accelerating voltage of 15 kV.

Dynamic mechanical testing was performed on resins to establish their flow behavior prior to blending. Frequency sweeps from .1 to 100 rad.s^{-1} to obtain complex viscosities at a strain of 10% and at temperatures from 190 to 290°C were made with a Rheometrics RMS 800 Spectrometer equipped with parallel plates (diameter 12.7 mm and gap height 1.5 mm).

3.3   Results and Discussion

3.3.1   Rheology

The viscosities of several materials were measured in order to decide upon which materials would be suitable for blending. Many researchers [1,17-19] have found that the viscosity of the TLCP must be lower than the matrix viscosity in order to get a favorable fibrillar morphology. The complex viscosity at 10 rad.s^{-1} frequency is plotted as a function of temperature in Figure 3.1. The matrix viscosity is compared to the TLCP cooling curves, because the dual extruder process allows the TLCP to be heated to a higher temperature before mixing with a cooler matrix. It can be seen that the HDPE viscosity actually intersects the cooling curves of the Vectras around 260°C. This implies that at temperatures above 260°C, the matrix viscosity is higher than that of the TLCP, which is favorable for the deformation of drops into fibrils. Therefore the drawing step has to occur above this temperature in order to ascertain effective fiber formation during strand processing. Meanwhile, the viscosity of the HDPE is almost 10 times higher than the MAPE viscosity and therefore HDPE should be more suitable to produce fibrillated TLCP blends.
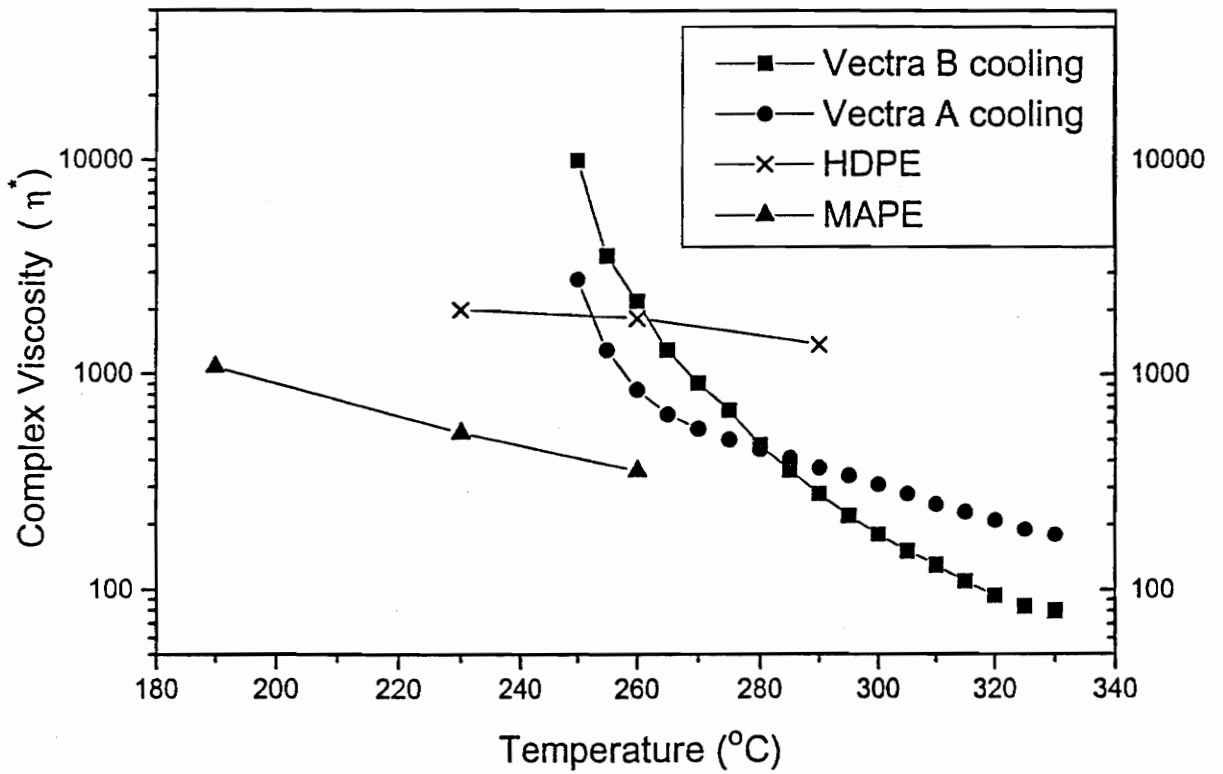
Figure 3.1   Complex viscosity at 10 rad.s^{-1} as a function of temperature for all
materials. Cooling curve data of Vectra A and B are from Sukhadia [2]

3.3.2   Strand Drawing

Strands drawn from single and dual extruder processes were first compared in order to decide upon the appropriate blending method. A single extruder was first equipped with a capillary die with length/diameter ratio (L/D) of 16, and later with 18 Kenics static mixer elements and a short die. The strand properties were compared in Table 3.1 to the tensile properties of blends obtained from the dual extruder process equipped with 18 Kenics mixers.

The addition of only 20 wt% TLCP improved the HDPE modulus up to 10 times the initial value, when the dual extruder blending system was used. Although it appeared to be possible to generate high modulus strands from a single extruder as well, the highest properties could only be obtained at much higher draw ratios and with use of a long, capillary die. These results are similar to earlier reports on PET/Vectra blends [2] and PP/TLCP blends [16]. According to Sabol [16], blends produced in the dual extruder process exhibit an axially continuous TLCP morphology which was maintained and further developed as the blend contracted into the die and drawn as a strand. In contrast, blending in a single extruder resulted in large axial concentration variations and a poor morhpology for mechanical property enhancement. Thus, the need for higher draw to obtain similar mechanical properties in single extruder blends resulted in a less stable drawing process with more frequent breakage of the thinner strands. Therefore, the dual extruder process was used for all further strand generation.

Table 3.1 Modulus and Tensile Strength of drawn strands of HDPE / 10% MAPE / 20% Vectra A under different extrusion conditions. ± Values indicate one standard deviation.

Extruder(s)	Die L/D	Modulus (GPa)	Tensile Strength (MPa)	Modulus (GPa)	Tensile Strength (MPa)
		Draw ratio ≈ 10		Draw ratio ≈ 20	
single, pure PE	16	0.9 ±.1	18 ±.2		
single	16	4.9 ±.8	81 ±3	9.9 ±2.6	147 ±38
single+mixers	1	5.0 ±.6	58 ±11	6.4 ±1.7	83 ±30
dual	1	9.0 ±1.4	113 ±16	10.0 ±1.6	120 ±32
dual	.5	7.0 ±1.2	95 ±11		

The properties of the strands were dramatically improved as the draw ratio was increased. The TLCPs were found to form fibrils, which became finer in a more extensional flow. When the draw ratio was increased during spinning, the orientation of the TLCP phase became larger, and the strength and modulus increased, as can be seen in Figure 3.2. The moduli of up to 10 GPa can be compared to theoretically predicted properties in fiber filled systems. The Tsai-Halpin equation predicts the blend modulus as a function of the fiber aspect ratio [20]:

$$E_{composite} = \frac{E_{HDPE} \left(E_{TLCP} + \xi \left(V_{HDPE} E_{HDPE} + V_{TLCP} E_{TLCP} \right) \right)}{V_{HDPE} E_{TLCP} + V_{TLCP} E_{HDPE} + \xi E_{HDPE}} \qquad (3.1)$$

where E is the modulus of the composite, the matrix (HDPE) or the TLCP, V the volume fraction and ξ the fiber aspect ratio ($\xi=2$ L/D). In the limit of infinitely long fibers, the modulus ultimately becomes the average of the volume-weighted average of the moduli of the two phases:

$$E_{composite} = V_{TLCP} E_{TLCP} + V_{HDPE} E_{HDPE} \qquad (3.2).$$

For a value of 65 GPa as the modulus of the TLCP phase [21], and an HDPE modulus of 1.1 GPa, a maximum modulus for a 20 wt% (15 vol%) blend of 10.7 GPa is predicted. As seen in Figure 3.2a, this maximum is approached at higher draw ratios, for both the Vectra A and B blends.
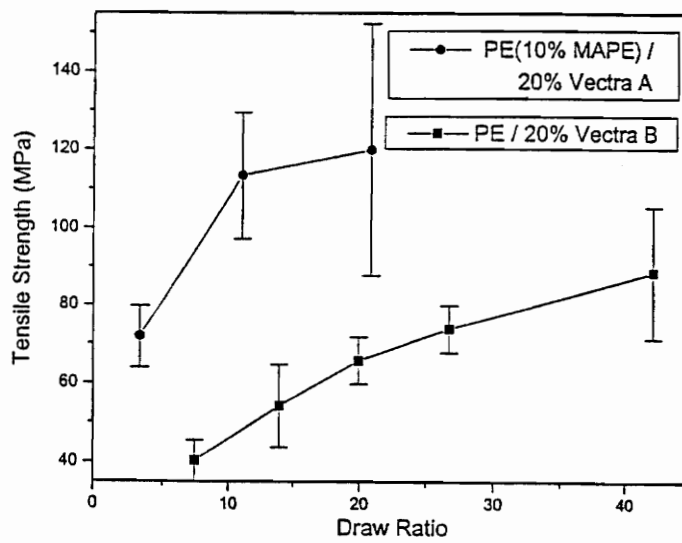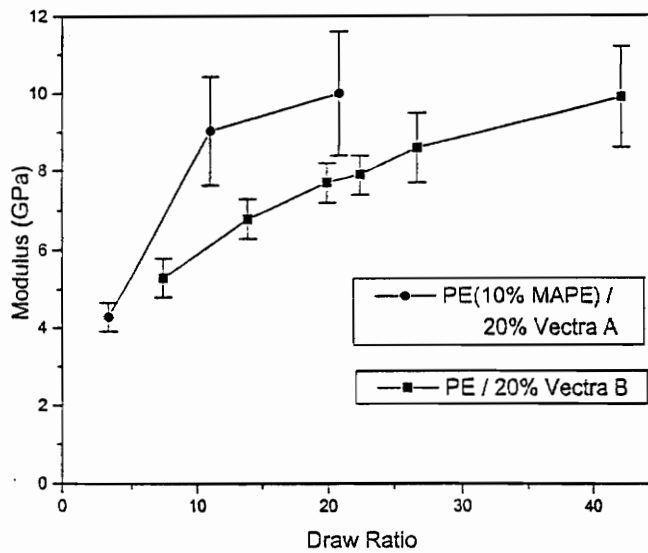
Figure 3.2   a)   Modulus of PE/ 20% Vectra A and B drawn strands versus Draw
                    Ratio

             b)   Tensile Strength of PE / 20% Vectra A and B strands

However, it has been predicted recently, that not only the fiber aspect ratio, but also the TLCP modulus, increase with draw. Lin and Yee [4] report moduli for Vectra A fibrils ranging from 2.2 to 75 GPa, and predict a modulus for Vectra B of 110 GPa. Robertson et al.[22] found that such a high modulus prediction could indeed be obtained in highly drawn PP / TLCP blends. This would imply that for a higher Vectra modulus, maximum orientation has not yet been obtained in the TLCP / HDPE strands.

The SEMs in Figure 3.3 show how the TLCP fibrils in higher draw ratio strands indeed become finer, down to a diameter of approximately 2 μm, which explains the better strand properties.
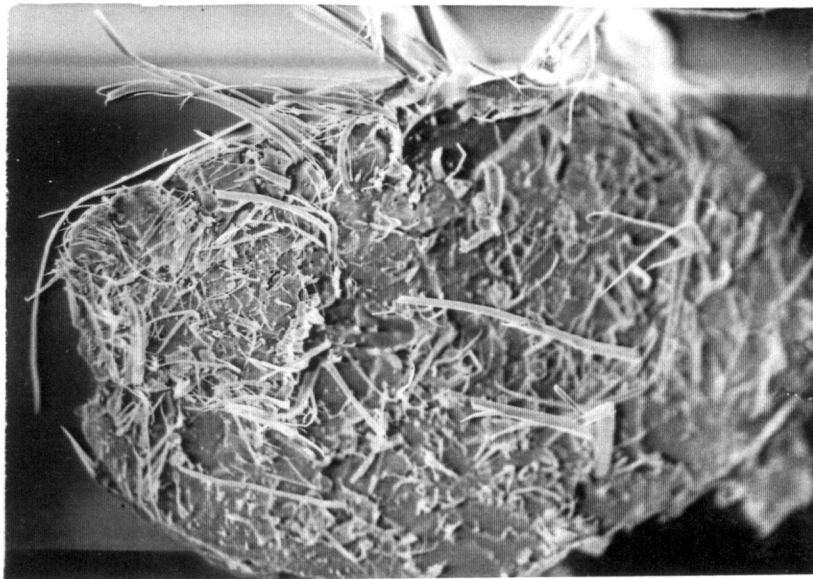
Thin Fibrils at High Draw Ratio (40)
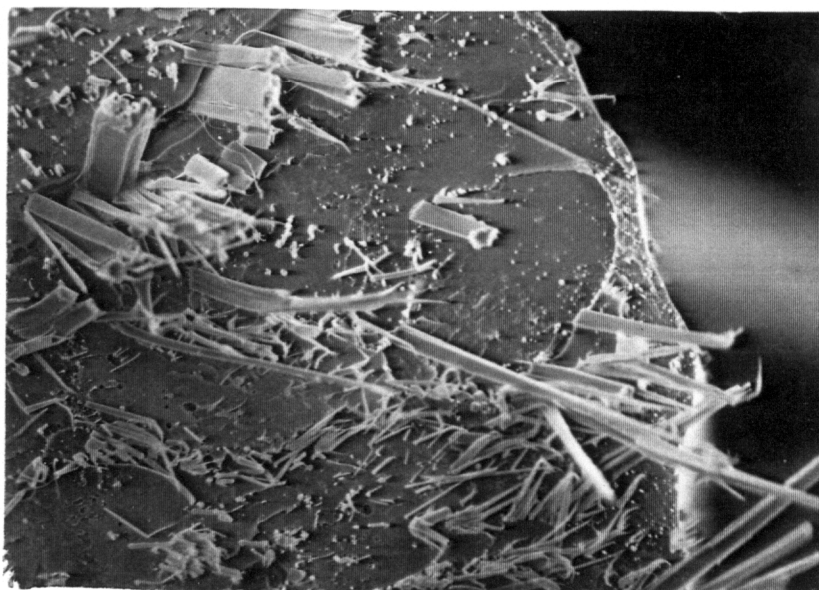
Thick Fibrils at Low Draw Ratio (5)

⟷
100µm

Figure 3.3   SEM's of low (5) and high (42) draw ratio strands of HDPE/20% Vectra B

3.3.3 Post-processing Methods: Effect of aspect ratio on properties

In order to understand what happens during further processing of pregenerated strands, it was useful to look at properties of compression and injection molded plaques, as seen in Table 3.2. First, when strands were uniaxially aligned and compression molded, the modulus in the fiber direction was found to decrease about 30% from the strand modulus. Samples appear to be weak in regions where fibers are poorly aligned, which explains the loss in strength and stiffness. However, when strands were first pelletized into pieces of approximately 3 mm length, the properties dramatically decreased. Similarly, injection molding of pellets into plaques at 190°C left the properties of the 20% Vectra A blend at a modulus of approximately 1.9 GPa and a tensile strength of 24 MPa. Although the initial infinite aspect ratio of the fibrils first remains well over a hundred during pelletizing (e.g. 3 mm/3μm = 1000), it is much further reduced during the processing, as is seen from the optical micrographs in Figure 3.4. This means that the upper limit of the Tsai-Halpin equation is no longer valid, which explains the lower properties. For aspect ratios approaching zero, the Tsai-Halpin equation reduces to a lower bound modulus prediction:

$$\frac{1}{E_{composite}} = \frac{V_{TLCP}}{E_{TLCP}} + \frac{V_{HDPE}}{E_{HDPE}}$$

(3.3)

For an HDPE / 20 wt% TLCP blend with moduli of 1.1 and 65 GPa respectively, equation 3.3 results in a composite modulus of 1.3 GPa. With an actual composite modulus value of 1.8 GPa, the Tsai-Halpin equation predicts a fiber aspect ratio of 3/2. Clearly, the post-processing methods resulted in material properties closer to the lower bound modulus prediction than the upper bound prediction, which is logical, because the fiber aspect ratio was reduced as fibrils were actually broken up during processing.

Table 3.2   Properties of strands, compression and injection molded plaques of HDPE /10% MAPE/ 20% Vectra A blends and glass filled HDPE

Material	Process	Modulus (GPa)	Tensile Strength (MPa)
HDPE	strands	0.9 ±.1	∞
	comp.mold pellets	1.6 ±.6	19 ±1
	inj.mold	1.1 ±.1	20 ±.3
HDPE (10%MAPE) 20% Vectra A	strands	10.0 ±1.6	120 ±32
	comp.mold strands	7.1 ±.3	89 ±6
	comp.mold pellets	1.8 ±.2	16 ±1
	inj.mold	1.9 ±.2	24 ±3
HDPE 20% glass	comp.mold	1.8 ±.2	24 ±1
	inj.mold	3.2 ±.4	33 ±2

The tensile properties of 20% glass filled HDPE from compression molded plaques, as reported in Table 3.2, were essentially the same as the TLCP reinforced microcomposites (modulus 1.8 GPa, tensile strength 24 MPa). However, due to the abrasive nature of glass, the injection molded samples showed contamination with material that was scraped from the extruder screw.
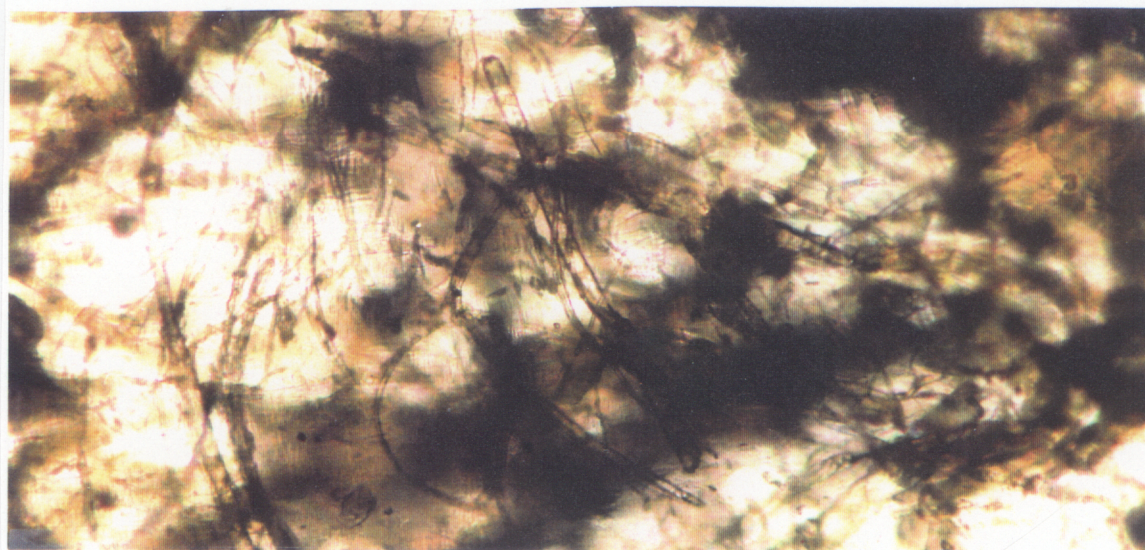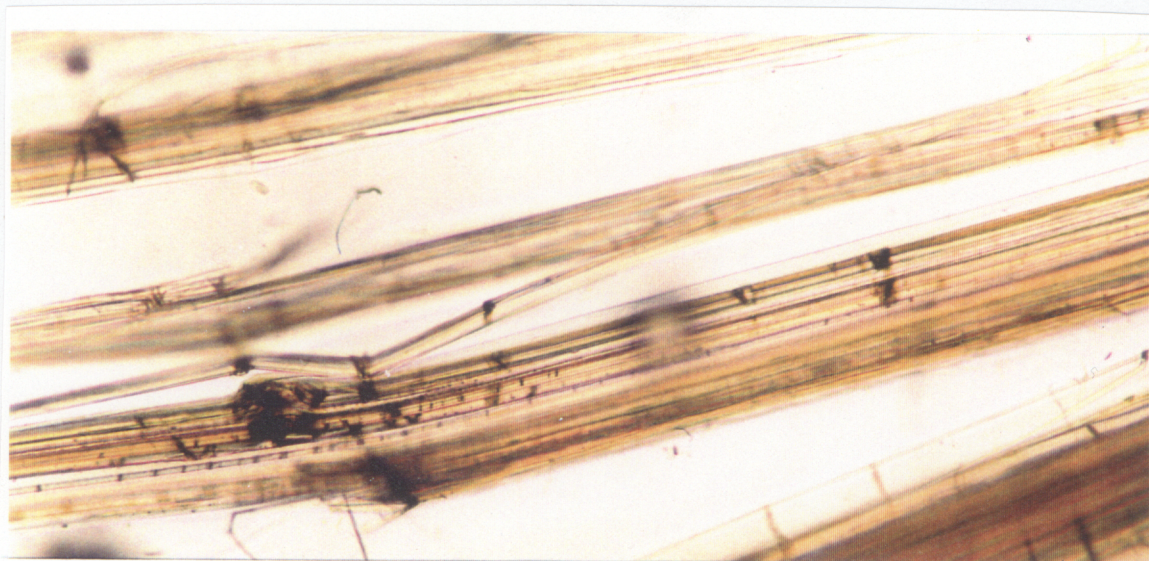
Figure 3.4   Optical micrographs of HDPE/ 20% Vectra B:

100µm

a)   In strands, fibers contain fine, infinitely long fibrils

b)   The injection molded microcomposites show agglomerates and fibrils.

3.3.4   Injection Molded Microcomposites

Now the high properties of strands need to be translated into the production of more useful parts and items. In the ideal case, it should be possible to maintain the strand properties when fibers remain long and are aligned uniaxially. For a two dimensional random fiber orientation, Piggott [23] derived the following composite theory to predict the composite modulus:

$$E_{composite} = \frac{3}{8} E_P + \frac{5}{8} E_T \tag{3.4}$$

where E_p and E_T are the rule of mixture and the lower bound modulus prediction respectively, as found in equations 3.2 and 3.3. Sabol [9] showed that it was possible to obtain composites with moduli approaching this limit, by compression molding long strands of PP / TLCP. However, compression molding of pelletized strands and injection molding at 250°C resulted in properties much lower than this composite theory prediction. With the assumption that the TLCP modulus remains constant at 65 GPa, a maximum modulus of 4.8 GPa is calculated for a random oriented long fiber reinforced composite with HDPE as the matrix. In the following section, an attempt is made to obtain this maximum level in injection molding, by varying the post-processing conditions. Pelletized HDPE/20% Vectra B strands were injection molded at several temperatures, in order to obtain microcomposite plaques. The effects of fiber aspect ratio, orientation, compatibilization and pre-mixing on the composite properties were also studied.
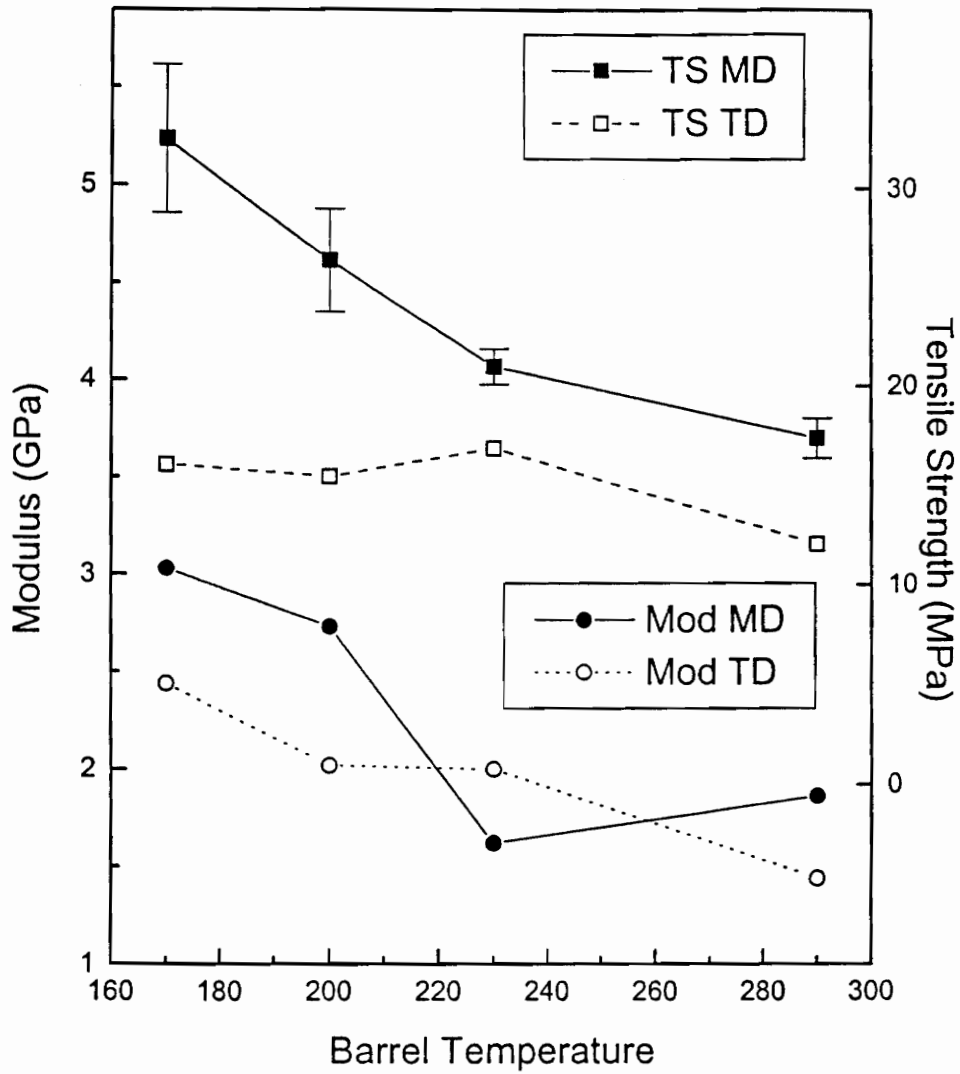
Figure 3.5   Properties of HDPE/20% Vectra B microcomposites as a function of the

barrel temperature in the last injection molding zones

Injection Molding Temperature

The tensile properties of injection molded plaques determined in both the machine and transverse direction are presented in Figure 3.5 as a function of the temperature in the last heating zone of the injection molder. Both the modulus and tensile strength of the HDPE/ 20% Vectra B composites in machine and transverse directions, increased significantly with lower temperatures, up to a 3.0 GPa modulus and 33 MPa tensile strength in the machine direction at the lowest temperature of 170°C. This is a more than 50% improvement over the 1.9 GPa modulus and 21 MPa tensile strength of samples molded at a 230°C barrel temperature. The SEMs of Figure 3.6 clearly illustrate why the mechanical properties increased. At a temperature of 170°C, the pregenerated fibers stayed intact, but at 230°C, the spun fibers deformed into large agglomerates (with low aspect ratio). Although Vectra does not start melting until 260°C, the deformation of the high aspect ratio fibrils dramatically decreased the tensile properties of the microcomposites. A similar trend was reported for PP/ 30% Vectra A microcomposites [5], but for this system the properties were best at the lowest temperature (190°C), as well as at the highest (280°C) temperature, while reduced around 250 °C. The fact that the properties of composites molded at temperatures above the TLCP melting point only further decreased for the HDPE / Vectra B system, indicate that there was no significant in situ fiber formation in the HDPE microcomposites.
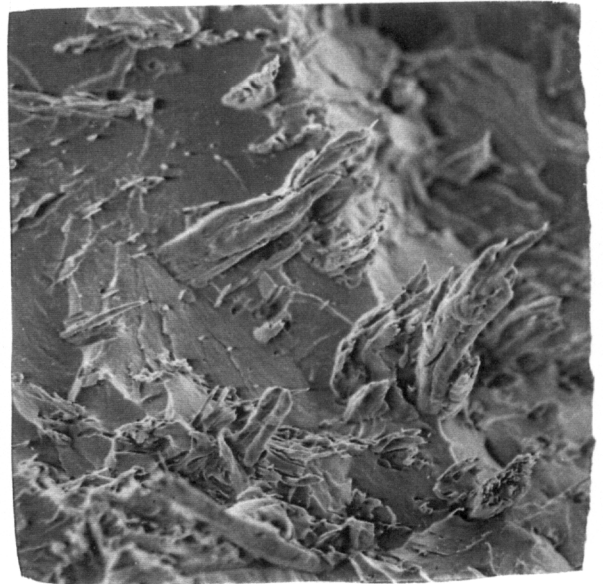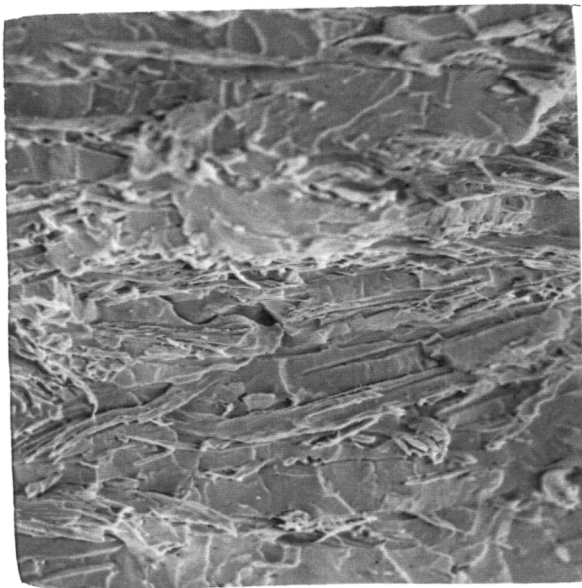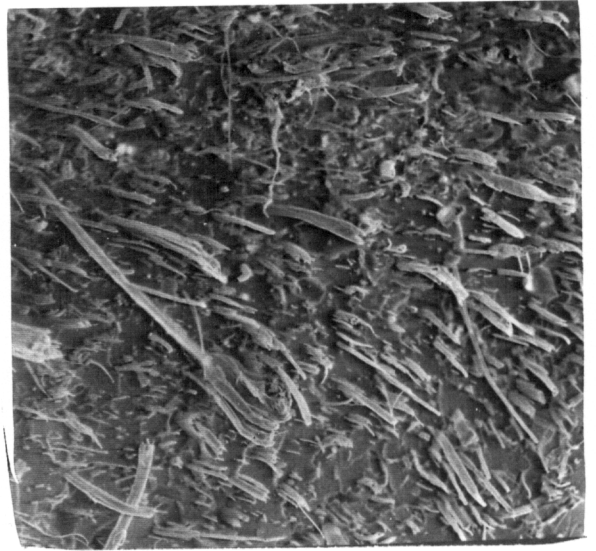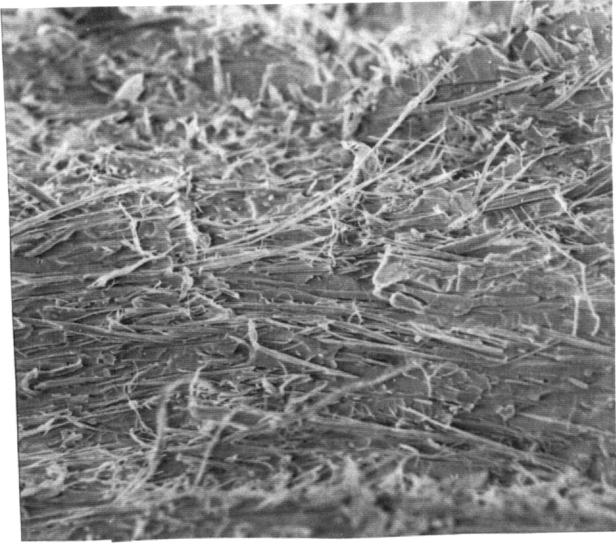
Figure 3.6   SEM's of HDPE/ 20% Vectra B microcomposites injection molded at low
(170°C) and high temperature (230°C), parallel and perpendicular to the
flow direction

25μm

Draw Ratio

When higher draw ratio strands are used for injection molding, it is expected that their better tensile properties would be translated into plaque properties, provided that the fiber aspect ratio is also transferred from the strands into the microcomposites. Although Handlos [5] reported this translation of better properties of higher draw ratio strands into injection molded microcomposites, Table 3.3 does not show this effect. The trend was likely too insignificant to show up within accuracy of results. This could also be due to the fact the initial fiber aspect ratio was well above 100, even for the lowest draw ratio blends, but reduced during the injection molding, as was shown for the composites molded at 230 °C in Figure 3.6. Also, the adhesion between HDPE and TLCPs was found to be poor (as can be seen from the long fiber pull-out in the SEMs of Figure 3.3). Therefore, an increased surface area from the higher aspect ratio may not have affected the HDPE/Vectra B properties as much, as was found for the PP/Vectra A microcomposites [5]. Also noteworthy in Table 3.3 is that the standard deviations at low temperature suddenly increased. This indicates that properties were not as uniform in low temperature injection molded plaques. This anisotropy effect will be addressed next.

Table 3.3 Properties of microcomposite plaques of HDPE/ 20% Vectra B with increasing strand draw ratio, injection molded at 230 and 170°C

Draw Ratio	230°C		170°C	
	Modulus (GPa)	Tensile Strength (MPa)	Modulus (GPa)	Tensile Strength (MPa)
7.4	1.49 ±.14	19.7 ±.8	2.73 ±.44	28.9 ±2.7
13.9	1.61 ±.17	20.8 ±.8	3.01 ±.83	28.4 ±2.8
22.4	1.64 ±.16	23.0 ±1.0	2.84 ±.74	27.8 ±2.5
42.2	1.62 ±.09	21.0 ±.9	3.03 ±.58	32.5 ±3.7

Orientation / Anisotropy

Fibers form much better reinforcement along the fiber direction than in the transverse direction. Because fibers are aligned in the machine direction during injection molding, the properties of transverse direction samples cut from plaques are up to 50% lower than machine direction properties, as seen in Figure 3.5. The orientation of the fibers in a plaque is known to depend on the location in the thickness direction: the skin is highly oriented in the flow direction, whereas the core is not. The orientation dependence over the thickness of the plaque is known to be formed during the fountain flow filling of the mold [24,25]. However, the plaques of the very viscous blends at low temperature showed a similar distinct flow pattern over the width of the plaque, as shown in Figure 3.7. The fibers oriented along the streamlines and therefore the machine direction samples cut from the side of the plaques had better tensile properties than tensile bars cut from the relatively unoriented middle.

The high standard deviations in the tensile properties of microcomposites produced at 170°C were related to the fiber orientation and the resulting anisotropy in the plaques. The average modulus and strength of the 170°C microcomposites of Table 3.3, split between the side and middle of the plaques, are also reported in Figure 3.7. The fact that the modulus in the side region was approximately 40% higher than in the center, is clearly a result from the fiber orientation. The SEMs in Figure 3.6 were actually all taken looking into the machine direction of the plaques, but the fractures on the side of the plaque showed fibers coming out of the surface, whereas in the center they were oriented in the plain of fracture. This means that the T-manifold mold did not produce uniform plaques, and shows once again that the fiber orientation is very important for final product properties.
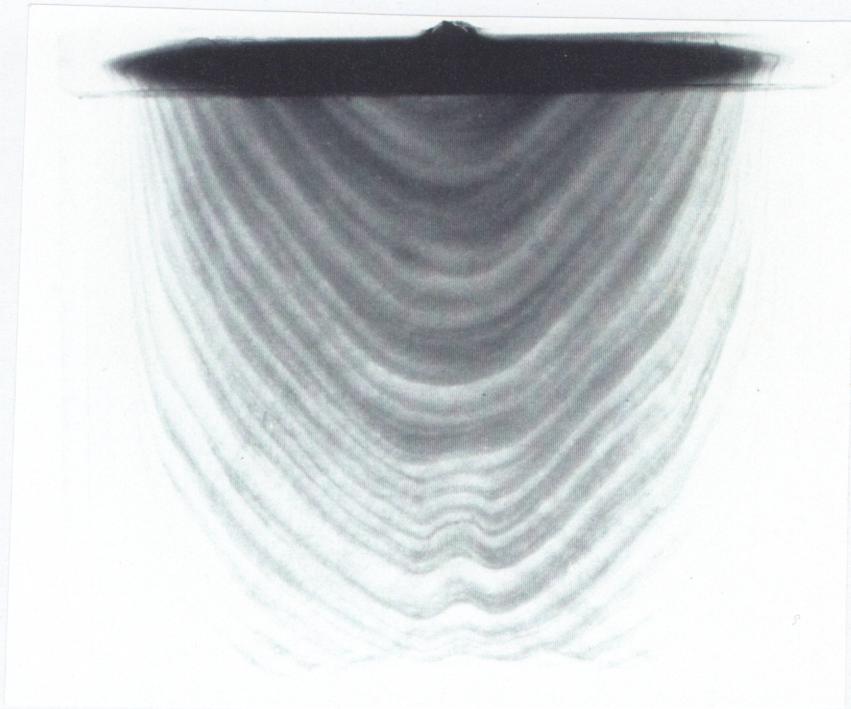
	Modulus	2.4±.1 GPa	3.3±.3
	Tens.Str.	27±2 MPa	32±2

Figure 3.7   Orientation in injection molded plaques from a T-manifold mold; flow lines and properties for machine direction cut bars of HDPE/ 20% Vectra B microcomposites

Addition of Maleic Anhydride grafted Polyethylene (MAPE)

To see whether a third phase, maleic anhydride grafted HDPE (MAPE), could improve adhesion between the TLCP fibrils and the matrix, strands were produced with and without addition of 10% MAPE to the HDPE matrix. Maleated polyolefins act as a compatibilizers, reducing the dispersed phase size, and are also known to improve adhesion between two phases [8]. However, the addition of MAPE clearly made the drawing process less stable and actually resulted in lower strand properties. Although the Vectra A strands were all produced with MAPE, the blends with Vectra B were all made without MAPE. The MAPE was already found to have a much lower viscosity than HDPE (Figure 3.1), and during rheological measurements it carbonized almost immediately when heated in air. Thus, the addition of MAPE in the relatively hot extrusion blending process resulted in more voids and unstable drawing. Also, a better dispersion of TLCP in the matrix, could imply that fibrils were no longer fully continuous, resulting in more fiber breakage.

O'Donnell [8] reported that the modulus of in situ PP / Vectra B blends was most improved upon addition of 20% Maleic Anhydride grafted PP (MAP) to the matrix. Meanwhile, the tensile strength of these in situ blends almost doubled upon addition of 50% MAP to the PP phase. To compare this to the HDPE blends, pregenerated fibers were diluted with 50% of mixtures of HDPE and MAPE and injection molded at 230°C. This resulted in the properties of the 10% Vectra B microcomposites of Figure 3.8. There is no increase of properties upon addition of MAPE.
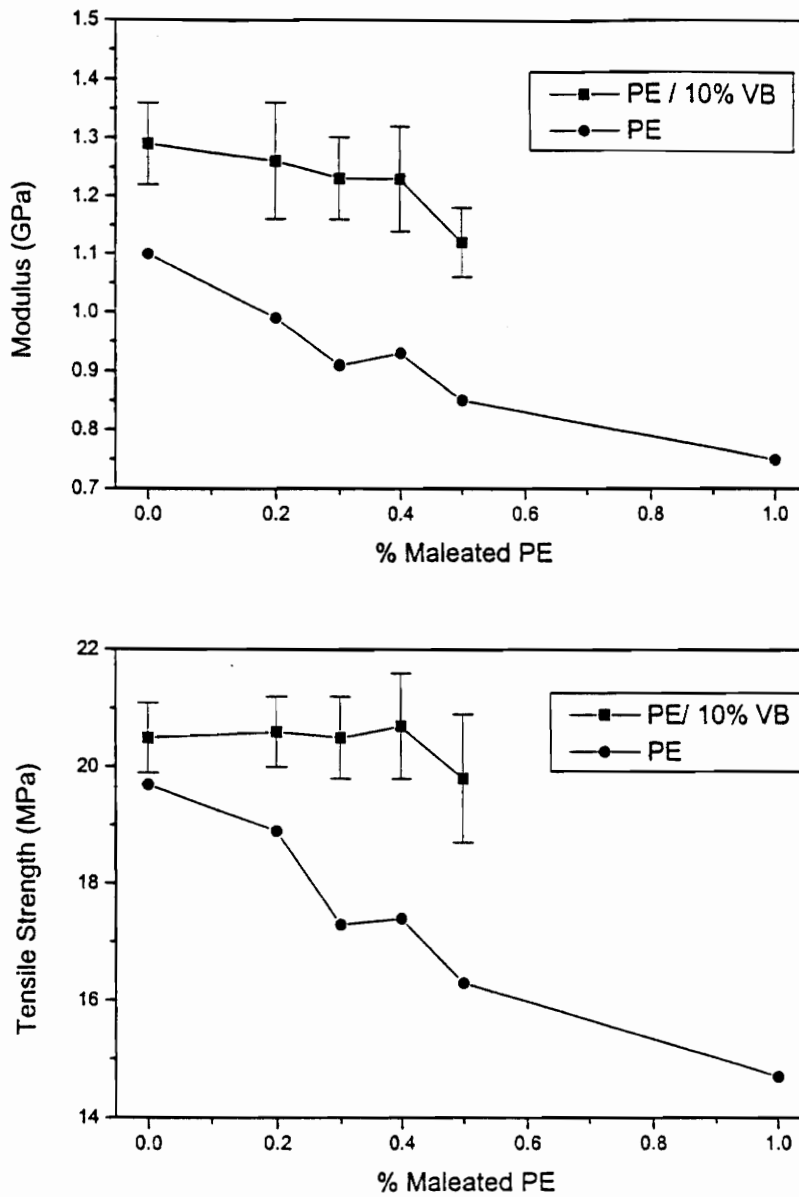
Figure 3.8   Properties of HDPE/10% Vectra B microcomposites with increasing
MAPE concentration, injection molded at 230°C. Modulus and tensile
strength of compatibilized blends are compared to original matrix
properties

Table 3.4 shows the same trend for HDPE / 20% Vectra B in situ composites: TLCP blend properties practically the same, while the HDPE / MAPE properties decreased with increasing maleation. The properties of the matrix decreased steeply upon the addition of MAPE to HDPE, which could be related to the lower viscosity (and molecular weight) as noted in Figure 3.1. However, this means that the composites with MAPE did have better properties compared to the matrix, than composites without MAPE. This also reflects the better phase dispersion that was noticed in the compatibilized material shown in Figure 3.9. However, it remains unknown whether the phase dispersion improved because of compatibilization or because of the lower MAPE viscosity.

Table 3.4   Properties of compatibilized in situ HDPE / 20% Vectra B plaques,
injection molded at 290°C

% MAPE in HDPE	Modulus (GPa)	Tensile Strength (MPa)	strain@break (%)
0	1.93 ±.31	20.3 ±2.5	1.4 ±.2
10	1.86 ±.26	20.7 ±2.0	2.0 ±.4
15	1.92 ±.32	27.6 ±2.8	1.6 ±.2
20	2.24 ±.32	23.6 ±3.0	1.6 ±.2
30	2.38 ±.42	22.2 ±1.8	1.4 ±.3
40	2.57 ±.66	23.3 ±3.9	1.3 ±.2
100	1.93 ±.32	20.3 ±2.5	2.2 ±.4
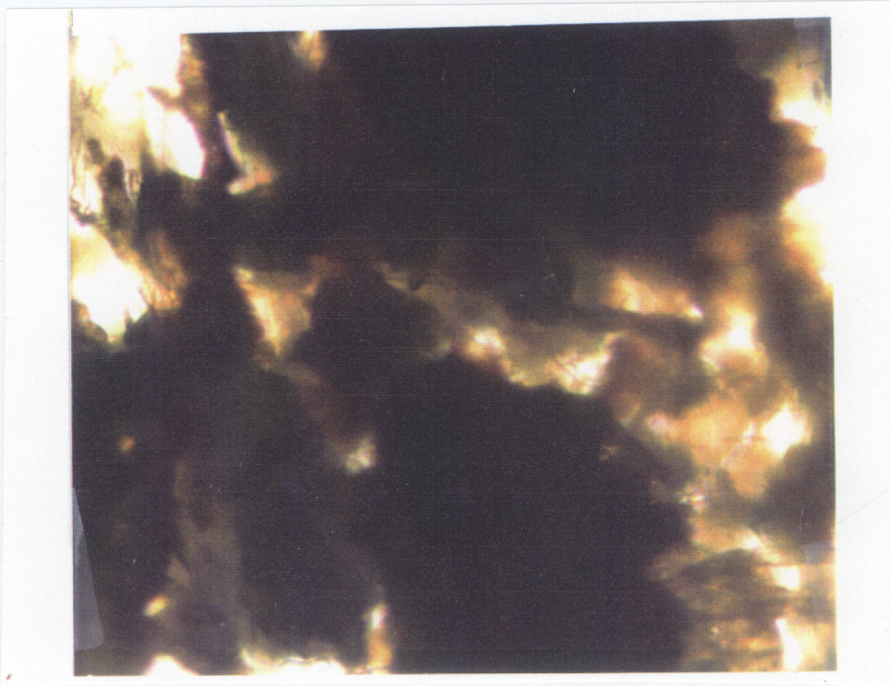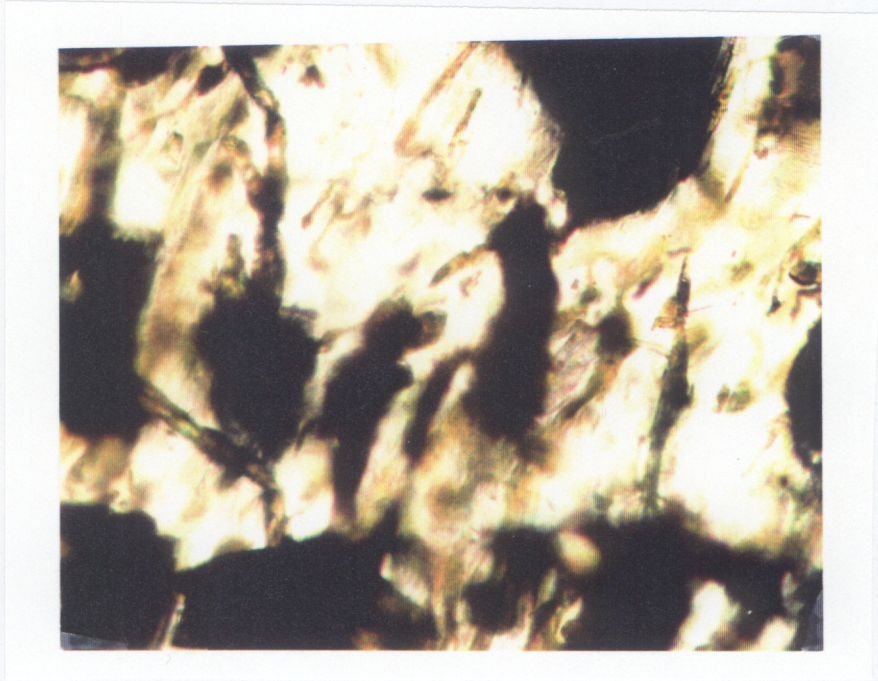
Figure 3.9   Micrographs of compatibilized and uncompatibilized plaques of HDPE /
10% Vectra B

$\longleftrightarrow$

100μm

Microcomposites vs. in situ composites

The modulus of 1.9 GPa and strength of 20 MPa of the HDPE / 20% Vectra B in situ composites, generated at 290°C, as was reported in Table 3.4, are in the same range as the values for higher temperature microcomposites, generated at 230 and 290°C. This is not surprising, because it was already found that the injection molding of HDPE blends did not provide enough extensional flow for sufficient fiber generation. The properties of in situ and microcomposites, generated at several temperatures, as well as the strain at which the samples broke, are reported in Table 3.5. Besides the improvement in tensile properties, the increased strain at break is significant for the low temperature microcomposites. Clearly, the microcomposites generated at low temperature, had much better properties than the composites made at higher temperatures.

Table 3.5   Properties of pregenerated high draw ratio and in situ composites of HDPE / 20% Vectra B

Temp (°C)	Modulus (GPa)	Tensile Strength (MPa)	strain@break (%)
InSitu 290	1.9 ±.3	20.3 ±2.5	1.4 ±.2
290	1.9 ±.3	17.4 ±1.0	2.1 ±.5
230	1.6 ±.1	21.0 ±.9	6.1 ±1.2
200	2.7 ±.8	26.4 ±.6	3.9 ±1.4
170	3.0 ±.6	32.5 ±3.7	3.2 ±1.5

3.4   Conclusions

In this study, it was shown that TLCP fibrils in an HDPE matrix can be generated by using a dual extruder process and these fibrils can be effectively used to produce reinforced composites, when fiber aspect ratios are maintained during processing. The dual extruder blended HDPE/20 wt% Vectra strands had moduli increasing from 5 GPa at low draw ratio to 10 GPa at draw ratios over 20. The tensile strengths of both Vectra A and B blended strands reached over 100 MPa. Increased drawing resulted in finer fibrils and improved strand strength and stiffness up to the predictions of the Tsai-Halpin rule of mixtures, using a TLCP modulus of 65 GPa. In high temperature injection molding, the high aspect ratio pregenerated fibers formed large agglomerates and the tensile modulus reduced to the lower bound modulus property prediction. However, when the high aspect ratio fibrils were maintained in strand compression molding and low temperature injection molding microcomposites, the tensile properties remained much higher (at levels of 70 and 30% of the strands, respectively). The strength and stiffness of injection molded plaques increased in both the machine and transverse direction, but the anisotropy in these solid fiber filled composites remained. Addition of maleic anhydride grafted polyethylene resulted in less TLCP agglomeration, but properties only improved relative to decreased matrix properties. The properties of in situ composites were also close to the lower bound prediction. Overall, microcomposites of HDPE and TLCPs showed best properties when a solid fiber morphology was maintained in low temperature injection molding.

3.5   References

1.   A. A. Handlos and D. G. Baird, *J. Macr. Sci. - Revs. Macromol. Chem.*, submitted

2.   A. M. Sukhadia, A. Datta and D. G. Baird, *Int.Polym.Proc.*, **VII** (1992) 3, 218-228

3.   W. Lee and A. T. Dibenedetto, *Polym.Eng.Sci.*, **32** (1992) 6, 400-408

4.   Q. Lin and A.F.Yee, *Polym. Comp.*, **15** (1994) 2, 156-162

5.   A. A. Handlos and D. G. Baird, *Int.Polym.Proc.*, submitted

6.   A. A. Handlos, E. A. Sabol and D. G. Baird, *SPE Antec '94*, 1594-1598

7.   A. I. Isayev, Y. Holdengreber, R. Viswanathan and S. Akhtar, *Polym.Comp.*, **15** (1994) 4, 254-260

8.   H. J. O'Donnell and D. G. Baird, *Polymer*, submitted

9.   E. A. Sabol and D.G. Baird, *Polym.Comp.*, submitted

10.   R. Juran (ed.), <u>Modern Plastics Encyclopedia</u>, **66** (1989) 11, 75

11.   T. C. Hsu, A. M.Lichkus and I. R. Harrison, *Polym.Eng.Sci.*, **33** (1993) 13, 860-864

12.   T. Harada, K. Tomari, A. Hamamoto, S. Tonogai, K. Sakaura, S. Nagai and K. Yamaoka, *SPE Antec '92*, 376-381

13.   S. Meretz, M. Kwiatkowski and C. Hinrichsen, *Int.Polym.Proc.*, **VI** (1991) 3, 239-246

14.   Quantum product literature, <u>Petrothene High Density Polyethylene for Blown and Cast Film</u>

15.   BP Product Bulletin, <u>PolyBond Chemically Modified Polyolefins</u>, **3** (1993)

16.   E. A. Sabol and D. G. Baird, *Int.Polym.Proc.*, accepted

17.   F. P. La Mantia, F. Cangialosi, U. Pedretti and A. Roggero, *Eur.Polym.J.*, **29** (1993) 5, 671-677

18.   R. Gonzalez-Nunez, B. D. Favis and P. J. Carreau, *Polym.Eng.Sci.*, **33** (1993) 13, 851-859

19. R. E. S. Bretas, D. Collias and D. G. Baird, *Polym.Eng.Sci.*, **34** (1994) 19, 1492-1496

20. K. Engberg, O. Stroemberg, J. Martinsson and U. W Gedde, *Polym.Eng.Sci.*, **34** (1994) 17, 1336-1345

21. Chung,T.S., *J.Polym.Sci., Polym.Phys.Ed.*, **26** (1988), 1549

22. C. G. Robertson, J. P. de Souza and D. G. Baird, *SPE Antec '95*, accepted

23. M. R. Piggott, Load Bearing Fibre Composites, Pergamon Press, Oxford (1980)

24. R. Bailey and B. Rzepka, *Intern.Polym.Proc.*, **VI** (1991) 1, 35-41

25. S. D. Hudson, A. J. Lovinger, S. K. Venkataraman, C. Liu and L. T. Manzione, *Polym.Eng.Sci.*, **34** (1994) 17, 1327-1335

4.   Recommendations

It was shown in this thesis that blends of polyethylene and liquid crystalline polymers could be developed and that composites made of these materials could exhibit improved properties using the right processing conditions. Research always initiates more research. The encouraging results from microcomposite blends of HDPE and TLCPs ask for further improvements in order to optimize properties. Meanwhile, the research could also be broadened with development of new techniques. Thus, the following recommendations are stated.

- Injection molding of HDPE/ Vectra B blends resulted in a much finer fibrillar morphology at temperatures as low as 170°C. However, some agglomerates were still present in these microcomposites. The morphology and mechanical properties of blends processed at even lower temperatures should be studied. This could be achieved by using a less viscous HDPE or, e.g., LDPE, which can be processed at even lower temperatures. It should be checked whether the actual melt temperature is close to the barrel temperature setting in the injection molder. It should also be studied whether the fiber breakdown is related to the narrow channels and thus high shear rates in the relatively small screw injection molder used in this study.

- The swell of polymer exiting the die could be reduced when a longer die would be used. Although this would increase the pressure drop during extrusion, it is expected that this would improve strand drawing.

- The temperatures during extrusion blending appear to be very critical, yet difficult

79

to control. It might help finding stable processing conditions when more thermocouples would actually be inserted in the flow, especially in the mixing and die section.

- The 20 wt% TLCP blends used in this study showed encouraging reinforcement. However, when diluted down, the reinforcement was largely overshadowed by measurement inaccuracies. Blends with higher TLCP content are easily drawable, because of the high TLCP melt strength. However, for the HDPE blends it appeared impossible to pelletize 40 wt% blends. These higher concentration blends are of interest, also because they can be diluted with other polymers, but a better pelletization process needs to be developed. Once this problem is overcome, it should be possible to obtain higher draw ratio blends, which should result in properties even better than the Rule of Mixtures prediction (as reported Lin and Yee, see Chapter 2) and hopefully translate into better microcomposite properties. The validity of the Lin and Yee prediction should be tested, because then we could obtain more significantly reinforced materials with prosperous applications.

- In order to improve processability of pelletized strands, a pultrusion process could be developed. This would increase the diameter of strands because a number of highly drawn strands could be molten into one thicker strand, thus also improving the pelletization efficiency, pellet size and the feed efficiency in further processing.

- In order to reduce the anisotropy found in the plaques made with a T-distribution mold, a coathanger design mold could be made to produce more uniform plaques. The anisotropy needs to be understood better and become more controllable, so that properties in injection molded parts can be uniform or at least desirably distributed.

- To provide a better comparison with other reinforced materials, the flex modulus and Izod impact resistance of composites could also be tested.

Vita

Born in 1969 in the worldfamous village of Jisp (Holland), the author was doomed to follow her parents in their pursuit of conquering the world. After having survived highschool in a commuter suburb, it was time to get as far away possible from these horrors and move to Turkey. Determined to become rich, returning to The Netherlands was inevitable, for only in Delft was the best school of engineering. After her parents decided to move to the center of the universe on the other side of the humongous Dutch country, nothing kept the author any longer from doing similar. Trips through Europe, back to Turkey, and eventually a life in America, guided her through education. With this thesis, the author eventually hopes to get the long-seeked college degree, helping her on the way to a successful career to start off in Belgium.