

**Reclamation and Reprocessing of a Thermotropic Liquid Crystalline
Polymer from Composites of Polypropylene Reinforced with Liquid
Crystalline Polymer**

by

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(ABSTRACT)

The composites industry can be positively influenced by composite materials that are processed faster, are lighter in weight, are higher in stiffness and strength, and that are more recyclable. There has been considerable interest in the use of thermotropic liquid crystalline polymers (TLCPs) to reinforce thermoplastic materials. In a novel process developed by Baird and coworkers, wholly thermoplastic composites are produced via a patented, dual extrusion process. This unique process yields a fiber which consists of numerous continuous fibrils of the liquid crystalline polymer encased in a thermoplastic matrix. These fibers have been used to form random mats and woven pre-forms, which have then been compression molded to form composite parts. Because of the high cost associated with these thermotropic liquid crystalline polymers and the desire to generate recyclable composites, a process was developed in this research to separate the liquid crystalline component from polypropylene (PP) composites.

The overall objectives of this work were to develop a process to reclaim the liquid crystalline component of these thermoplastic composites, to determine the effect the process had on the properties of the reclaimed liquid crystalline polymer, and finally to determine whether or not the reclaimed liquid crystalline polymer could be used again to generate a reinforcing component. An ancillary objective was to see if the polypropylene could also be reclaimed, and if it had further use as a polymeric resin.

In the present work, a novel process was developed that allows the liquid crystalline component to be reclaimed for further use in the composite material or in other applications that require thermotropic liquid crystalline polymers. The polypropylene component, which has undergone molecular weight reduction, can also be reclaimed by this process. This process consisted of using an organic peroxide and reactive extrusion to selectively degrade only the polypropylene, and not the thermotropic liquid crystalline polymer. The degraded polypropylene was selectively dissolved away from the liquid crystalline polymer by stirring the extruded melt in boiling mineral oil. The remaining solids, of thermotropic liquid crystalline polymer, were collected via centrifugation, cleaned of the mineral oil by boiling in kerosene, and then dried in a convection oven. The purity of the reclaimed thermotropic liquid crystalline polymer was determined by density measurements, while the physical properties of the reclaimed material were determined by rheological tests. The mechanical properties were determined via Instron testing of injection molded plaques made from mixtures of reclaimed material and pure thermotropic liquid crystalline polymer.

From this work, it was found that over 70 wt% of the thermotropic liquid crystalline polymer, DuPont HX8000, could be successfully separated from the polypropylene to a degree of 96.0%. From Instron testing, it was found that up to 40 wt% of the reclaimed HX8000 could be blended with the pure HX8000, with no loss in mechanical properties. Furthermore, it was seen that up to 83 % of the HX8000 component (40 wt%) of PP 6523 (60 wt%) composites could be replaced with reclaimed HX8000 without seeing any losses in mechanical properties. It was also found that the degraded polypropylene could be successfully separated, via centrifugation at a temperature of 253 K, and could be potentially used as resin for non-wovens. The projected material cost of the reclaimed HX8000, based on the ability to purchase and to process in bulk, was determined to be 90 % less than the virgin HX8000.

Acknowledgments

The author would like for all who read this thesis to know that the success of this work was only possible by the grace of God. I give all the credit to my Lord and Savior, Jesus Christ. Additionally, I would like to thank my wife, Christina K. Collier, for all of her support, prayers, and encouragement that she gave me throughout my graduate career. None of this would have been possible without her commitment and understanding for all of the long hours.

The author would also like to thank my research advisor, Dr. Donald G. Baird, for the support and confidence entrusted by him to allow me the latitude to pursue my ideas and suggestions in this research, but also for the perfect amount of help that kept the project on target.

The author would also like to thank the following:

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- Soon-to-be Dr. Robert Young for his extreme patience in answering all of my questions. Most of all, for the constant help and support in my research that also was a key and integral part of my success.
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- I would like to thank the Army Research Office, Grant # DAAH04-94-G-0171, for their support of my project.
- Lastly, I would like to thank the Department of Chemical Engineering and more specifically, the Graduate School Secretaries.

Original Contributions

The following are considered to be the significant original contributions of this research:

- It was determined that the reactive extrusion of the HX8000 / PP composite, with dicumyl peroxide, rather than the use of a batch reactor was essential in successfully reacting the composite system and in separating the two phases of PP and HX8000 prior to selective dissolution.
- The use of light mineral oil was established as the best solvent for the dissolution of degraded PP and reclamation of HX8000. This solvent allowed for selective melting of the PP, for selective dissolution of the PP, and it allowed for the selective flotation of degraded PP and subsequent sinking of HX8000 which facilitated collection.
- The use of a centrifuge and the use of solvents such as Kerosene and Hexanes were also essential in the successful reclamation of relatively pure particles of HX8000. The centrifuge allowed the differences in densities to be utilized for separation. The use of kerosene to remove excess oil and the use of a volatile solvent, like Hexane, to remove excess kerosene allowed the reclaimed solids of HX8000 to be dried and collected.

Table of Contents

1. Introduction	1
1.1 Thermotropic Liquid Crystalline Polymer	2
1.1.1 Chemical Structure and Phase Behavior of TLCPs	2
1.1.2 Mechanical and Physical Properties of TLCPs	7
1.2 Composites Based on TLCP / Thermoplastic Blends	12
1.2.1 In situ Composites	13
1.2.2 The Need for a Reclamation Process	19
1.3 The Separation of Two Intimately Blended Species	23
1.3.1 Mixed Plastics Recycling	24
1.3.2 Selective Dissolution of Polymers	25
1.4 Reclamation of TLCPs	31
1.5 Research Objectives	32
1.6 References	35
2. Literature Review	38
2.1 Introduction	38
2.2 Plastics Recycling	40
2.2.1 Reclamation via Shredding and Density Separation	41
2.2.2 Recycling of TLCP / Thermoplastic Composites	51
2.3 Polymer Solubility	59
2.3.1 Important Factors in Polymeric Solubility	60

2.3.2 The Solubility of Polypropylene	68
2.4 Reactive Extrusion	76
2.4.1 The Mechanical Aspect of Reactive Extrusion	77
2.4.2 Controlling Factors and Reaction Kinetics	81
2.5 The Reprocessing of Reclaimed or Recycled Polymer	92
2.6 References	100
3. Separation of a Thermotropic Liquid Crystalline Polymer from Polypropylene Composites	103
3.1 Introduction	106
3.2 Experimental	113
3.2.1 Materials	113
3.2.2 Reactive Extrusion	114
3.2.3 Mineral Oil Separation	115
3.2.4 Physical Properties	115
3.2.5 Injection Molding	116
3.2.6 Mechanical Properties	117
3.3 Results and Discussion	118
3.3.1 Development of the Reclamation Process	118
3.3.2 Physical Properties of the Reclaimed HX8000	121
3.3.3 Mechanical Properties of the (Reclaimed/Pure) HX8000/PP Plaques	123
3.3.4 Rheological Testing of the Reclaimed HX8000	129

3.3.5 Proposed Explanations for the Differences in Rheological Properties	134
3.3.6 Projected Material Cost Analysis	135
3.4 Conclusions	137
3.5 Acknowledgments	139
3.6 References	139
4. Reprocessing of a Recycled Thermotropic Liquid Crystalline Polymer	142
4.1 Introduction	145
4.2 Experimental	149
4.2.1 Materials	149
4.2.2 Physical Properties	150
4.2.3 Injection Molding	151
4.2.4 Mechanical Properties	152
4.2.5 Scanning Electron Microscopy	152
4.2.6 Differential Scanning Calorimetry	152
4.3 Results and Discussion	153
4.3.1 The Reclamation Process	153
4.3.2 Physical Properties of the Reclaimed HX8000	154
4.3.3 Mechanical Properties of the Reclaimed and Pure HX8000 Plaques	154
4.3.4 Rheological Testing of the Reclaimed HX8000	159
4.3.5 Proposed Explanations for the Differences in Rheological Properties	161

4.3.6 Scanning Electron Microscopy (SEM) of the Reclaimed	
HX8000 Samples	164
4.3.7 Differential Scanning Calorimetry (DSC) Testing	168
4.4 Conclusions	171
4.5 Acknowledgments	172
4.6 References	172
5. Recommendations	174
Appendix A: Reclamation Process Pictures	178
Appendix B: Rheological Data	185
Appendix C: DMTA Data	193
Vita	197

List of Figures

CHAPTER 1:

Figure 1.1 The Dual Extrusion Process	17
Figure 1.2 Single Solvent Dissolution Process Flow Sheet	27

CHAPTER 2:

Figure 2.1 Schematic of Japan Steel Work's Nikko Waste Plastics Reclamation Line	42
Figure 2.2 Single Solvent Dissolution Process Flow Sheet	48
Figure 2.3 Tensile Strength vs. LCP Content for PP Strands	54
Figure 2.4 Process by which Sasaki et al. [13] Generated In situ LCP Composite Strands from Polypropylene and then Reground and Reprocessed the Material	55
Figure 2.5 Tensile Strength as a Function of Successive Regrinding and Reprocessing for Composite Strands of 30 wt% LCP and 70 wt% PP	57
Figure 2.6 The Lattice Model of Solubility with respect to Small Molecules and Large Polymeric Molecules	62
Figure 2.7 Determination of the Solubility Parameter for a Polymer by Swelling the Lightly Cross-linked Polymer in Different Solvents, and therefore different Solubility Parameters	65
Figure 2.8 Thermodynamic Properties of Various Solvents and their Effect on the %Elongation of Polypropylene Films	71
Figure 2.9 Comparison of the Yield Properties for the Polypropylene Films as a Function of Exposure Time and Solvent	73
Figure 2.10 Cross-sectional View of a Common, Single-Screw Extruder	78
Figure 2.11 Cross-sectional Representation of the Melting, Mixing, and Pumping Zone of a Single-Screw Extruder	80
Figure 2.12 Reaction Mechanism for the Peroxide Degradation of PP	82

Figure 2.13 Various Industrially Important Organic Peroxides	83
Figure 2.14 The Effect of Peroxide Concentration and Screw Speed on the Melt Flow Index of the Polypropylene	87
Figure 2.15 Melt Flow Index as a function of Peroxide Concentration in the Reactive Extrusion of Polypropylene performed by Dorn	89
Figure 2.16 Shear Viscosity as a Function of Peroxide Concentration and Molecular Weight as a Function of Peroxide Concentration for the Reactive Extrusion	90
Figure 2.17 Stress at Maximum Load and Percent Strain at Maximum Load as a Function of PET Concentration for Recycled Composites	93
Figure 2.18 Effect of the Recycling on the Melt Flow Index as a Function of the Number of Cycles for the two Liquid Crystalline Polymers	96
Figure 2.19 Effect of the Recycling on Young's Modulus and the Tensile Strength as a Function of the Number of Cycles	97

CHAPTER 3:

Figure 3.1 Schematic of the Reclamation Process	122
Figure 3.2 A Comparison of the Machine Direction, Tensile Modulus of In Situ Composites of 40 wt% Pure HX8000 / 60 wt% PP 6523 (Control) and Three Composites whose 40 wt% HX8000 Component contains Various Fractions of Reclaimed HX8000	124
Figure 3.3 A Comparison of the Machine Direction, Tensile Strength of In Situ Composites of 40 wt% Pure HX8000 / 60 wt% PP 6523 (Control) and Three Composites whose 40 wt% HX8000 Component contains Various Fractions of Reclaimed HX8000	125
Figure 3.4 A Comparison of the Machine Direction, Flexural Modulus of In Situ Composites of 40 wt% Pure HX8000 / 60 wt% PP 6523 (Control) and Three Composites whose 40 wt% HX8000 Component contains Various Fractions of Reclaimed HX8000	127

Figure 3.5 A Comparison of the Machine Direction, Flexural Strength of In Situ Composites of 40 wt% Pure HX8000 / 60 wt% PP 6523 (Control) and Three Composites whose 40 wt% HX8000 Component contains Various Fractions of Reclaimed HX8000 128

Figure 3.6 Complex Viscosity ($|\eta^*|$) vs. Angular Frequency (ω) Comparison between Pure HX8000 = (—□—) and 97% Pure Reclaimed HX8000 = (—Δ—) 130

Figure 3.7 Shear Viscosity vs. Shear Rate Comparison between the Pure HX8000 = (—□—) and the 97% Pure, Reclaimed HX8000 = (—Δ—). Run at 290°C 132

Figure 3.8 Complex Viscosity ($|\eta^*|$) vs. Temperature (Cooling Curve) for Pure HX8000 = (—●—) and Reclaimed HX8000 = (—□—). Run at 2.3°C/min and 10 rad/sec 133

CHAPTER 4:

Figure 4.1 Thermogravimetric Analysis (TGA) of the Pure HX8000 = (—), Reclaimed HX8000 = (—), and of the Control Sample of 40 wt% HX8000 / 60 wt% PP 6523 = (—), which were held at 300°C for ~25 minutes 155

Figure 4.2 A Comparison of the Machine Direction, Tensile Properties of Injection Molded Plaques of Pure HX8000 and Two Blends of Reclaimed HX8000 with Pure HX8000. (—●—) = Tensile Strength and (—□—) = Tensile Modulus 157

Figure 4.3 A Comparison of the Machine Direction, Flexural Properties of Pure HX8000 and Two Blends of Reclaimed HX8000 with Pure HX8000. (—●—) = Flexural Strength and (—□—) = Flexural Modulus 158

Figure 4.4 Complex Viscosity ($|\eta^*|$) vs. Angular Frequency (ω) Comparison among the Pure HX8000 = (—□—), the 40 wt% Reclaimed / 60 wt% Pure HX8000 = (—x—), and the 97 wt% Pure, Reclaimed HX8000 = (—Δ—) 160

Figure 4.5 Shear Viscosity vs. Shear Rate Comparison among the Pure HX8000 = (—□—), the 40 wt% Reclaimed / 60 wt% Pure HX8000 = (—x—), and the 97 wt% Pure, Reclaimed HX8000 = (—Δ—) 162

Figure 4.6 Scanning Electron Micrograph of the 96 wt% Pure HX8000 Compression Molded Plaque (cross-section) showing the Dominance of HX8000 with an Inclusion of Degraded PP 6523 165

Figure 4.7 Scanning Electron Micrograph of an Injection Molded Plaque (cross-section / transverse) of the 20 wt% Reclaimed HX8000 / 80 wt% Pure HX8000 showing the Very Small Inclusions of Degraded PP 6523	166
Figure 4.8 Scanning Electron Micrograph of the Same 20 wt% Reclaimed / 80 wt% Pure HX8000 Plaque showing a Closer View of the Scale of the Degraded PP 6523 Inclusions	167
Figure 4.9 DSC Heating Scans of Pure HX8000, Reclaimed HX8000, and Pure PP 6523, using a Heating Rate of 10.0°C/min and Normalized to 1.0 mg.	169
Figure 4.10 DSC Cooling Scans of Pure HX8000, Reclaimed HX8000, and Pure PP 6523, using a Cooling Rate of 10.0°C/min and Normalized to 1.0 mg	170

APPENDIX A:

Figure A.1 Cumberland Polymeric Material Granulator used to render the In situ Composites (40 wt% HX8000 / 60 wt% PP 6523) into Pieces	179
Figure A.2 Spool of Composite Fiber (40 wt% HX8000 / 60 wt% PP 6523) that was generated in the Dual Extrusion Process and the Granulated Pieces for Reactive Extrusion	180
Figure A.3 Reclamation Process which consists of the Single Screw Extruder for Reactive Extrusion and the Light Mineral Oil Bath for PP Dissolution	181
Figure A.4 Close-up of the Mineral Oil Dissolution Process that shows the Impeller and the Screening System with leftover Reclaimed HX8000 Pieces	182
Figure A.5 Fisher Scientific Marathon 21K/R Centrifuge used to Separate the Pieces of Reclaimed HX8000 from the Mineral Oil, the Kerosene, and the Hexanes	183
Figure A.6 Arburg Allrounder Injection Molder (Model 221-55-250) used to generate the Injection Molded In situ Composites and Plaques	184

APPENDIX B:

Figure B.1 Complex Viscosity ($ \eta^* $) vs. Angular Frequency (ω) Comparison among Pure HX8000 = (\square), Pure HX8000 run through the Reactive Extrusion Process = (x), 40 wt% Reclaimed / 60 wt% Pure HX8000 = (*), and 97 wt% Pure Reclaimed HX8000 = (Δ). Run at 290°C, 5.0% strain, 25 mm parallel plates, and a 1.0 mm gap	186
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Figure B.2 Complex Viscosity ($|\eta^*|$) vs. Angular Frequency (ω) Comparison among Pure HX8000 = (\square), Pure HX8000 run through the Reactive Extrusion Process = (x), 40 wt% Reclaimed / 60 wt% Pure HX8000 = (*), and 97 wt% Pure Reclaimed HX8000 = (Δ). Run at 310°C, 5.0% strain, 25 mm parallel plates, and a 1.0 mm gap 187

Figure B.3 Complex Viscosity ($|\eta^*|$) vs. Angular Frequency (ω) Comparison among Pure HX8000 = (\square), Pure HX8000 run through the Reactive Extrusion Process = (x), 40 wt% Reclaimed / 60 wt% Pure HX8000 = (*), and 97 wt% Pure Reclaimed HX8000 = (Δ). Run at 330°C, 5.0% strain, 25 mm parallel plates, and a 1.0 mm gap 188

Figure B.4 Complex Viscosity ($|\eta^*|$) vs. Angular Frequency (ω) Comparison among Pure HX8000 = (\square), 40 wt% Reclaimed / 60 wt% Pure HX8000 = (x), and 97 wt% Pure Reclaimed HX8000 = (Δ). Run at 310°C, 5.0% strain, 25 mm parallel plates, and a 1.0 mm gap 189

Figure B.5 Complex Viscosity ($|\eta^*|$) vs. Angular Frequency (ω) Comparison among Pure HX8000 = (\square), 40 wt% Reclaimed / 60 wt% Pure HX8000 = (x), and 97 wt% Pure Reclaimed HX8000 = (Δ). Run at 330°C, 5.0% strain, 25 mm parallel plates, and a 1.0 mm gap 190

Figure B.6 Complex Viscosity ($|\eta^*|$) vs. Angular Frequency (ω) for Pure Polypropylene, Montell PP 6523 at 5 Different Temperatures. 190°C = (\square), 210°C = (o), 230°C = (Δ), 250°C = (x), and 270°C = (+). Run at 5.0% strain, 25 mm parallel plates, and a 1.0 mm gap 191

Figure B.7 Complex Viscosity ($|\eta^*|$) vs. Angular Frequency (ω) for 1.0 wt% Dicumyl Peroxide Reacted, Polypropylene (Montell PP 6523) at 5 Different Temperatures. 190°C = (\square), 210°C = (o), 230°C = (Δ), 250°C = (x), and 270°C = (+). Run at 5.0% strain, 25 mm parallel plates, and a 1.0 mm gap 192

APPENDIX C:

Figure C.1 DMTA Data of Storage Modulus (G') and Loss Modulus (G'') for Two Separate Runs of Pure HX8000 Injection Molded Plaques (Machine Direction). Run from 30°C to 300°C at a Rate of 2.5°C/min, at a Angular Frequency (ω) of 10 rad/sec, and at a Strain of 0.1%. Run #1 Storage Modulus = (\square), Run #1 Loss Modulus = (o), Run #2 Storage Modulus = (Δ), and Run #2 Loss Modulus = (∇) 194

Figure C.2 DMTA Data of Storage Modulus (G') and Loss Modulus (G'') for 20 wt% Reclaimed / 80 wt% Pure HX8000 Injection Molded Plaque. Run from 30°C to 300°C at a Rate of 2.5°C/min, at a Angular Frequency (ω) of 10 rad/sec, and at a Strain of 0.1%. Storage Modulus = (\square) and Loss Modulus = (o) 195

Figure C.3 DMTA Data of Storage Modulus (G') and Loss Modulus (G'') for the 40 wt% Reclaimed / 60 wt% Pure HX8000 Injection Molded Plaque. Run from 30°C to 300°C at a Rate of 2.5°C/min, at a Angular Frequency (ω) of 10 rad/sec, and at a Strain of 0.1%. Storage Modulus = (\square) and Loss Modulus = (o) 198

List of Tables

CHAPTER 1:

Table 1.1 Examples of Thermotropic and Lyotropic Liquid Crystalline Polymers that can be found in Industry	3
Table 1.2 Commercially Available Thermotropic Liquid Crystalline Polymers	5
Table 1.3 General Mechanical and Physical Properties for certain Thermotropic Liquid Crystalline Polymers	8
Table 1.4 Properties of Amoco Xydar and Hoechst-Celanese Vectran Series	9
Table 1.5 Moduli for Some Spun Fibers of Thermotropic Liquid Crystalline Polymers	11
Table 1.6 The Composition and Commercial Names for Some TLCs	14
Table 1.7 Mechanical Properties (Machine Direction) of In situ Composites	15
Table 1.8 A Comparison of Modulus from Conventional Injection Molded Plaques and Pre-generated Micro Composite Fibers	20
Table 1.9 Experimental Extraction Efficiencies Using Single Solvent Selective Dissolution	29

CHAPTER 2:

Table 2.1 Data from the Process for the Separation of Carpet Materials	44
Table 2.2 Experimental Extraction Efficiencies Using Single Solvent Selective Dissolution	49
Table 2.3 Various Blends of an Undisclosed Liquid Crystalline Polymer and Thermoplastics, and their Mechanical Properties, that were used in the Japanese Study for Regrinding / Reprocessing Recycling	52
Table 2.4 Half-lives and their Temperature Dependence for Various, Industrially Important Organic Peroxides	84

CHAPTER 3:

Table 3.1 The Composition and Commercial Names for Some TLCPs 107

Table 3.2 Experimental Extraction Efficiencies Using Single Solvent
Selective Dissolution 112

Table 3.3 Properties of the Thermotropic Liquid Crystalline Polymer
(HX8000) and the Polypropylene Matrix (PP 6523) 119

CHAPTER 4:

Table 4.1 The Composition and Commercial Names for Some TLCPs 146

1.0 Introduction

The purpose of this chapter is to introduce the reader to composite materials based on thermoplastics (TPs) reinforced with thermotropic liquid crystalline polymers (TLCPs) and to discuss the importance of reclaiming these components from such intimately blended systems. Thermotropic liquid crystalline polymers, with respect to their composition and to their reinforcing potential, are discussed in Section 1.1. The area of In situ composites and pre-generated micro-composites, that are generated from TLCPs and thermoplastics, is discussed in Section 1.2. Current recycling technology, for the separation of intimately blended systems, is discussed in Section 1.3. The need to recycle thermotropic liquid crystalline polymers is discussed in Section 1.4. Lastly, the objectives of this research are given in Section 1.5.

1.1 Thermotropic Liquid Crystalline Polymer

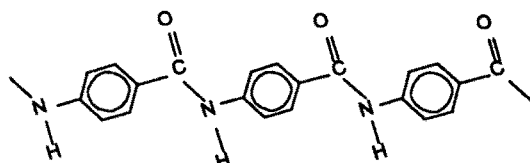
A brief review of thermotropic liquid crystalline polymers and their reinforcing potential is discussed in this section. It is focused on the structure and the phase behavior of these polymers, and how these areas led to their use as a reinforcing agent in thermoplastic materials. The basic chemical structure and the phase behavior of these polymers are discussed in Section 1.1.1. The mechanical and physical properties of these materials are discussed in Section 1.1.2.

1.1.1 Chemical Structure and Phase Behavior of TLCPs

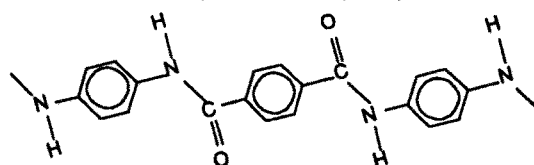
The discovery of aramids, such as Kevlar or poly (p-phenylene terephthalamide), by DuPont in the mid 1970's has resulted in unparalleled academic and industrial research over the past 28 years in the area of liquid crystalline polymers [1]. These aramids, or aromatic polyamides, form liquid crystalline states when dissolved in solvents such as sulfuric acid, and therefore are termed lyotropic liquid crystalline polymers. More recently, a new series of aromatic copolyesters, that form liquid crystalline states upon melting (thermotropic), have seen tremendous commercial growth. Some examples of these new thermotropic liquid crystalline polymers are Xydar (made by Amoco) and Vectra (made by Hoechst-Celanese). These two thermotropic liquid crystalline polymers, as well as some lyotropic liquid crystalline polymers, can be seen in Table 1.1.

Table 1.1 Examples of Thermotropic and Lyotropic Liquid Crystalline Polymers that can be found in Industry. (Table from M.A. McLeod, *Ph.D. Dissertation*, Virginia Polytechnic Institute and State University, 1997.)

Lyotropic Liquid Crystalline Polymers

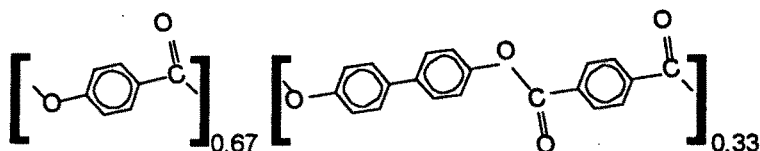


Polybenzamide (PBA)

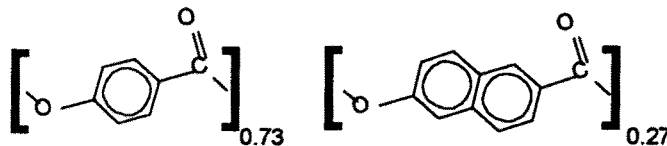


Poly(1,4-phenylene terephthalamide) (PPTA)

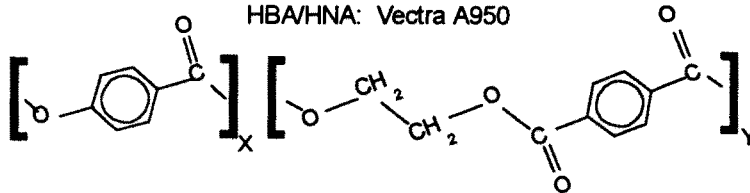
Thermotropic Liquid Crystalline Polymers



HBA/BP-TA: Xydar (formerly Ekkcel I-2000)



HBA/HNA: Vectra A950



HBA/PET: Rodrun (formerly XG-7)

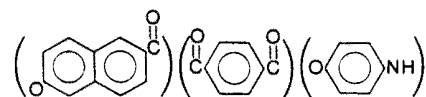
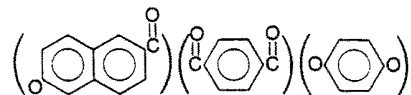
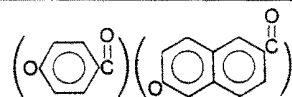
Liquid crystallinity is a term that signifies materials that contain partially ordered states and whose molecular order lies somewhere between the crystalline and liquid state. Due to this molecular ordering, liquid crystalline phases are anisotropic in nature. Therefore, their properties are strongly dependent on direction. This liquid crystalline state or phase is a function of either plate-like structures or rigid segments with a high axial ratio. These segments or structures are often referred to as mesogenic units.

Liquid crystalline polymers commonly have the same type or form of backbone along the polymeric chain. This backbone is comprised of the before mentioned mesogenic units or structures. For instance, the thermotropic aromatic polyesters usually consist of one or more of the following combinations of units: 1) long runs of rectilinear units, 2) an alternating sequence of flexible and rigid units, or 3) rigid unit spacers along the main backbone of the polymer. These mesogenic units usually contain two or three aromatic or aliphatic rings that are joined together by ester or amide linkages, which help to maintain a linear arrangement of the rings.

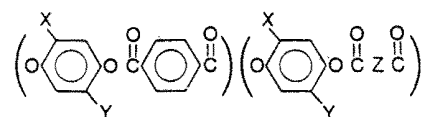
Synthesis of these mesogenic units typically comes in the form of reacting the following species: 1) terephthalic acid, 2) 2,6-naphthalene dicarboxylic acid, 3) p-hydroxybenzoic acid, 4) hydroquinone, and 5) p,p'-biphenol. In the case of Xydar, the reaction of p-hydroxybenzoic acid, terephthalic acid, and p,p'-biphenol is utilized to generate this thermotropic liquid crystalline polymer. Some more examples of commercially available thermotropic liquid crystalline polymers, that contain these mesogenic units, can be seen in Table 1.2.

Table 1.2 Commercially Available Thermotropic Liquid Crystalline Polymers. (Table from W.A. MacDonald, *Polymeric Materials Encyclopedia*, J. C. Salome (ed.), **5**, 3697, 1996.)

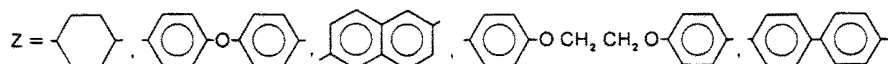
Celanese



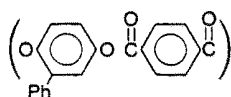
Dupont



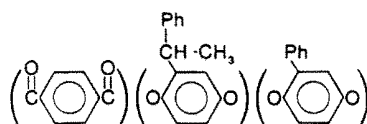
X and Y = -H, -Cl, -Br, -CH₃



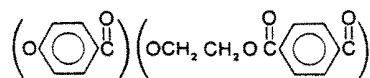
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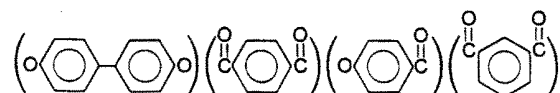
Owens Corning
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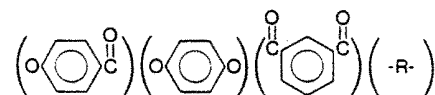
Eastman Kodak



Carborundum
(Amoco)



ICI



R - aromatic diol, carboxylic acid, hydroxy acid (less than 2%)

Source: Reference 25.

From both Table 1.1 and Table 1.2, it can be seen that these thermotropic and lyotropic liquid crystalline polymers have basically the same units in their backbones. Lyotropic liquid crystalline polymers usually contain many aromatic groups that are coupled together, along the main chain, by amide bonds. It is these amide bonds, that interact with solvents such as sulfuric acid, which lead to the partially ordered states of liquid crystallinity. As for the thermotropic liquid crystalline polymers, the main chain in these type of polymers consist of the same aromatic groups, but are instead bound together by ester bonds. What is common among both, aside from the aromatic groups or mesogenic units, is that there are no aliphatic linkages along the main chain backbone.

In conclusion, thermotropic liquid crystalline polymers contain mesogenic units that are comprised of aromatic or aliphatic rings bonded together by ester or amide linkages. These ester or amide linkages help maintain the linear nature of the backbone for these thermotropic liquid crystalline polymers. These same linkages also allow for some conformational mobility of the rigid backbone which leads to liquid crystalline phases in the melt state. These liquid crystalline phases, brought on by the molecular ordering of these units, are anisotropic in nature. Therefore, the properties of these polymers are strongly dependent on direction. The next section will deal with the properties of these thermotropic liquid crystalline polymers.

1.1.2 Mechanical and Physical Properties of TLCPs

Thermotropic liquid crystalline polymers exhibit many physical and mechanical properties which make them commercially attractive. These properties include high modulus, high strength, good barrier properties, excellent surface features, low coefficient of thermal expansion, thermal stability, great dielectric properties, and a high resistance to chemicals [4, 5, 6]. Some commercially available (unfilled) thermotropic liquid crystalline polymers, that exhibit these properties, are: 1) DuPont HX2000, 2) Hoechst-Celanese Vectran A950, 3) Hoechst-Celanese Vectran B950, 4) BASF Victrex SRP1500G, and 5) BASF Victrex SRP2300G. The general physical and mechanical properties, and not necessarily the maximum properties attainable, of these thermotropic liquid crystalline polymers can be seen in Table 1.3. With densities as low as 1.27 g/cm^3 and mechanical properties as high as 230 MPa for tensile strength and 28.3 GPa for tensile modulus, these TLCPs are very attractive to such industries as the automotive, aerospace, and aeronautical industries.

Much work has been done on the processing, and subsequent property determination, of these thermotropic liquid crystalline polymers [2, 6-13]. The main forms of processing these thermotropic liquid crystalline polymers are injection molding, fiber spinning, filament extrusion / drawing, and film extrusion / drawing. The properties of injection molded bars of two of the leading thermotropic liquid crystalline polymers on the market, Amoco Xydar and the Hoechst-Celanese Vectran series, can be seen in Table 1.4.

Table 1.3 General Mechanical and Physical Properties for certain Thermotropic Liquid Crystalline Polymers. (Table from G.D. Figuly, *Polymeric Materials Encyclopedia*, J.C. Salome (ed.), 5, 3731, 1996.)

Properties	Values ^a
A. General Properties	
Specific Gravity (g/cc)	1.27–1.40
Water absorption (immersion to equilibrium at 23 °C) (%)	0.02–0.20
Mold shrinkage (flow direction) (%)	0.0–0.20
(Transverse Direction) (%)	0.2–0.3
Tolerance (%)	0.006–0.023
B. Mechanical properties (at 23 °C)	
Tensile strength at break (MPa)	117–230
Tensile impact strength (KJ/m ²)	59–115
Tensile modulus (GPa)	9.7–28.3
Tensile elongation at break (%)	0.6–8.0
Flexural strength (MPa)	169–276
Flexural modulus (GPa)	9.0–17.9
Compressive strength (MPa)	70
Compressive modulus (GPa)	6.3
Izod impact strength: Notched (J/m)	197–931
Unnotched (J/m)	785–no break
Hardness (Rockwell) (M scale)	66–80
Shear strength (MPa)	105–129
Taber abrasion (mg/1000 cycles)	56
Coeff. of friction against metal: dynamic	0.12
static	0.14
C. Thermal properties	
Melting point (°C)	Amorphous–280
Heat deflection temperature (at 264 psi 1.82 N/mm ²) (°C)	180–200
Coefficient of thermal expansion: flow direction	(–5)–14
–50 °C to 200 °C (cm/cm/°C × 10 ^{–6}); transverse to flow	27–76
Glass transition temp. (°C)	110–150
Thermal conductivity (W/m-K)	0.15–0.21
Heat distortion temperature (°C)	170–190
D. Electrical properties	
Dielectric strength (KV/mm)	22–39
23 °C, 50% RH, short term, 1.5 mm thickness	
Dielectric constant 1 KHz	3.3–3.6
1 MHz	3.0–3.6
Dissipation factor 1 GHz	0.0015–0.007
Arc resistance (seconds)	74–137
Volume resistivity (ohm-cm)	10 ¹⁶ –10 ¹⁷
Comparative tracking index (V)	150–175
E. Flammability	
Limiting oxygen index (LOI)	35–50
Underwriters laboratory ratings (UL94) @ minimum thickness (mm)	V-O at 0.43–3.2 mm
Smoke density: flaming mode (3.2 mm thick sample)	95–221
Glow wire test (2 mm thick sample) (°C)	960
Flammability rating: avg. extent of burn (AEB) (mm)	< 5
(1.8 mm thick sample): avg. time of burn (ATB) (sec)	< 5

^aRanges of properties reported for unfilled grades of Vectran® (A950 and B950) (Hoechst-Celanese), HX®-2000 (DuPont), Victrex® (SRP1500G and SRP2300G) (ICI) LCPs.

Table 1.4 Properties of Injection Molded Bars of Amoco Xydar and Hoechst-Celanese Vectran Series. (Table from J. Jin, *Polymeric Materials Encyclopedia*, J.C. Salome (ed.), 5, 3645, 1996.)

Property	Xydar	Vectra
Tensile strength, MPa	126	138–241
Tensile modulus, GPa	8.3	9.6–38
Elongation, %	5	1.2–5.5
Flexural strength, MPa	131	151–296
Izod impact strength, J/m		
Notched	208	53–534
Unnotched	454	
Density, g/cm ³	1.35	
T_m or Vicat softening point, °C	358	275–330
Coefficient thermal expansion, ppm, °C		
Flow		0–27
Transverse		27–54
Mold shrinkage		0.006
Mold temperature, °C		50–150

Source: Reference 84. With permission.

What can be seen from both of these tables is that the Vectran series can generate a broad range of mechanical properties. For instance, the tensile strength ranges from 138 to 241 MPa, while the tensile modulus ranges from 9.6 to 38 GPa for injection molded samples.

Higher properties are realized in the fiber spinning of these thermotropic liquid crystalline polymers. The moduli of these spun fibers, made from a few of these thermotropic liquid crystalline polymers, can be seen in Table 1.5. The modulus for the Vectran series, Vectran A950 and Vectran B950, increases from 38 GPa to 65 and 75 GPa, respectively, for the spun fibers as compared to the injection molded bars. The other form of processing, film extrusion / drawing, is omitted due to the lower mechanical properties seen in this form of TLCP processing.

In conclusion, thermotropic liquid crystalline polymers exhibit a wide range of commercially attractive properties such as: 1) high modulus, 2) high strength, 3) good barrier properties, 4) excellent surface features, 5) low coefficient of thermal expansion, 6) thermal stability, 7) great dielectric properties, and 8) a high resistance to chemicals. The highest mechanical properties are realized in the form of spun fibers. However, these polymers are very expensive to produce. Therefore, the addition of these TLCPs to cheap engineering thermoplastics represents a way to generate composites that have excellent properties and a lower cost. The next section will deal the area of wholly thermoplastic composites generated from thermoplastics reinforced with thermotropic liquid crystalline polymers.

Table 1.5 Moduli for Some Spun Fibers of Thermotropic Liquid Crystalline Polymers.
 (Table from D.G. Baird and A.M. Sukhadia, *U.S. Patent No. 5,225,488*, 1993.)

Fiber	Composition	Modulus (GPa)
Vectran A	73/27 HBA/HNA	65
Vectran B	Copolyesteramide	75
60% HBA/PET	HBA/PET	50
B-7	HBA/BBA/TA/IA	100
B-6-2	HBA/BBA/TA/IA	90

HBA, *p*-hydroxybenzoic acid; HNA, 2-hydroxy-6-naphthoic acid; PET, poly(ethylene terephthalate); BBA, *p,p*-biphenol bisacetate; TA, terephthalic acid; IA, isophthalic acid.

1.2 Composites Based on TLCP / Thermoplastic Blends

A short synopsis of In situ composites and of pre-generated micro composites is given in this section. The focus will be on how these composites are generated, what the inherent properties of these composites are, and how the physical properties of these composites led to the current work of developing a process to separate and reclaim the liquid crystalline component. The area of In situ composites, how they are processed, and the level of mechanical properties generated by these composites is discussed in Section 1.2.1. And the physical and mechanical properties of these composites, with respect to their importance in developing a successful reclamation process, are discussed in Section 1.2.2.

1.2.1 In situ Composites

In situ composites are typically generated by subjecting the blend of a thermotropic liquid crystalline polymer (TLCP) and a thermoplastic (TP) to an extensional flow during processing. During this extensional flow, the thermotropic liquid crystalline polymer drops are elongated from spheres into fibrils. These fibrils are oriented and cooled to lock in orientation and morphology. Because the reinforcing fibrils are generated during the processing step, these composites are referred to as *In situ* composites. Generally, the main forms of processing these TLCP / TP composites are: 1) injection molding, 2) fiber spinning, 3) filament extrusion / drawing, and 4) film extrusion / drawing.

Much work has been done on the addition of thermotropic liquid crystalline polymers to thermoplastics to enhance the overall mechanical properties of the thermoplastic materials [2, 9-13]. One of the first studies that reported on In situ composites was done by Kiss [8]. In this study, various thermoplastics were reinforced with a thermotropic copolyester and a copolyesteramide. Some of the thermoplastics used were: 1) polycarbonate (PC), 2) poly(butylene terephthalate) (PBT), 3) poly(ether ether ketone) (PEEK), 4) poly(ether imide) (PEI), and 5) polyarylate (PAR). Even more work has been done, since this study, on the addition of TLCPs to such other thermoplastics as polypropylene (PP), polyethylene terephthalate (PET), and polystyrene (PS) [8, 9, 16-22]. The composition and commercial names of a few of these thermotropic liquid crystalline polymers can be seen in Table 1.6. The mechanical properties, only in the machine direction, that were reported in these studies can be seen in Table 1.7. From this table, it

Table 1.6 The Composition and Commercial Names for Some TLCs. (Table from D.G. Baird, *Polymeric Materials Encyclopedia*, J.C. Salome (ed.), 5, 3207, 1996.)

Article name	Commercial name	Supplier	Composition
PET/60% HBA	—	Unitca	PET/HBA
Vectra A	Vectra A900/950	Hoechst-Celanese	HBA/HNA
Vectra B	Vectra B900/950	Hoechst-Celanese	HBA/HNA/AP
Vectra RD500	Vectra RD500	Hoechst-Celanese	HBA/HNA/HQ
SBH	—	Eniricerche	SA/HBA/BP
K161	—	Bayer	HBA/TA/TA/HQ/BP
—	Granular	Granmont	TA/PhHQ/StHQ
HX1000	—	DuPont	Based on HQ and TA ^a
HX4000	—	DuPont	Based on HQ and TA ^a

PET, poly(ethylene terephthalate); HBA, 4-hydroxybenzoic acid; HNA, 2-hydroxy-6-naphthoic acid; TA, terephthalic acid; SA, sebacic acid; AP, aminophenol; HQ, hydroquinone; IA, isophthalic acid; BP, 4,4'-dihydroxybiphenol; PhHQ, phenyl hydroquinone; and StHQ, styryl hydroquinone.

^aOther molar constituents are proprietary.

Table 1.7 Mechanical Properties (Machine Direction) of In situ Composites. (Table from D.G. Baird, *Polymeric Materials Encyclopedia*, J.C. Salome (ed.), **5**, 3207, 1996.)

Thermoplastic	TLCP composition	Injection-molded parts				Test part	Fibers/strands				Test part
		<i>E</i> (GPa)	σ (MPa)	% ΔE	% $\Delta\sigma$		<i>E</i> (GPa)	σ (MPa)	% $\Delta\sigma$	% ΔE	
PP	20% 60% HBA/PET ^a	2.90	30.21	110.1	12.3	PQ					
	20% 60% HBA/PET ^a	3.59	41.19	162.0	31.9	TB					
	30% Vectra A ^a	3.79	34.45	174.6	14.0	PQ					
	30% Vectra A ^a	4.26	49.88	210.9	59.7	TB					
	30% Vectra B ^a	4.01	37.55	190.6	39.6	PQ					
	30% Vectra B ^a	5.28	50.31	285.4	61.0	TB					
	20% SBH						5.00	130	31.6	-3.84	F
	30% Vectra A	2.94	44	62.7	29.4	TB					
	28% Vectra A						4.71	—	584.5		S ^a
	26% Vectra B						13.47	—	1857		S ^a
24% 60% HBA/PET						2.67	—	288.1		S ^a	
PET	30% Vectra A						18.99	—	840.1		S ^a
	20% Ultrax						8.28	—	309.9		S ^a
	30% Vectra A	5.50	84	109.1	37.7	TB					
	20% Vectra A	3.42	103.7	82.9	67.1	PQ					
	20% HX4000	4.71	57	151.9	-13.6	PQ					
	10% 60% HBA/PET						1.2	57	20	42.5	F
PS	20% Vectra A						11.1	—	344		S
	10% 60% HBA/PET	1.67	22.5	15	-20	PQ					
	25% Vectra A	3.80	33.4	19	4	PQ					
	25% Vectra B	4.80	38.7	50	21	PQ					
PC	10% 60% HBA/PET						1.6	1.6	6.6	-33.3	F
	40% Vectra B						23	—	360	—	F
PC	30% Vectra A	5.72	121	147	81	TB					
	30% Vectra B	6.55	154	182	130	TB					
	10% 75/25 HBA/HNA	3.50	80	133	33	PQ					
	30% Vectra A						9.9	—	267	—	F
	30% Granlar						5.9	—	118	—	F
PEI	30% Vectra A	8.10	—	170	—	TB					
	30% HX1000	8.70	129	190	22.9	TB					
	30% HX4000	9.80	152	226	44.8	TB					
	30% K161						7	—	133		F
	30% Granlar						10.1	—	170		F

E, elastic modulus; σ , tensile strength; % ΔE , percent change in modulus; % $\Delta\sigma$, percent change in strength; F, spun fibers; S, extruded strand; PQ, plaques; TB, tensile bars.
^aCompatibilized with 10% maleic anhydride-modified PP (MAP).

can be seen that the addition of a small amount of a thermotropic liquid crystalline polymer into a thermoplastic results in increased mechanical properties. It can also be seen from this table, Table 1.7, that the highest tensile properties are generated by the fiber spinning or filament (strand) extrusion and drawing.

As can also be seen from Table 1.7, the main form of generating In situ composites is injection molding. However, some work has been done on improving the mechanical properties of injection molded plaques by blending the TLCP and thermoplastic in an extruder prior to injection molding [16, 23]. In other cases, the extrusion system is fit with a static mixer that will thoroughly mix and fibrillate the TLCP prior to injection molding [23, 24]. These other methods were also performed in order to eliminate the problem of anisotropy found in these In situ composites. These composite were found to be anisotropic in nature as a function of cross-section. For instance, a cross-sectional view along the transverse direction, showed that there were more TLCP fibrils along the outer skin region, than in the core region [6]. This type of morphological anisotropy has been termed as skin-core effects. Although these techniques are successful in further enhancing the mechanical properties, the problem of anisotropy was not eliminated.

However, there is one blending method, represented in Table 1.7, that is very different and seems to greatly reduce this problem of anisotropy. This method is the dual extrusion technique patented by Baird et al. [10]. This unique process, which utilizes two single-screw extruders, represents a novel method of generating excellent mechanical properties in In situ composites. In this system ,see Figure 1.1, the two extruders separately plasticate the thermotropic liquid crystalline polymer and the engineering

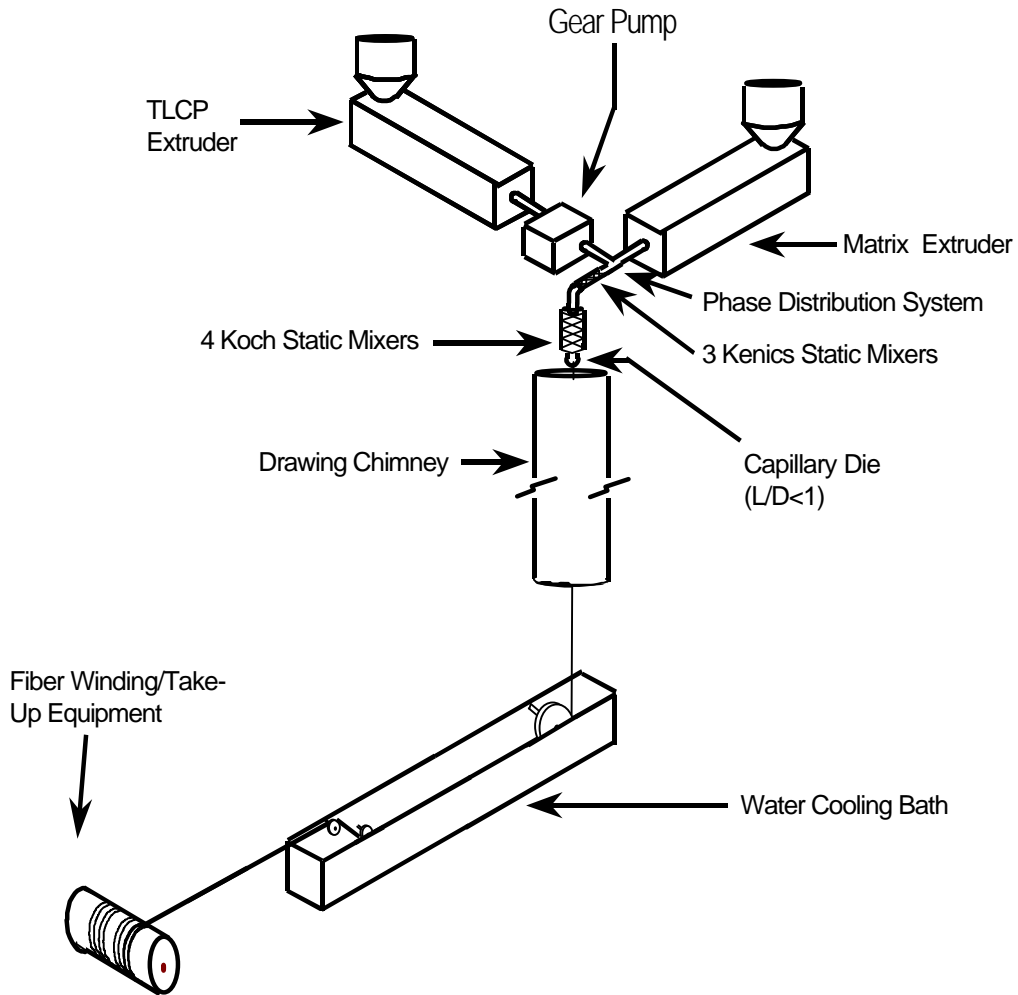


Figure 1.1 The Dual Extrusion Process developed by Baird and Sukhadia (9). (Figure from M.A. McLeod, 1996.)

thermoplastic. From Figure 1.1, it can be seen that the two extruders are connected to a static mixer, where each stream is separated into multiple layers and combined together. Once the two polymeric streams are combined, the resulting strand from the capillary die can be drawn and collected on a take-up device. There are numerous advantages to this system: 1) since the two composite components are extruded separately, a TLCP and a thermoplastic, whose processing temperature ranges do not overlap, may still be processed into a composite, 2) because the mixing method uses a static mixer, continuous strands of the thermotropic liquid crystalline polymer can be generated, 3) because these composites have higher melt strengths, the composite fibers can be further drawn to increase properties.

In conclusion, there are many methods in which to generate these wholly thermoplastic composites. Traditional processing comes in the form of injection molding, strand extrusion, and film extrusion. However, these forms of processing are limited to systems of TLCPs and TPs with overlapping processing conditions. Furthermore, these processing methods produce In situ composites that exhibit anisotropy due to skin-core morphologies. Therefore, a new processing method was developed that not only reduced anisotropy, it allowed polymers with different processing windows to be used to generate composites. The next section will deal with a property comparison between this method and the others, why the ability to recycle these composites is advantageous, and why reclamation of the TLCP component is paramount to the recycling process.

1.2.2 The Need for a Reclamation Process

The differences in the mechanical properties of conventional injection molded plaques and pre-generated micro composites generated by using the dual extrusion process have been studied for various TLCPs and matrices [9, 13]. As can be seen in Table 1.8, there is a dramatic increase in the modulus for the pre-generated micro-composites over traditional, injection molded composites. For the 30 wt% Vectra A950 in polypropylene, there is a six fold increase in modulus for the fiber from the dual extrusion process over the injection molded plaque. Another major difference, as was stated in section 1.2.1, is that the pre-generated micro-composites are free of skin-core morphologies that are present in injection molded plaques. Therefore, the optimum processing method for generating In situ TLCP/TP composites is the dual extrusion process.

Unfortunately, the high cost of TLCPs represents a problem only when comparing this new form of composites to composite systems that are reinforced with glass fiber, because Kevlar and carbon fiber are more expensive [26, 27]. Currently, the cost of pure thermotropic liquid crystalline polymers ranges from \$8.00 to \$12.00 dollars a pound [28]. This is quite comparable to other traditional reinforcements used in thermoplastics. For instance, carbon fiber is around \$8.00 to \$30.00 per pound and Kevlar fiber is around \$15.00 per pound [29, 30]. However, with respect to the glass fiber used in composites, the cost of the TLCP is much higher than the \$1.00 per pound cost of this fiber [31]. Therefore, even though TLCP / TP composites have excellent mechanical and physical

Table 1.8 A Comparison of Modulus from Conventional Injection Molded Plaques and Pre-generated Micro Composite Fibers. (Data from A.A. Handlos, *Ph.D Dissertation*, Virginia Polytechnic Institute and State University, 1994.)

Composite System	Injection Molded Plaque Reported Modulus (GPa)	Pre-generated Micro Composite Fiber Reported Modulus (GPa)
30 wt% Vectra A / PP	2.16	13.5 DR = 40
20 wt% Vectra B / PET	3.42	11.1 DR = 35
30 wt% Vectra A / PET	5.50	13.0 DR = 80

properties, the overall cost of the thermotropic liquid crystalline polymer / thermoplastic composites is substantially higher than the cost of the glass filled composites. However, the cost of these TLCP / TP composites can be lowered and the marketability can be increased if there exists a way in which these composites can be recycled.

In order to recycle these wholly thermoplastic composite blends, and therefore lower their cost and increase their market potential, the proper method for recycling must be determined. Many recycling methods rely on merely grinding the composite blends and then reprocessing the materials into further composite blends [32]. These methods would work for the injection molded or the strand extruded composites, since these processes already involve compounding or mixing the materials together in one step. There has already been some work done in this area of reprocessing wholly thermoplastic composite strands by grinding up the recovered waste and then reintroducing them back into the process [33]. Sasaki et al. [33] found that polypropylene reinforced with an undisclosed TLCP can undergo ten of these grinding / reprocessing cycles and see no loss in tensile strength. Unfortunately, this form of recycling would only work for composites, whose components have overlapping processing temperatures, and for composites that are processed in the same device. Except for the dual extrusion method, these other processes do not require the separation of the polymers in order to reprocess them. Therefore, in order to utilize the dual extrusion process, recycling would require complete separation of the components in these TLCP / TP composites.

In conclusion, the dual extrusion process produces the highest properties of composites generated with thermotropic liquid crystalline polymers and engineering thermoplastics. This process also eliminates the problem of morphological anisotropy or skin-core morphologies by producing continuous strands of TLCP fibrils within the composite fiber. Furthermore, by being able to extrude the two components separately, TLCPs and TPs with non-overlapping processing windows can be used and the highest mechanical properties can be obtained. Additionally, the overall cost can be reduced and the marketability can be increased, if a method of recycling can be developed. However, only with complete separation can the pre-generated micro-composite be truly recycled. The next section will deal with the separation of well blended or mixed polymers.

1.3 The Separation of Two Intimately Blended Species

In recent years, the area of mixed plastics recycling has seen an increase in the amount of research performed [34]. Due to a desire to reuse the components of these blends, much work has been done on the separation of plastics from heterogeneous blends that consist of macroscopic pieces of each plastic component [34]. Unfortunately, no work has been found that deals with the separation of two, intimately blended polymers. Intimate blending refers to a state in which, the size of a pure phase in a blend is smaller than the size of the smallest particle possible from mechanical grinding. Therefore, this section deals with the current technologies for the separation of heterogeneous blends, what the important points are, and how they can be used for developing a new technology to separate well blended systems. Current industrial and academic technology, for the recycling of heterogeneous plastics mixes, is discussed in Section 1.3.1. The selective dissolution of polymers is discussed in Section 1.3.2. And, finally, the area of separating thermotropic liquid crystalline polymers from thermoplastic matrices is discussed in Section 1.3.3.

1.3.1 Mixed Plastics Recycling

In the area of recycling plastics, three methods are used to separate mixtures of polymers [34]. The first method of separation is called macro separation and it deals with separating large, pure components of polymers from each other. The second method of separation is called micro separation and it deals with the grinding of polymeric mixtures and then using density differences to effect a separation. The third method of separation is called molecular separation and it deals with dissolving the polymer(s) and then using temperature to bring about a separation. Therefore, depending on the system in question and how well the polymers are mixed, one of these three methods can be used to bring about the desired separation.

For the macro separation method to work, the mixture of polymeric pieces must contain large fractions of pure polymer within the mixed system. A good example of this method is the separation of different colored plastic components within a mixture of polymers. The differences in the way the polymeric materials reflect or absorb light, along with some form of mechanical, segregating device, can be used to bring about the desired separation. However, this method fails when the pure, polymeric components are adhered or blended together due to gluing or melt blending. Once this level of attachment has been reached, and depending on the level of blending, one of the other two separation methods must be used.

In the case of micro separation, since the respective polymers are adhered together, the pieces must be pre-processed in the form of grinding. Once the materials are ground into small enough pieces, the polymers can be separated using differences in

density. This type of separation relies on the principle that, though the polymers are adhered to each other, grinding of the materials results in a distribution of particles that contain some pure components of each of the polymers present. These pure components can then be separated by utilizing differences in density. However, this method only works if the polymers are not intimately blended. This level of mixing, or intimate blending, exists if the size of the pure component domain is smaller than the size of the ground particle. If this condition is present, then this method can not be used and the molecular method must be used. The next section will deal with the molecular separation method.

1.3.2 Selective Dissolution of Polymers

One of the new areas of separating mixed plastics is called molecular separation, and it deals with the use of a solvent to dissolve the polymers away from each other [34, 35]. Currently, this method is only being studied on the academic scale due to the use of expensive and / or toxic solvents. There are two methods used for this type of selective dissolution and separation method. The first method involves using one solvent to dissolve all of the mixed polymers and the second method involves using one solvent to only dissolve one polymer at a time. However, both techniques utilize the same basic steps in the separation process and both techniques lead to the relatively complete separation of two or more well mixed polymeric systems.

The first major step in the molecular separation method is called selective dissolution, while the second major step is called flash devolatilization [35]. As can be seen in Figure 1.2, the mixed polymeric material is ground up into very small pieces and then sent to the separation unit. The separation unit, or selective dissolution step, consists of adding the polymeric mixture to a solvent and then using the temperature to selectively dissolve certain components of the mixture. Once one of the polymers has been thoroughly and selectively dissolved, the next step is to filter the solution of non-dissolved contaminants and then to blend in some stabilizers. Once the stabilizers have been added, the next step is to take this solution to the flash devolatilization process. This process involves evaporating all of the solvent away from the plastic and thereby leaving a pure, solvent-free polymeric material. This technology is a hybrid of the technology used to generate microdispersions of one polymer in another polymer that are normally incompatible with each other. This process, of dispersing one incompatible polymer into another incompatible polymer, is known as compositional quenching [34]. The solvent vapor is then condensed and returned to the main solvating chamber to help in selectively dissolving the next polymer.

An example of some specific work, using this recycling method, was the separation of six engineering thermoplastics [34]. The solvent chosen to separate these thermoplastics was tetrahydrofuran (THF), which is a cyclic, aliphatic ether. The six engineering plastics chosen were: 1) polyvinyl chloride (PVC), 2) polystyrene (PS), 3) low density polyethylene (LDPE), 4) polypropylene (PP), 5) high density polyethylene (HDPE), and 6) polyethylene terephthalate (PET). This mixture of polymers was ground

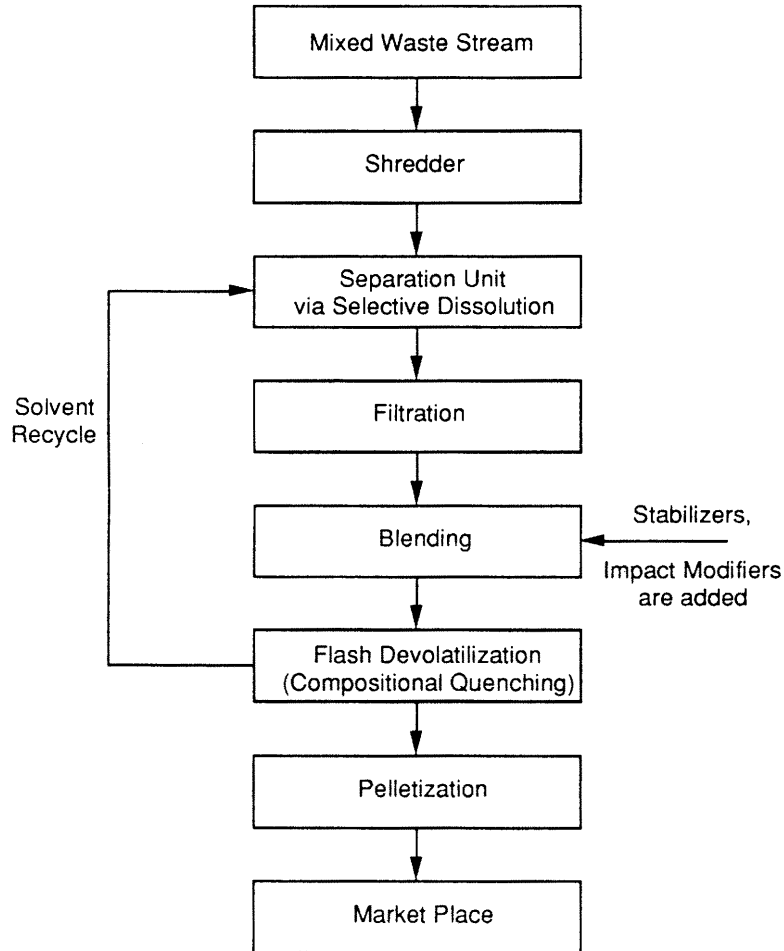


Figure 1.2 Single Solvent Dissolution Process Flow Sheet. (Figure from B.A. Hegberg, G.R. Brenniman, and W.H. Hallenbeck, *Mixed Plastics Recycling Technology*, Noyes Data Corp., Park Ridge, NJ, 1992.)

into small pieces and then dumped into the THF. Three different temperatures were used in the selective dissolution process (25, 160, and 190 °C), and three different extracts were sent to the flash devolatilization process. From Table 1.9, the efficiency and selectivity of each temperature can be seen. The first extraction led to the separation of both PVC and PS from the mixture to a degree of >99%. The second extraction led to the successful separation of only the LDPE from the mixture at an efficiency of >99%. The third extraction led to the separation of both HDPE and PP from the mixture at a degree of >99%. Finally, the last extraction led to the complete isolation of PET from the mixture at an efficiency of >99%. Even though the efficiencies of each separation were very high, only two of the six polymers were successfully reclaimed by themselves. The other four polymers were left commingled with another polymer. Therefore, it would still have been necessary to separate these polymers further by utilizing another solvent or solvents.

This type of separation method seems to be a viable process to utilize in order to separate well mixed polymers. Unfortunately, in the case of the Hegberg et al. [34] study, the level of mixing of these polymers was not very intimate. Intimately blended, polymeric systems, in which the size of the pure polymer components is on the order of microns, are not currently being separated using this technology. Since this process also relies on the ability of a chosen solvent to be able to dissolve all of the polymers present, not much work has been done on systems whose polymers are chemically and physically very different.

Table 1.9 Experimental Extraction Efficiencies Using Single Solvent Selective Dissolution. (Table from B.A. Hegberg, G.R. Brenniman, and W.H. Hallenbeck, *Mixed Plastics Recycling Technology*, Noyes Data Corp., Park Ridge, NJ, 1992.)

Material	Extraction	Temperature (°C)	Efficiency (%)
PVC	First	25	>99
PS	First	25	>99
LDPE	Second	70	>99
PP	Third	160	>99
HDPE	Third	160	>99
PET	Fourth	190	>99

- a. Experiments were conducted using virgin polymers. Tetrahydrofuran was the solvent used in dissolution.

In conclusion, traditional recycling of mixed plastics comes in the form of grinding down the mixture and either using density or solvent to bring about the desired separation. However, the grinding / density technique relies on the condition that the pure, polymeric phases are larger than the size of the ground particles. Furthermore, the selective dissolution technique relies on the ability of one solvent to be able to completely dissolve all or at least one of the polymers present. This process would not be able to handle encapsulated polymers or well blended polymers, where the solvent can only dissolve the trapped polymer and not the encasing polymer. Therefore, no work can be found that deals with the separation of a thermotropic liquid crystalline polymer from a wholly thermoplastic polymer. This seems to be a function of the level of mixing, the large differences in chemical properties between these two materials, and the fact that most forms of processing these composites do not require separation of these two materials in order to recycle them. However, as was seen in section 1.2.2, the optimum processing method, that realizes the highest mechanical properties, is the dual extrusion process. Therefore, in order to reproduce TLCP / TP composites, with the highest mechanical properties, the recycling method should be able to completely separate these two polymeric materials. Since the most important aspect of this recycling process is the reclamation of the expensive TLCP component, the next section will be a brief discussion on the area of reclaiming thermotropic liquid crystalline polymers.

1.4 Reclamation of TLCPs

As has been shown, much work has been done on the use of thermotropic liquid crystalline polymers to enhance the mechanical properties of traditional engineering thermoplastics. These works have been concerned with developing a wholly thermoplastic composite that can compete with and / or replace traditional carbon or glass fiber composites. These TLCP / TP composites offer the unique ability to be able to be melt processed, thermoformed, or compression molded rapidly, in order to form complex parts. These types of processing methods would prove almost impossible for glass or carbon fiber composites. Since the carbon fiber and the glass fiber are not thermoplastics, melt processing of these two fibers is either impossible or would require such high temperatures that the matrix would thermally degrade. However, the current cost associated with these TLCP based composites is higher than the cost associated with these carbon or glass fiber composites.

The ability to recycle or reclaim the thermotropic liquid crystalline polymer component of these wholly thermoplastic composites would be very cost effective. It would also make these composites more economically and environmentally attractive than the traditional composites. Unfortunately, due to the relative youth of these pre-generated micro-composites, no work can be found that deals with the separation and reclamation of the TLCP component. Because of the lack of work, and the benefit it would bring, this work will be about the development of such a reclamation process.

1.5 Research Objectives

As has been shown in Section 1.2.2, these composites have excellent mechanical properties relative to their overall weight or density, but the overall cost of these composites is high in relation to traditional composites or metals. In order to realize the highest mechanical properties and in order to eliminate anisotropy, the composites must be generated using the dual extrusion process. This process represents the only method to achieve both of these criteria. Since this process requires that the two polymers to be processed separately, in order to use polymers with non-overlapping processing temperatures, any form of recycling must include the separation of these two polymers from the composite. Furthermore, the overall cost of these composites can be driven down if a way to reclaim the expensive, TLCP component can be successfully developed in a way that is economically and environmentally feasible.

And, if it could be shown that these composites could be recycled in such a way that the reclaimed liquid crystal could not only be used to make further composites, but could also be used in other processes, then the overall marketability of these composites is increased. This can be better understood by noting that most recycling performed stays within the same cycle of product. An example of this is the recycling of plastic food trays, such as those you would find at your local fast food restaurant. These trays are recycled by grinding them up and then re-blending them with pure material to make further food trays. Now, if a process could be developed that reclaimed a polymer from a

well blended system in such a way that it could be successfully used in other systems, and there was no cross-contamination, then this process would represent a novel and beneficial impact on mixed plastics recycling.

An important factor to pay attention to when developing any type of process for the chemical industry is the environmental impact the process has on the surroundings. A process that can compete with the demanding codes set by the EPA (environmental protection agency) should be realized. More importantly, an economically feasible process should be designed and developed that consists of readily available technologies. Basically, this process must consist of equipment, technologies, and chemicals that are easily obtained and meet the rigors of an industry that is environmentally conscious.

It also becomes important when developing a process that the highest yields possible are reached and the highest purity is also achieved. This can only be accomplished by having a good understanding of the most important process variables and how these variables effect the overall efficiency of the system. Once the important variables are understood, then the process can be optimized for the highest yields and the highest purity. However, in order to optimize the purity of the product, a method or methods must be developed that will effectively give the correct purity of a reclaimed material. This method should give reliable and accurate measurements of purity. Once the purity is determined, then testing can be done to determine the overall ability of this reclaimed material to be reused in the polymer industry.

The overall objective of this research is to develop a process that will reclaim the thermotropic liquid crystalline polymer from composites generated from this thermotropic liquid crystalline polymer and polypropylene. Once this has been accomplished, the subsequent objectives are to determine the purity of the reclaimed polymer and then to determine if the reclaimed polymer can be used as a blending resin to make further composites with polypropylene. Another objective is to determine if the reclaimed TLCP can be used as a blending resin with only pure thermotropic liquid crystalline polymer. Lastly, the final objective is to determine the economic feasibility of the reclamation process. In the following chapter, typical recycling processes will be examined for their potential to be used in this research. Along with that, the area of reactive extrusion will be developed for its potential uses in a reclamation process. Also in this chapter, the solubility of polypropylene will be briefly examined. Finally, the area of reprocessing of reclaimed or recycled polymeric material will be discussed.

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