

2.0 Literature Review

2.1 Introduction

The ability to reclaim the thermotropic liquid crystalline polymer component (TLCP), from composites generated from TLCPs and polypropylene (PP), would result in a number of attractive advantages. First, any technology that can reclaim components from such a well blended system, would have a positive impact on plastics recycling. Second, the ability to reclaim this expensive component would lower the overall cost of producing these wholly thermoplastic composites. And last, this recycling ability would make these composites more attractive over other composites that lack such a recycling capability. Currently, no work has been done in the area of reclaiming thermotropic liquid crystalline polymers from thermoplastic composites. Although much work has been done on the recycling of mixed plastics, nothing can be found that deals with the separation of such an intimately blended system. Therefore, this review will deal with what has been done on other systems, that will help in the development of such a reclamation process.

In this review, a summary of mixed plastics recycling technologies will be investigated for their use in effectively separating polymeric blends or mixtures. The area of reactive extrusion will also be investigated for its potential impact on a reclamation process. Hence, this investigation will try to understand or answer the following questions: 1) Can existing technologies be used to separate polymeric blends with a high degree of purity and yield: 2) Can existing technologies be used to separate TLCPs from composites generated with TLCPs and thermoplastics (such as PP): 3) how can the purity

of a reclaimed polymer be determined: 4) can solvents be used to bring about an effective separation of two well blended polymers: and 5) what happens to the physical and mechanical properties of a recycled or reclaimed polymer in the area of re-processing. This last investigation will help to understand the potential for polymers to be long range, reusable media in the infrastructure of buildings, bridges, and other structures.

Therefore, section 2.2 is a discussion on the current state of mixed plastics recycling and how these existing technologies may be used to develop a process to reclaim thermotropic liquid crystalline polymers. Section 2.3 is a brief discussion on the area of polymeric solubility and how it might help in affecting a physical separation of two polymers in a blended system. Section 2.4 is an investigation of how reactive extrusion is used to control the molecular weight of a polymer and how this might be beneficial in a reclamation process. And in section 2.5, the field of processing recycled or reclaimed polymeric material is briefly investigated to get a better understanding of the potential for engineering plastics to be reused.

2.2 Plastics Recycling

In recent years, there has been a dramatic increase in investigating ways in which mixed plastics can be recycled or reclaimed for reprocessing. There are usually two methodologies when dealing with recycling mixed plastics that consist of different polymers. One method is to grind up the mixed material and then to add in a small amount of this regrind back into the process of making new parts or products. The other method is to separate the mixed polymers, in order to re-obtain the pure components. In section 2.2.1, the area of separation is investigated to determine its technological potential to be used to separate thermotropic liquid crystalline polymer from composites generated from polypropylene and these liquid crystalline polymers. And in section 2.2.2, the area of recycling thermotropic liquid crystalline polymer / thermoplastic composites is explored to demonstrate how this technique not only leads to losses in properties, but can not be used to process new composites that have the highest properties possible.

2.2.1 Reclamation via Shredding and Density Separation

A common form of mixed plastics recycling is shredding the mixture and then using differences in density to bring about a flotation separation [2, 10-12]. This type of process works on the assumption, that the blended system can be shredded into small enough pieces, that the resulting mixture contains a distribution of pure component pieces. These pieces are then separated by using some type of device that utilizes the difference in densities to bring about a bulk separation of the various materials. In Figure 2.1, a schematic of such a device, that is used in industry, can be seen [2]. This particular device works by first shredding the material, then washing the material to remove contaminants, then blowing the material into a tower for density classification, then grinding the material down into smaller pieces, then passing the pieces through an air classifier system, then washing and drying the pieces, and then passing the pieces through an extruder for compounding purposes. However, even after two density-type separations, the material is still very impure and the mechanical properties are lower than the virgin material.

Another device or system that works along this same principle is a very new invention for the separation of carpet materials. Dilly-Louis and coworkers [12], developed a process for separating carpet materials into three distinct components: nylon, polyester, and polypropylene. This system works on the same principle that if the compounded material can be shredded into small enough pieces, the resulting distribution will contain only pure components of all three plastics. And, because these materials have

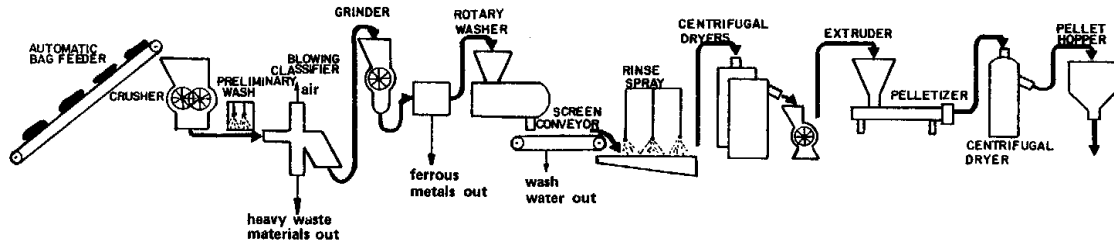


Figure 2.1 Schematic of Japan Steel Work's Nikko Waste Plastics Reclamation line. (Figure from J. Leidner, *Plastics Waste: Recovery of Economic Value*, Marcel Dekker Inc., New York, 1981.)

different densities, the particles can be separated by using a flotation type device. The uniqueness to this particular invention is that the process for density separation utilizes liquids, instead of air, as the separation media.

This type of difficult separation, using liquids, is only possible by controlling the density of the separating solution. . The density of the aqueous solution is manipulated by adding in various amounts of an aqueous salt, such as $\text{CaCl}\cdot 2\text{H}_2\text{O}$. The pre-shredded pieces are dumped into a double-cone full-jacketed screw centrifuge that contains this liquid, whose density has been selectively adjusted to be higher than one of the pure materials and lower than the other materials. Therefore, only the pure component of one of the materials will float to the top to be screened off after centrifugation. Then, the density of the solution is adjusted again so that it is higher than only one of the leftover materials, but is still lower than the remaining pieces. This material is then centrifuged and screened off. This process is repeated over and over again, until all of the pure components have been removed.

The ability of this device to provide pure reclaimed material is substantiated by the following values that are reported by Dilly-Louis and coworkers [12]. From Table 2.1, it can be seen that this process affords Nylon fiber that is around 96 % pure, polypropylene that is 98 % pure, and latex that is 94 % pure. Even though the materials are separated, each of the separation fractions still contain small amounts of the other materials. However, this process is still quite successful in the separation of such a well mixed system.

Table 2.1. Data from the Process for the Separation of Carpet Materials. (Data from W. Dilly-Louis, J. Seeligh, and R. Wolf, *U.S. Patent No. 4,809,854*, 1989.)

Component	Nylon (wt%)	Polypropylene (wt%)	Latex (wt%)
Starting Material	40.0	5.0	55.0
Separated Fractions			
Pile Fiber	96.0	2.0	2.0
Carrier Fabric	1.0	98.0	1.0
Carpet Backing	5.0	1.0	94.0

The most important factor for the success of this type of process is that, although the starting material consists of multiple polymers, these polymeric materials are not intimately blended. Intimate blending refers to the state in which the sizes of the pure polymeric phases, within the blend, are much smaller than the size of the smallest ground particles. Carpeting consists of Nylon fibers, interwoven in a polypropylene mesh, and then backed with a synthetic rubber. These materials are merely attached to each other, and are not dispersed within each other. Therefore, it is possible to shred this mixture into small enough pieces in order to obtain a distribution of relatively pure pieces. It becomes apparent then, that though this is a successful process, it can not be used to separate materials that are melt blended enough that the size of the pure phase is smaller than the ground material.

In the previous techniques, it was seen that recycling was a function of separating only mixed, heterogeneous systems of polymers that were adhered together due to glues, resins, or melt welding. These polymers were not intimately blended to a degree that the size of the pure polymeric phases was on the order of microns. Because this level of blending is found in the thermotropic liquid crystalline polymer / thermoplastic composites, these techniques can not be utilized. However, these techniques do support the probability that the TLCP/TP composite system can be separated if the right conditions can be determined and met. The same principles of utilizing differences in physical properties, to effect a separation, can be used in developing a new process of separating these well blended systems.

Fortunately, there is another method of separating well mixed polymeric materials. This method is called selective dissolution and it deals with utilizing temperature and a

solvent to bring about the desired separation [13]. This method works on the principle of solubility, as a function of temperature, to dissolve only certain polymers at certain temperatures. Each of the polymers present can be dissolved and then crystallized separately.

The selective dissolution technique is broken down into two main process steps. The first step involves adding the polymeric mixture to a solvent that has been specially chosen, and which depends on the polymers present within the blend. This solvent is able to dissolve all of the polymers included within the mixture, but only as a function of temperature. After dissolution, the next step in the process is called flash devolatilization and it involves evaporating the solvent away from the separated polymer. The separated polymer is removed and then the evaporated solvent is condensed and returned to the dissolution chamber for further use.

This selective dissolution process can be further broken down into two main categories: 1) one solvent is used to dissolve all of the polymers in the mixture or 2) one solvent is used to dissolve only one polymer in the mixture. The first category is used to dissolve all of the polymers in the mixture and then to use different temperatures to selectively crystallize out each polymer. The main drawback to this process is finding a solvent that will dissolve all of the polymers present in the mixture. The more common method used, category 2, is to find a solvent that will either only dissolve the desired polymer, or it will dissolve all of the other polymers except the desired one.

Some work has been done on using this method to separate six engineering plastics from a mixture [14]. The six engineering plastics used 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). The particular solvent chosen was tetrahydrofuran (THF), which is a four carbon, aliphatic heterocyclic ether. This polymeric mixture was shredded down and then combined with the THF in a tubular vessel. The flow of THF across the solids was started and the system was heated to 25 °C. The first extraction of solvent was sent to the devolatilization chamber, where the solvent was evaporated away from the dissolved polymer(s). The solvent was condensed and then sent back into the selective dissolution chamber. The temperature was raised to 70 °C and then the next extraction was sent to the flash devolatilization chamber. The same evaporation process was performed and the dissolved polymer(s) was collected. This entire process, see Figure 2.2, was repeated for temperatures of 160 and 190 °C.

The resulting extracts, see Table 2.2, were examined for polymeric content and percent efficiency of separation. The first extract, at 25 °C, resulted in the separation of both the PVC and the PS from the polymeric mixture. The next extract, at 70 °C, resulted in the separation of only the LDPE from the polymeric mixture. The subsequent extract, at 160 °C, resulted in both the PP and the HDPE being separated from the mixture. Finally, the 190 °C extract resulted in the separation of only the PET from the six polymer mixture. All of the extractions resulted in a greater than 99% efficiency of separation from the polymeric mixture in the selective dissolution chamber. However, only the PET and the LDPE were successfully isolated from the six polymer mixture. The rest of the extracts contained two polymers that were still commingled together. Overall, this type of selective dissolution process is somewhat effective in separating polymers that are well mixed.

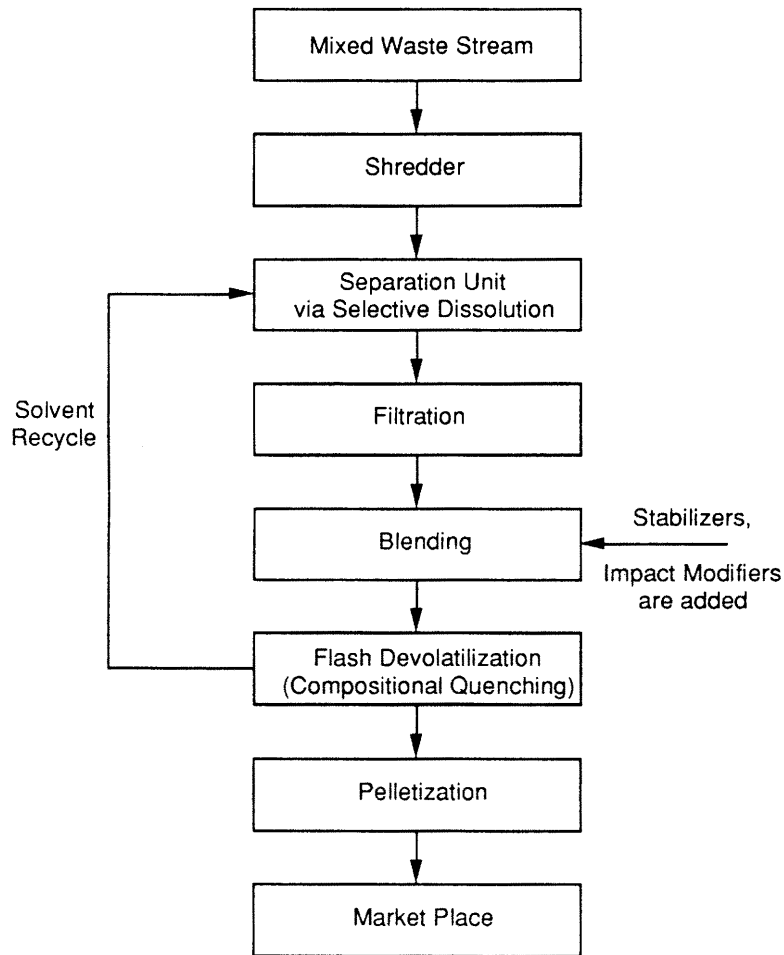


Figure 2.2 Single Solvent Dissolution Process Flow Sheet. (Figure from B.A. Hegberg, G.R. Brenniman, and W.H. Hallenbeck, *Mixed Plastics Recycling Technology*, Noyes Data Corp., Park Ridge, NJ, 1992.)

Table 2.2 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.

There are many advantages and disadvantages to this selective dissolution type of process, especially when dealing with the separation of well mixed plastics. The main disadvantages of this process are that it may only separate certain polymers from the mixture, the chosen solvent must be able to dissolve all or at least one of the polymers present, and it utilizes solvents that are hazardous and / or toxic to use. The most important point of this process is that it can successfully separate well mixed systems, but it may run into difficulties in dissolving intimately blended polymers. The starting materials used in this study were not well blended, but were just a mixture of pure components.

Currently, no work can be found that utilizes this technology to dissolve polymers that are intimately blended. More specifically, this technology has not been attempted on the separation of thermotropic liquid crystalline polymers from thermoplastic matrices. Therefore, this selective dissolution method could be utilized to separate the thermotropic liquid crystalline polymer from the TLCP / TP composites, if the problem of intimate blending can be overcome.

Before such a process could be performed on this composite system, it becomes necessary to investigate the ability of these composites to undergo multiple processing steps. It is unwise to develop a reclamation process if the desired material can not undergo multiple processing steps without seeing losses in mechanical properties. Fortunately, some work has already been done on the recycling of TLCP/TP composites to determine if there will be any losses in properties for these composites. The next section will deal with the mechanical and physical stability of these thermotropic liquid crystalline polymer / thermoplastic composites.

2.2.2 Recycling of Thermotropic Liquid Crystalline Polymer/ Thermoplastic Composites

Based on the current technology available for mixed plastics recycling, there seems to be an absence of processes that can successfully reclaim or separate components from a well blended system. The absence of work done in this area stems from the fact that this type of separation can be very difficult and costly. Therefore, instead of separating the polymers, the main form of recycling used is to only reprocess the material. In the case of wholly thermoplastic composites, in which the reinforcing phase and the matrix material are melt processable thermoplastics, recycling comes in the form of regrinding the composite and then reprocessing it back into a composite.

Sasaki et al. [15] found that it is possible to recycle liquid crystalline polymer / thermoplastic in situ composites and see no loss in strength. This form of recycling consisted of shredding the composites and then re-extruding the material into in-situ composites. This process, of merely grinding up the composite and reprocessing it without separating the two polymers, was merely performed to determine if there would be any loss in mechanical properties. In this study, see Table 2.3, various systems of a liquid crystalline polymer (Vectra A950) and different thermoplastics were examined.

Sasaki et al [15] generated the in-situ composites by dry mixing the reinforcing polymer (LCP) with the matrix polymer (thermoplastic) in a twin screw extruder, and then extruding a filament. This processing method resulted in the fibrillation of the LCP component and encasement from the thermoplastic component. It was found, from their process, that increased properties could be realized from the addition of the LCP

Table 2.3 Various Blends of a Liquid Crystalline Polymer (Vectra A950) and Thermoplastics, and their Mechanical Properties, that were used in the Japanese Study for Regrinding / Reprocessing Recycling . (Data from K. Sasaki and T. Tomita, (Japanese) *Kobunshi Ronbunshi, Japan. J. of Poly. Sci. and Tech.*, **50**, 11, 855, 1993.)

LCP Composite Matrix	LCP Content (wt%)	Tensile Strength (MPa)
PS / PPE	50.0	160.0
PP	50.0	150.0
PBT	50.0	170.0
ABS	50.0	120.0
PA6	50.0	100.0
PS / PPE / PA6	50.0	140.0
PC / PBT	50.0	170.0

where PS is polystyrene, PPE is polyphenylene ether, PP is polypropylene, PBT is polybutylene terephthalate, ABS is acrylonitrile-butadiene-styrene, PA6 is nylon 6, and PC is polycarbonate.

into the thermoplastic matrix. Originally, the driving force behind this process was to demonstrate that cheap materials, with low mechanical properties, can be used in making composites with excellent mechanical properties from the addition of a LCP. And though the LCP is high in cost, the overall blended composite has substantial properties at a lower average cost. In concurrence with this review, one of the composites studied (see Table 2.3) was a blend of LCP and PP, which is consistent with the form of the composite system that is to be recycled / reclaimed in this work.

Sasaki et al. [15] showed that by mixing in various amounts of the high cost LCP into the PP, the mechanical properties of the low cost thermoplastic matrix (PP) could be enhanced with little increase in the overall cost of the composite. In Figure 2.3, it can be seen that the tensile strength of the thermoplastic can be increased from the addition of the high strength liquid crystalline polymer. This result, and the fact that the entire composite is made up of thermoplastics, makes these type of composites very desirable and marketable over other traditional composites. Therefore, it became necessary for Sasaki et al [15] to investigate how the mechanical and physical properties of these composites changed after repeated recycling in the form of reprocessing.

To study these changes, Sasaki et al. [15] developed a process to recycle the composites. This process, see Figure 2.4, consisted of extruding composite strands and then performing mechanical testing on the strands to determine their properties. Then, the composite strands were pelletized and then re-extruded into new, recycled composite strands. The mechanical properties were then determined for this first recycle composition. This same process was repeated over and over again until the 10th recycle.

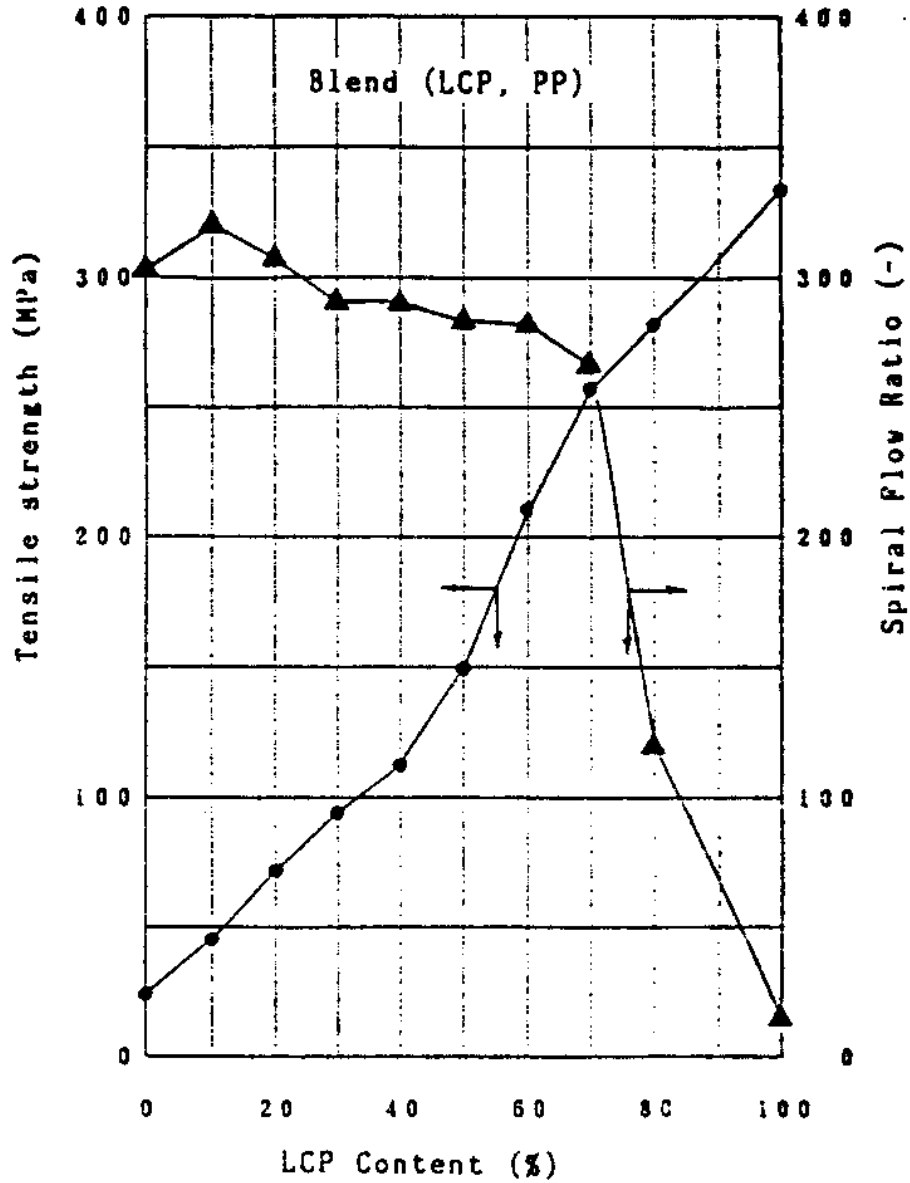


Figure 2.3 Tensile Strength vs. LCP Content for PP Strands. (Figure from K. Sasaki and T. Tomita, (Japanese) *Kobunshi Ronbunshi, Japan. J. of Poly. Sci. and Tech.*, **50**, 11, 855, 1993.)

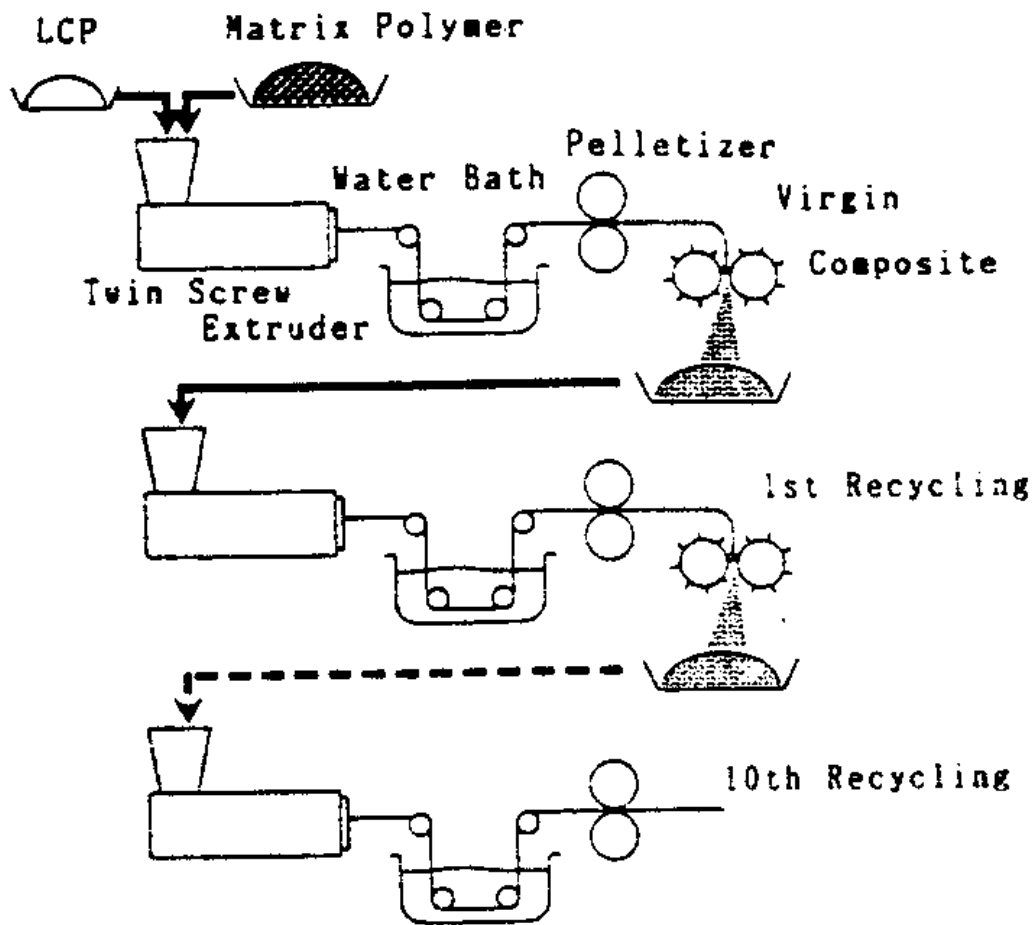


Figure 2.4 Process by which Sasaki et al. [13] Generated In situ LCP Composite Strands from Polypropylene and then Reground and Reprocessed the Material. (Flow Chart from K. Sasaki and T. Tomita, (Japanese) *Kobunshi Ronbunshi, Japan. J. of Poly. Sci. and Tech.*, **50**, 11, 855, 1993.)

A plot of the tensile strength vs. number of recycles, see Figure 2.5, showed that there was no appreciable loss in tensile strength with successive reprocessing. And, even after the 10th recycle, the tensile strength for the LCP / PP composites had not changed. This is an important result in the sense that it demonstrates the ability of the liquid crystalline polymer to withstand multiple processing steps and not degrade under the thermal and mechanical history. However, though the strength was not being lost with successive recycling cycles, there was no mention about what was happening to the other mechanical properties. This could only mean that Sasaki et al [15] did see losses in tensile modulus and tensile toughness.

If losses in tensile modulus and toughness were occurring, it could be attributed to a loss in the high aspect ratios of the reinforcing fibrils of the unknown LCP due to the grinding step. Based on other works, it is this high aspect ratio, in the form of LCP fibrils, that give these composites their excellent mechanical properties [16-19]. Upon inspection by scanning electron microscopy (SEM), Sasaki et al [15] did find that the fibrils of the liquid crystalline polymer, in the recycled composite strands, were either twisted or broken. This effectively reduced the apparent aspect ratio, and therefore the reinforcement ability suffered due to this loss. However, this work did show that the tensile strength of a liquid crystalline polymer is relatively capable of handling multiple thermal and mechanical processing steps.

In conclusion, two main techniques of plastics recycling were discussed: 1) the grinding and selective dissolution of the polymer mixture and 2) the other was to grind the polymeric mixture and reprocess it back into the same product. The disadvantages to the

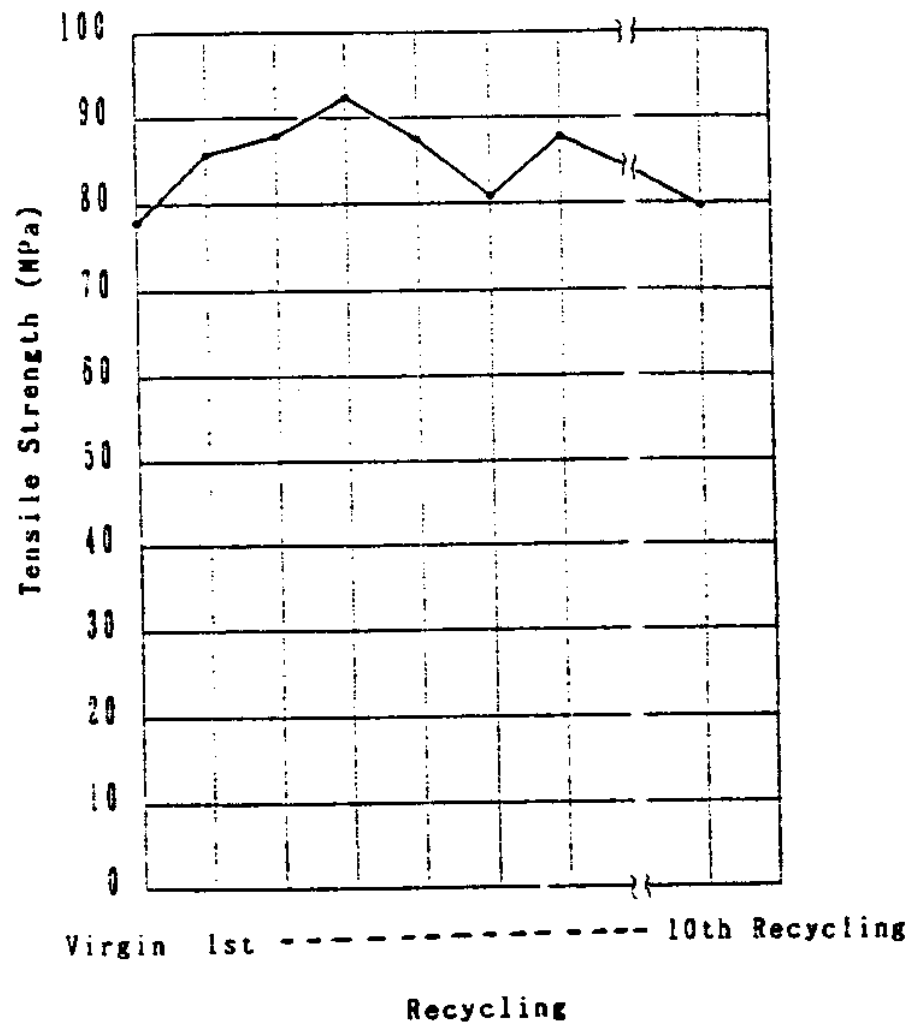


Figure 2.5 Tensile Strength as a Function of Successive Regrinding and Reprocessing for Composite Strands of 30 wt% LCP and 70 wt% PP. (Figure from K. Sasaki and T. Tomita, (Japanese) *Kobunshi Ronbunshi, Japan. J. of Poly. Sci. and Tech.*, **50**, 11, 855, 1993.)

selective dissolution process were that complete separation was not always being accomplished and the process could require the use of hazardous and / or toxic solvents. As for the recycling of the LCP / PP composites, while the strength did remain constant, more than likely there were losses in modulus and toughness. Furthermore, because these in-situ composites have inferior properties compared to the pre-generated micro-composites (see section 1.2.2), this type of recycling must be abandoned anyway. In order to be able to recycle the pre-generated micro-composites, separation of the two polymers must occur to be utilized in the dual extrusion process.

The most promising method of separating well mixed polymers was the selective dissolution method. However, the success of this type of process relies on the ability of a particular solvent to selectively dissolve only one of the polymers and not the rest. If a solvent or set of solvents could be found that would only dissolve one of the polymers in these composites, then the possibility exists that the TLCP could be reclaimed. And, based on the studies by Sasaki et al [15], it stands to reason that these TLCPs would not show substantial losses in mechanical properties. It, therefore, becomes important to determine all of the important factors involved in polymeric solubility.

2.3 Polymer Solubility

Based on the previous section, it was found that traditional recycling methods could not be used to bring about a successful separation of the liquid crystalline polymer component of in-situ or pre-generated micro-composites. The fact that the reinforcing phase, the thermotropic liquid crystalline polymer, is well dispersed within the polypropylene, makes any type of mechanical separation extremely difficult and nearly improbable. Because of this problem and based on the success of Lynch et al [14], the area of potentially dissolving the matrix material away from the reinforcing phase needs to be examined for its potential use in developing a reclamation process.

However, when looking at using solvents to dissolve a polymer, some very important issues arise that are applicable to developing a process that is industrially and environmentally suitable. The area of toxicity, volatility, and cost are the main issues that must be addressed when dealing with using solvents to generate a new, recycling process. Another important area in using solvents is that, due to the large molecular structures of polymeric materials, the thermodynamics begin to play a very important role in solubility. More specifically, can a solvent be found that can dissolve the polypropylene away from the thermotropic liquid crystalline polymer. Therefore, the area of polymer solubility and what the most important factors are when trying to bring about an effective dissolution of a polymeric material is discussed in section 2.3.1. And, the area of polypropylene dissolution is discussed in section 2.3.2.

2.3.1 Important Factors in Polymeric Solubility

The area of polymeric solubility has been widely studied over the years and much work has been done to get at a good fundamental understanding of what influences solubility in the area of polymers [23-28]. And although much is known in the area of small molecular solubility, less is known about polymeric solubility. What is understood is that there are three main factors which control the thermodynamics of polymeric solubility within a solvent [29]. All of these factors are a function of the thermodynamics behind the mixing of two species. The first factor is the combinatorial entropy of mixing. This term comes from the entropic effect of mixing the two species together and relates to the fact that the amount of disorder in the system must increase when going from a solid polymer to a dissolved polymer. The next important factor in polymeric solubility is the enthalpic effect arising from the mixing of the two species. This change can be either positive (the components prefer to be with themselves) or it can be a negative (the polymer likes the solvent more than itself). And lastly, the other important factor is the free volume effects between the polymer and the solvent. This factor deals with the solvent's ability to surround and contain the polymeric molecule in solution. The combination of the first two factors is the basis for an important thermodynamic relationship.

In order for a polymeric material to be dissolved, or any other solute, then the Gibb's free energy of mixing must be zero or negative [29-31]. As can be seen in equation (2), in order for the total Gibb's free energy of mixing (ΔG_{mix}) to be negative, then the

enthalpy of mixing (ΔH_{mix}) needs to be negative or weakly positive and the entropy of mixing (ΔS_{mix}) needs to be positive:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} \quad (2)$$

However, because one of the terms will always be positive, the entropy of mixing (ΔS_{mix}), then the only terms that influence the solubility are the absolute temperature (T) and the enthalpy of mixing (ΔH_{mix}). But, in order for this to be true, then the entropic contribution needs to be substantially large and positive. It has been seen that for polymeric solutions, the entropy of mixing is not substantially large in comparison to equivalent masses or volume [23]. This is due to the nature of polymeric materials and their ability to move and get into different configurations. Small molecules can pack tightly together and can rotate around, whereas polymeric chains are confined to a lower number of conformations.

A good representation of this phenomena is the lattice model of solubility [23]. A solution is treated as a volume that consists of a number of smaller volumes or cells that make up a total volume. Now, each molecule can only occupy one cell at a time, but they can distribute themselves in any number of ways. However, due to the rigid conformational mobility of a polymeric chain, there exists only a few ways in which the polymer can pack itself into the lattice. From Figure 2.6, it can be seen that the smaller molecules have more choices of where they reside than does the polymer chain. It is this confined nature that generates a lower difference in the value for the entropy of mixing for polymeric solutions as compared to traditional, small molecule solutions. With this being the case, the temperature and the enthalpy of mixing become very important when dealing with polymer solubility.

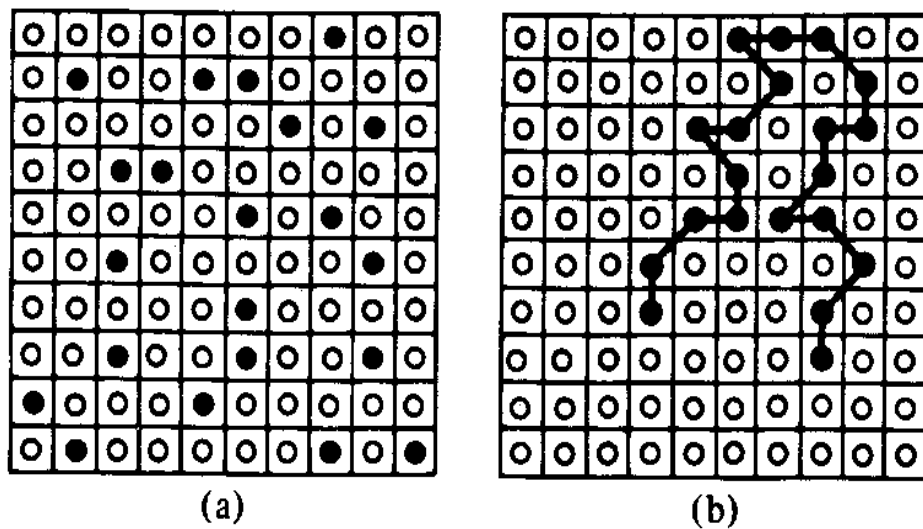


Figure 2.6 The Lattice Model of Solubility with respect to Small Molecules (●) and Large Polymeric (●—) Molecules. (Figures from R.L. Rosen, *Fundamental Principles of Polymeric Materials*, 2nd ed., John Wiley & Sons, New York, 1993.)

From regular solution theory, the enthalpy of mixing may be estimated by assuming that there are no specific interactions between the polymer and the solvent, and therefore it can be equated to the change in internal energy per unit volume of solution [23]. The form of this equation, see Equation (3), uses the solubility parameter (δ) and the volume fraction (Φ) to determine the change in internal energy for the solution:

$$\Delta H \approx \Delta E = \Phi_1 \Phi_2 (\delta_1 - \delta_2)^2 \quad (3)$$

where 1 represents the solvent and 2 represents the polymer or solute.

From looking at this equation, it becomes obvious that the value for the enthalpy of mixing will always be positive. This is true, because for regular solution theory, there are no specific interactions like hydrogen bonding. And even though the difference between the solubility parameter for the polymer and the solubility parameter for the solvent may be negative, this value is squared and therefore will always result in a positive number. Therefore, to increase the possibility of solubility, the internal energy of mixing must be minimized by picking a solvent with a solubility parameter that is very close or equivalent to the solubility parameter of the polymer. A good guideline for polymeric solubility is for the absolute value of the difference between the solubility parameters to be around $1.0 (\text{cal} / \text{cm}^3)^{1/2}$.

Determining the values of solubility parameters involves using the following equation:

$$\delta = (\text{CED})^{1/2} = (\Delta E_v / v)^{1/2} \quad (4)$$

where CED stands for the cohesive energy density, which is a measure of the attraction between the molecules in the liquid state; ΔE_v is the molar change in internal energy with respect to vaporization; and v is the molar volume of the liquid [23]. Unfortunately, when

dealing with polymeric materials, before the value of the molar vaporization energy can be determined, the polymer has started to degrade before vaporization can occur.

One way around this is to lightly cross-link the polymer and then measure the swelling of the polymer in different solvents. The resulting curve, see Figure 2.7, shows the swelling as a function of solvent solubility parameters. And from this curve, the maximum point of the curve can be determined, and thereby correlated to the solubility parameter for the uncross-linked polymer. With the value of the polymer's solubility parameter known, then a solvent can be matched up to this polymer so that the enthalpy of mixing goes to zero.

A large problem with regular solution theory is that it does not deal with the difference in size between the polymer and the solvent molecules. There are no terms to deal with the number of units in the polymer chain compared to the number of units in the solvent species. This becomes important when dealing with solvents that consist of long chain molecules themselves, and therefore have a better chance at dissolving the polymer molecules.

Work has been done to determine what effect molecular size has on polymer solubility [24, 26]. The most recognizable theory that deals with these interactions is the Flory-Huggins theory:

$$\Delta H = R T \chi \Phi_2 n_1 x_1 \quad (5)$$

where χ is the Flory-Huggins interaction parameter, n_1 is the number of moles of solvent, Φ_2 is the volume fraction of the polymer, x_1 is the number of segments in the solvent

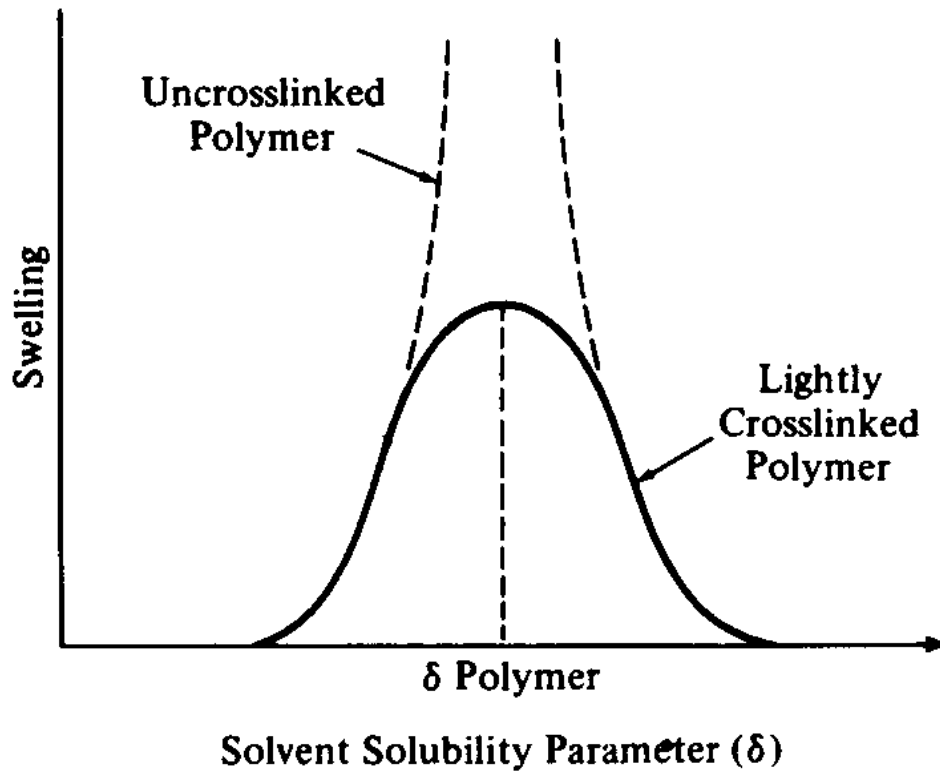


Figure 2.7 Determination of the Solubility Parameter for a Polymer by Swelling the Lightly Cross-linked Polymer in Different Solvents, and therefore different Solubility Parameters. (Figure from R.L. Rosen, *Fundamental Principles of Polymeric Materials*, 2nd ed., John Wiley & Sons, New York, 1993.)

molecule, and R is the gas constant. The value of the interaction parameter comes from the solubility parameters and the molar volume of the solvent:

$$\chi = \frac{v(\delta_1 - \delta_2)^2}{RT} \quad (6)$$

On looking at Equation (5), a means to handle the size of the solvent molecule comes about through the two terms n_1 and x_2 . Therefore, it becomes necessary to match the polymer molecule up with a solvent that is large enough to handle the macromolecule, but not too large that it rapidly enlarges the value for the enthalpy of mixing. Based on Equations (5) and (6), in order to generate a low enthalpy of mixing, the difference in solubility parameters must be close to zero and the molar volume must be very small. The smaller the molar volume, the larger the solvent molecule. However, the larger the molecule, the larger the values for n_1 and x_1 , which ends up expanding the overall enthalpy of mixing. In order to maximize solubility, a polymer solvent must either be very small, and therefore the large difference in solubility parameters does not matter, or the polymer solvent must be very large and have an equivalent solubility parameter to the polymer.

Hence, it becomes important to determine the solubility parameter for the polypropylene and to find a solvent that will potentially dissolve the polypropylene away from the thermotropic liquid crystalline polymer. If a solvent can be found that has a low molar volume and one that has a solubility parameter that is very close to the solubility parameter for the polypropylene, then conditions could be reached for solubility. These conditions can be further adjusted by understanding that the temperature, see Equation (2), greatly influences the solubility. With the enthalpy of mixing close to zero, by increasing the temperature, the entropy of mixing term will go to larger and larger

negative values. This has the overall effect of reducing the Gibb's free energy of mixing to larger and larger negative numbers, and thereby increasing the thermodynamics for dissolution.

Polymeric solubility has been shown to be a function of density or molar volume, temperature, and molecular weight, but there does exist another important factor to pay attention to when trying to dissolve a polymer [29]. This factor is the chemical structure of the solvent, in relation to the chemical structure of the polymer. An old rule of solubility is that "like dissolves like." This phrase stems from that fact that self-association is a strong interaction among molecules. Solvents that are similar in chemical structure to polymers will have a better chance in dissolving a polymeric molecule.

Any solvent, that is similar in structure to a polymeric molecule, will also be very large, will have a very small molar volume, and will dramatically effect the thermodynamics of solubility. Therefore, the values for n_1 and x_2 from Equation (5) will be quite large, because these values are a direct function of the size of the solvent molecules. This increase, in the values for these parameters, will result in an increase in the enthalpy of mixing. This is a condition that is very unfavorable for polymeric solubility. However, this unfavorable condition can be negated, through the interaction parameter of equation (6), if the solvent's solubility parameter is close enough to the polymer's solubility parameter. This relationship between size, molar volume, solubility parameter, similarity, and solubility needs to be kept in context with the choice of a solvent.

The thermodynamics of solubility can also be altered, advantageously, by noting how changing the dissolution temperature effects the solvent's ability to dissolve the

polymer. If a solvent is chosen that has a favorable size, density, and solubility parameter than the value of the enthalpy of mixing is small or zero. And, because the value of the entropy of mixing is always positive, based on Equation (2), by increasing the temperature of the system, the solubility of the polymer in the solvent can be dramatically increased. Therefore, in order to maximize solubility, a solvent must be found that meets all of the above criteria and that can also handle very high temperatures. For in order to dissolve a polymeric molecule, the solvent needs to be able to reach temperatures that are close to the melting point of the polymer.

In conclusion, polymeric solubility is strongly influenced by temperature, chemical structure, molar volume, and the value for the solubility parameter. It was seen that the conditions for solubility can be advantageously increased by not only increasing the temperature, but by matching the solubility parameters of the solvent and the solute. Because the main objective of this research is to remove the TLCP component from the polypropylene matrix, but because dissolving the TLCP is not probable due to its complex chemical structure, it becomes necessary to determine the solubility and solubility parameter of polypropylene.

2.3.2 The Solubility of Polypropylene

Work has been done to determine the solubility of polypropylene in many different solvents and under many different conditions [28, 29]. More specifically, Drain [29] found that the solubility of polypropylene was differential due to the semi-crystalline

nature of the polymer. It was found that when a film of the semi-crystalline polypropylene was dissolved in tetrachloroethylene at room temperature, the amorphous phase dissolved much faster than the crystalline phase. This can be attributed to the large difference in the effective densities of these two phases, which has been established as an important parameter for polymeric solubility. The crystals were harder to penetrate by the solvent due to the close packing found in this phase. And although there exist a concentration potential across the crystal / solvent layer, once the first fraction of solvent penetrates the crystal layer, the solvent starts to act as a barrier to keep more solvent from penetrating.

However, Drain [29] did notice that as the temperature of the system was taken above the glass transition, but below the melting point, the solubility of the amorphous phase went up as well. Unfortunately, the crystalline phase still had a harder time being dissolved, due to strong, self-association interactions. This discovery, that the amorphous phase is more soluble than the crystalline phase, is very important to note when designing a system that will allow for good solubility of the matrix material. It would be undesirable for only the amorphous phase of the matrix material to be dissolved, while the crystalline phase still remains with the target material.

But more importantly is the fact that temperature plays a pivotal role in designing a process to effectively dissolve a polymer. One beneficial factor, for solubility and crystallinity, is that both are directly effected in the same way. Therefore, as the temperature of the system is increased, the solubility goes up, the crystallinity goes away, and the mobility of the polymer chains go up. The preferential state for the best solubility should occur when the polymer is totally melted and the crystalline phase is gone. For

polypropylene, the general melting point is around 165 °C. Therefore, the best window, for effective solubility, will be at a system temperature that is above 165 °C.

Because most organic solvents are in the gas phase and are, therefore, unsuitable for a dissolution system at this temperature, some stringent criteria must be met by the solvent chosen for this type of selective dissolution process. The dissolution solvent needs to be similar in structure to the PP, have a similar or an equivalent solubility parameter to the polypropylene's parameter, be large enough to accommodate the large size of the polymeric chain, and also needs to have a boiling point that is near or above the melting point of the polypropylene. Fortunately, the chemical structure, the melting point, and the size of polypropylene is readily obtainable. Therefore, in order to choose the best solvent for dissolution, the solubility parameter for polypropylene is needed.

There has been some work done on the determination of the solubility and solubility parameter for various polymers, including polypropylene [35, 36]. Ugbohue et al. [35] found that relatively short periods of submersion, of polypropylene films into various solvents, resulted in changes in the percent elongation before break due to the dissolution of the solvent into the polymer [35]. This form of dissolution, of the solvent by the polymer, results in the plastication of the polymer.

In this study, see Figure 2.8, it was seen that the closer the solubility parameters of the solute and solvent were to each other, the higher the % elongation that was achieved. The value for the solubility parameter of polypropylene, $18.8 \text{ (J/cm}^3\text{)}^{1/2}$ or $\text{(MPa)}^{1/2}$, was determined from a previous work done by Hayes [36]. Concurrent with the Flory-Huggins Equation (6), the smaller the difference between the solubility parameters, the higher the degree of solubility. However, it is important to note that these films were

Liquid	Boiling Point (°C)	Molar Heat of Vaporization ΔH_v (KJ mol ⁻¹)	Solubility Parameter at 25°C		98 mN Pretension			49 mN Pretension		
			δH (MPa)	$ \Delta\delta $ (MPa ^{1/2})	%E	Thickness (mm) $\times 10^{-2}$	Increase (%)	%E	Thickness (mm) $\times 10^{-2}$	Increase (%)
Reformate	115–118	—	19.0	0.2	5.0	1.30	8	6.0	1.30	8
Chloroform	61	29.6	19.0	0.2	7.3	1.20	8	7.6	1.20	8
Toluene	110.6	33.2	18.2	0.6	5.9	1.30	8	5.8	1.30	8
<i>O</i> -xylene	144.4	36.8	18.0	0.8	5.6	1.30	8	4.0	1.24	3
Teralin	204–207	—	18.0	0.8	1.6	—	—	1.1	—	—
Carbon tetrachloride	75.6	29.9	17.8	1.0	6.4	1.26	5	6.6	1.26	5
Dichloromethane	39.8	36.3	20.3	1.5	5.5	1.30	8	5.1	1.30	8
Petroleum motor spirit	94–96	—	17.1	1.7	4.6	—	—	5.9	—	—
Naphtha	126–130	—	17.1	1.7	2.7	1.26	5	3.5	1.26	5
Petroleum ether	60–80	—	15.2	3.6	6.4	1.30	3	5.7	1.30	3

Untreated polypropylene (control): solubility parameter,¹⁵ δH 18.8; film width, 0.5 mm; thickness of film, (mm $\times 10^{-2}$) 1.2; % Elongation; 10.4.

Figure 2.8 Thermodynamic Properties of Various Solvents and their Effect on the % Elongation of Polypropylene Films. (Table from S.C.O. Ugbolue and T.C. Uzomah, *J. Appl. Polym. Sci.*, **62**, 1693, 1996.)

immersed at temperatures well below the melting point of the polypropylene. Therefore, instead of dissolving the polypropylene, the solvents only swelled the polymer.

Inspection of Figure 2.8 shows that the best solvents were reformat, petroleum motor spirit, naphtha, *o*-xylene, carbon tetrachloride, and petroleum ether. The highest boiling solvents were reformat, *o*-xylene, and petroleum motor spirits. These particular solvents resulted in the highest percent elongation and the highest solubility. Another important feature to note is that these particular solvents resemble the basic chemical structure of polypropylene. Although some of these solvents do contain aromatic rings, carbonyl groups, amine groups, and ether groups, these solvents do consist of aliphatic linkages which are also found in the polypropylene.

Another part of this study was to see what effect a long exposure to these solvents had on the % elongation of the polypropylene films. From Figure 2.9, it can be seen that the longer the polypropylene films were exposed to the solvents, the greater the plastication of the polypropylene. From this part of the study, it can be seen that the best solvents, for the plasticization of the polypropylene films, were the reformat and the decalin. Both of these solvents resulted in a ~ 1.7 fold increase in the % elongation based on the control sample of untreated polypropylene. Conversely, it can be seen that the petroleum ether had little to no effect on changing the % elongation as compared to the control sample. This can be attributed to the fact that this solvent's solubility parameter is much different than the solubility parameter for the polypropylene.

The main point that can be deduced from all of these results is that it seems possible to find a solvent whose chemical structure, solubility parameter, size, and boiling point are favorable for the dissolution of polypropylene at high temperatures. The best

Solvent	$\Delta\delta$ (MPa ^{1/2})	10-h Exposure			1-h Exposure		
		σ_y (MPa) $\times 10^{-1}$	IM (MPa)	% E_y	σ_y (MPa) $\times 10^{-1}$	IM (MPa)	% E_y
Reformate	0.2	208	23.8	19.0	196	25.0	1.6
<i>o</i> -Xylene	0.8	195	16.0	21.7	206	20.0	2.0
Decalin	0.8	196	23.5	16.8	—	—	—
CCL	1.0	186	12.3	27.0	199	21.5	2.2
Acetone	1.5	221	17.0	26.5	—	—	—
Naphtha	1.7	182	21.8	19.2	218	21.9	2.3
Isoamyl acetate		204	14.0	22.9	—	—	—
Petroleum ether	3.6	204	14.0	21.1	196	36.0	2.6
Control sample (No tension; non-solvent-treated)		198	17.9	17.2	—	—	—

Figure 2.9 Comparison of the Yield Properties for the Polypropylene Films as a Function of Exposure Time and Solvent. (Table from S.C.O. Ugbole and T.C. Uzomah, *J. Appl. Polym. Sci.*, **62**, 1693, 1996.)

solubility should occur when the polypropylene has no crystalline morphology present, when the chains are shorter than the typical polymeric length, and when the temperature is favorable for dissolution. It is intuitively obvious that two of these conditions can be met by performing the dissolution at a temperature above the melting point of the polypropylene. The last criteria seems to demand that the polymer chain be somehow reduced in overall size and molecular weight. The reduction in molecular weight of the polypropylene will result in shorter chains, which will be more suitable for dissolution into an aliphatic solvent.

The reduction of the molecular weight of a polymer can be accomplished by two main techniques: 1) thermal degradation of the material and 2) chemical degradation of the material. For the case of polypropylene, thermal degradation should start to occur at long times and at temperatures significantly higher than the melting point of the polymer. Although this form of degradation results in a product of smaller polypropylene chains, it also results in the formation of burned or charred polymeric particles that are usually unwanted in a process. These charred or carbonized particles act as an abrasive or contaminant in the rest of the process. The other form of degradation is brought on by the chemical breakdown of the polymer from using other chemicals to react with the molecule.

For most aliphatic polymers, like polypropylene, a common technique of degradation is brought on by reacting the material with organic peroxides [37]. This type of reaction results in reducing the molecular weight of the polypropylene, which results in increasing the free volume available for solubility. Typically, this reaction is run in an

extruder in order to melt out the polymeric material. The following section will deal with reactive extrusion, and what work has been done on the molecular weight modification of polypropylene.

2.4 Reactive Extrusion

There are many examples of the use of reactive extrusion to carry out chemical reactions in polymeric systems [42-45]. Fortunately, much of this work has been done on the degradation of polypropylene by reactive extrusion with organic peroxides [37, 38, 40]. From these studies, it was determined that, by adjusting certain parameters in the reactive extrusion, the molecular weight and the molecular weight distribution of polypropylene could be selectively controlled. These controlling parameters include the amount of peroxide used, the temperature of the reaction, the speed or reaction time, and the degree of mixing in the system. Therefore, the mechanical aspect of reactive extrusion is discussed in section 2.4.1. The controlling factors and the kinetics of the reaction are discussed in section 2.4.2.

2.4.1 The Mechanical Aspect of Reactive Extrusion

The first area of investigation that needs to be addressed is in the equipment used for reactive extrusion. Because there are many other types of chemical reactors, such as plug flow and batch systems, it becomes important to understand the need for an extruder to perform this type of chemical degradation [46]. Two of the important differences between a traditional reactant and having a polymer for a reactant are that the polymer usually has a higher viscosity and a higher melting point [23]. These two factors require large heaters and large pumps or mixers to effectively process this type of material. And, because the polymer is suspect to thermal degradation leading to charring, the reaction needs to be carried out without long contact between the polymer and the heaters. This short contact time between the heaters should allow for the polymer to be melted, but it should not allow enough time for it to be thermally degraded. These stringent criteria can only be met by an extrusion type of device.

For years, the extruder has been the main plastication and pumping device for polymeric material [23, 42, 47]. This type of device is capable of melting out and pumping a polymeric material with good control of the heating and of the pumping speed. Therefore, it is intuitively obvious to use this type of device for a chemical reactor when dealing with polymeric material. From Figure 2.10, we see a good cross-sectional representation of a common, single-screw extruder. It can be seen that the solid polymer, in the form of pellets, is fed into the extruder through the hopper. The first section that

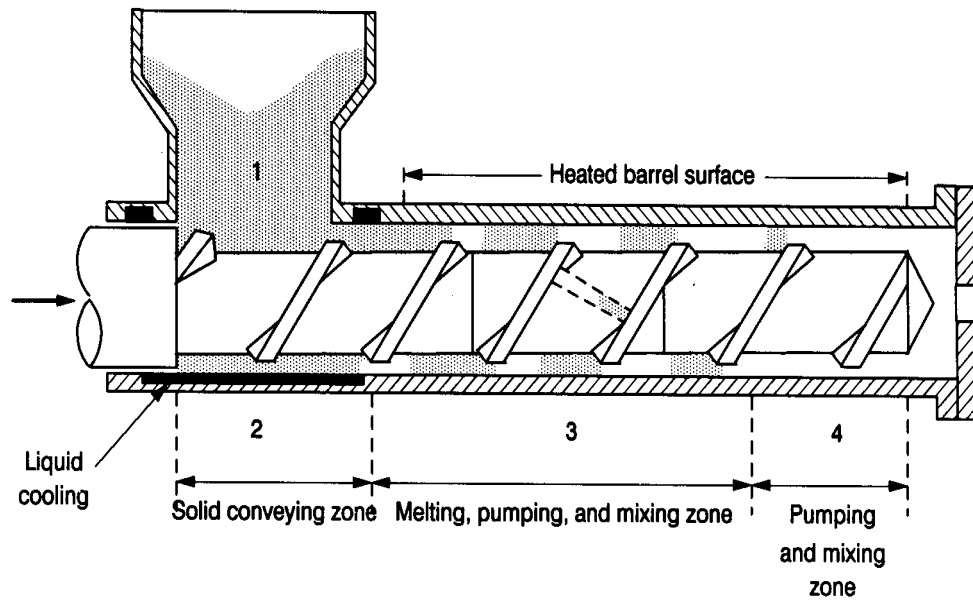


Figure 2.10 Cross-sectional View of a Common, Single-Screw Extruder. (Figure from D.G. Baird and D.I. Collias, *Polymer Processing: Principles and Design*, Butterworth-Heinemann, Boston, 1995.)

the polymer encounters is the solids conveying section. This section is used to begin to melt out the polymer via frictional heating between the barrel and the screw. The next section is the melting, pumping, and mixing zone. In this section, the melting of the polymer continues via frictional, viscous, and conductive heating. Next, the polymer melt goes through the pumping and mixing zone. In this section, the polymer is fully melted and mixed, and the gap between the screw and the barrel begins to narrow to bring about the desired pressure increase needed to pump the melt into some type of shaping device.

A good representation of the different aspects of mixing and melting that is going on inside of the extruder can be seen in Figure 2.11. This representation, of the melt and solids, is a cross-sectional view of the melting, mixing, and pumping zone. From this figure, it can be seen that the melting of the polymer is predominantly occurring at the head of the flight, as the material traverses down the extruder. It is in this section in which intimate contact between the reactant and the polymer is occurring for reactive extrusion.

In conclusion, there exists a good ability to control the necessary parameters for a chemical reaction in an extruder. The variables of barrel temperature, screw speed, and the addition of the polymer and reactant into the extruder can all be controlled with this piece of equipment. Furthermore, the direction and speed of the post-extrusion melt can be controlled by choosing an appropriate die. This is important when designing a process that requires further processing after the reactive extrusion.

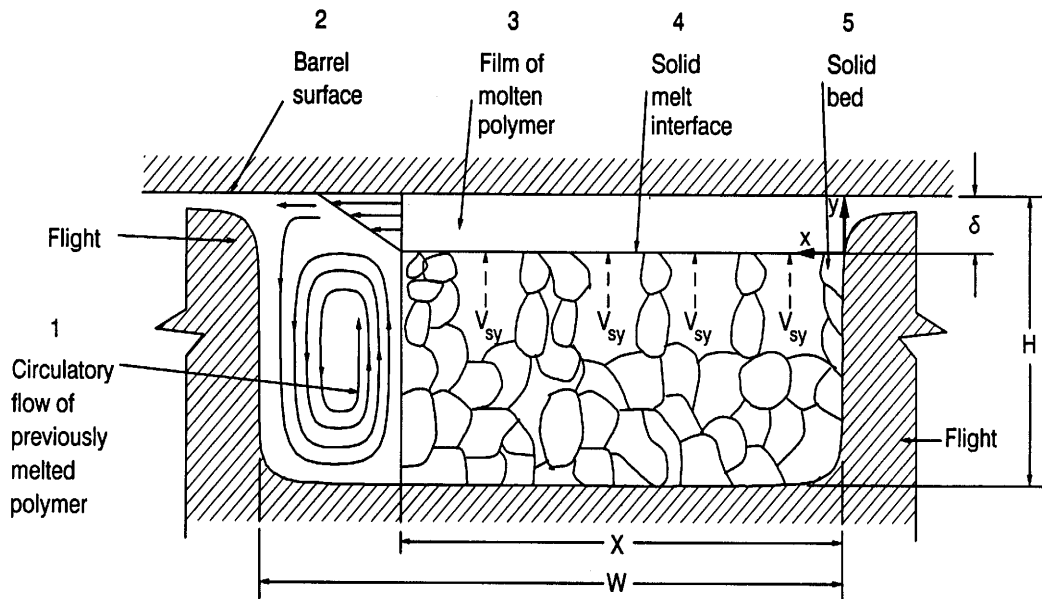
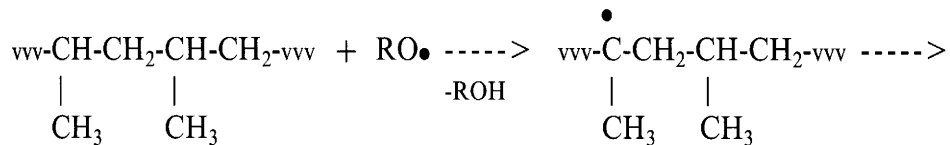


Figure 2.11 Cross-sectional Representation of the Melting, Mixing, and Pumping Zone of a Single-Screw Extruder. . (Figure from D.G. Baird and D.I. Collias, *Polymer Processing: Principles and Design*, Butterworth-Heinemann, Boston, 1995.)

2.4.2 Controlling Factors and Reaction Kinetics

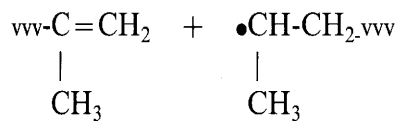
When dealing with reactive extrusion, or any other type of reaction, it is important to understand the controlling factors and the kinetics of the reaction. For the case of the controlled degradation of polypropylene, much work has been done in this area [37-40]. Both Dorn [40] and Tzonganakis et al. [37, 38] have done a lot of work behind determining the overall kinetics of the degradation of polypropylene via reactive extrusion with organic peroxides. The first area to investigate, when developing a reaction system, is the determination of the reaction scheme. Knowledge of the reaction scheme leads to a better understanding of the kinetics of the reaction and therefore leads to better control of the chemistry [46].

In the case of the degradation of polypropylene, the work done by both Dorn [40] and Tzonganakis [37] et al. have led to the same simplified reaction scheme. This simplified reaction scheme, along with the sub-reactions, can be seen in Figure 2.12. The first step of reaction is the initiation step or radical generation step. This step consists of the generation of the carbon radicals that will be used to react with and thereby degrade the polypropylene. Currently, there are many different organic peroxides used in industry, see Figure 2.13, and therefore are available for use in a reactive extrusion type of process. The choice of peroxide, see Table 2.4, is usually dominated by the desired half-life of the peroxide at the reaction temperature [43]. The predominant organic peroxides used in the controlled degradation of polypropylene are peroxides B and C from Table 2.4.



Radical attack

Hydrogen abstraction



Degradation (beta scission)



Termination (disproportionation)

Figure 2.12 Reaction Mechanism for the Peroxide Degradation of Polypropylene. (Figure from M. Xanthos, *Reactive Extrusion: Principles and Practice*, Hanser, New York, 1992.)

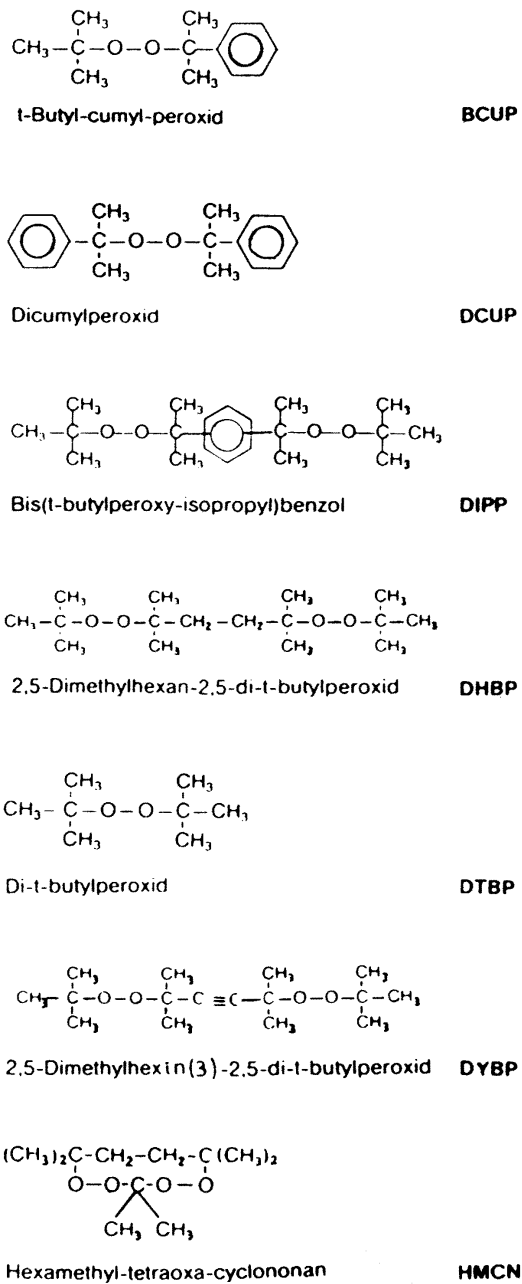


Figure 2.13 Various Industrially Important Organic Peroxides. (Figure from M. Dorn, *Adv. Polym. Tech.*, **5**, 87, 1985.)

Table 2.4 Half-Lives and their Temperature Dependence for Various, Industrially Important Organic Peroxides. (Tables from M. Xanthos, *Reactive Extrusion: Principles and Practice*, Hanser, New York, 1992.)

Peroxide	Half-Life in Dilute Solution*			
	seconds			
	180 °C	200 °C	220 °C	240 °C
B. Dicumyl peroxide	50	9	1.8	0.4
C. 2,5-dimethyl-2,5-di(t-butylperoxy) hexane	68	12	2.4	0.6
E. 2,5-dimethyl-2,5-di(t-butylperoxy) hexyne-3	216	36	6.8	1.4

* Estimated from decomposition kinetic data in dilute decane or dodecane solutions (Atomchem, 1990).

Peroxide	1 hr. Half-Life Temp.*, °C
A. Bis(t-butylperoxy) diisopropyl benzene	137,0
B. Dicumyl peroxide	137.0
C. 2,5-dimethyl-2,5-di(t-butylperoxy) hexane	140.3
D. Di-t butyl peroxide	149.1
E. 2,5-dimethyl-2,5-di(t-butylperoxy) hexyne-3	151.8

* From decomposition kinetic data in dilute decane or dodecane solutions (Atochem, 1990).

These two particular peroxides, dicumyl peroxide and 2,5-dimethyl-2,5-di(t-butylperoxy) hexane, are used due to their favorable half-lives and their ability to reach higher temperatures. Both of these peroxides generate radicals, at the melting temperature of polypropylene (165 °C), in around 2 minutes maximum. Once the radicals are formed, than the next part of the reaction mechanism, see Figure 2.12, is the radical attack of the polymer chain.

Radical attack is brought about by the abstraction of a hydrogen radical from the tertiary carbons along the polymer chain. Once this tertiary radical is formed, beta scission occurs vary rapidly. This beta scission, or subsequent bonding of the alpha and beta carbons, results in a stable, polymeric olefin and another tertiary radical. This new radical can go about beta scission as well, which ends up producing further polymeric olefins and new tertiary radicals. This process happens very fast, and these new radicals can go on to abstract hydrogen radicals from chains that have not yet participated in the degradation process. The last step in this reaction mechanism is the termination step.

Termination of these series of reactions can occur in three ways: 1) by radical combination with other polymeric radicals, 2) by disproportionation (see Figure 2.12), or 3) by radical combination with a peroxide radical. Due to the high volume of polymeric radicals present in the reaction, as compared to the part per million of peroxide radicals present, steps 1) and 2) are the predominant ways of termination.

Based on this simplified reaction scheme, it is important to understand which part of this reaction mechanism is the rate limiting step [46]. In the study performed by Tzonganakis et al [37], this was determined by varying the peroxide concentration and by

varying the screw speed. By varying the peroxide concentration, while maintaining a constant screw speed, a plot of the drop in molecular weight vs. peroxide concentration would show any dependence on peroxide concentration. This would show if the first step of the reaction mechanism, the radical initiation, was the rate controlling step. By varying the screw speed, while maintaining peroxide concentration, the dependence of the drop in molecular weight could be examined as a function of time. This type of study would show if the hydrogen abstraction and termination steps were the rate controlling steps. But, in order to perform this study, Tzonganakis et al. [37] needed to develop a method to determine the changes in molecular weight.

A common measure of molecular weight, or at least a qualitative measure, is to determine the melt flow index of a polymeric material [42, 49]. The melt flow index is a measure in the amount or material, mass, that will flow through a certain capillary die under a constant weight (2.16 Kg) over a period of 10 minutes. And, another method, is to measure the steady-shear viscosity vs. shear rate of the material [23, 42]. Both of these techniques were used by Tzonganakis et al [37] to determine the effect of varying the peroxide concentration and the screw speed or residence time on the molecular weight of the polypropylene. In the case of the melt flow index, as the molecular weight is decreased, than the melt flow index should go up in value. And, in the case of the shear viscosity, as the molecular weight goes down, the viscosity of the material should go down as well.

The results obtained by Tzonganakis et al. [37], on the dependence of the molecular weight as a function of peroxide concentration and screw speed in the form of the melt flow index, can be seen in Figure 2.14. From this figure, it becomes obvious that

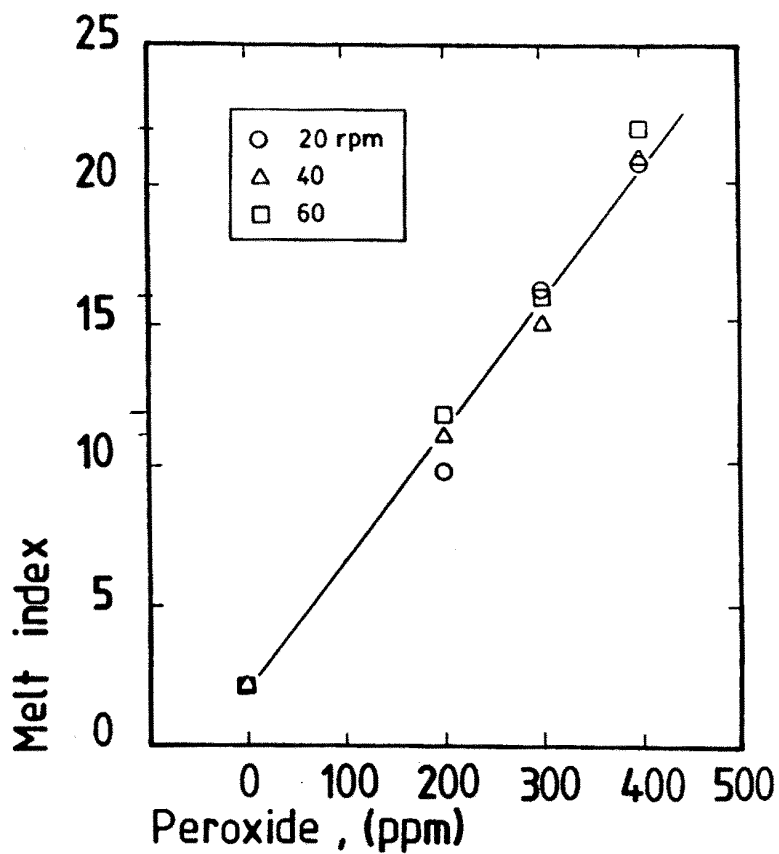


Figure 2.14 The Effect of Peroxide Concentration and Screw Speed (rpm) on the Melt Flow Index of the Polypropylene. (Figure from C. Tzonganakis, J. Vlachopoulos, and A.E. Hamielec, *Intern. Polym. Process.*, III, 3, 141, 1988.)

the peroxide concentration has a larger effect on the molecular weight than the screw speed. By doubling the peroxide concentration from 200 ppm to 400 ppm, there is a two fold increase in the melt flow index of the material. The same doubling of the residence time, or dividing the screw speed by two, only results in 1.2 fold increase in melt flow index. This same result, see Figure 2.15, is also seen in the study done by Dorn [40]. As the peroxide concentration is doubled, the melt flow index is doubled as well. Both of these results confirms the speculation by both Dorn [40] and Tzonganakis et al. [37], that the rate limiting step of this overall reaction is controlled by the peroxide generation. Therefore, the major factor that controls the molecular weight reduction in this degradation experiment is the initial concentration of the organic peroxide.

The effect on the shear viscosity vs. shear rate for the polypropylene, as a function of peroxide concentration, can be seen in Figure 2.16. From this figure, it can be seen that as the peroxide concentration is increased ten fold, the shear viscosity response goes down an order of magnitude [38]. However, it also becomes obvious, see Figure 2.16, that as the peroxide concentration is increased to even higher parts per million, the drop in molecular weight begins to level off and plateau. Therefore, it appears that as a value of 0.1 wt% peroxide concentration is reached, there is no further reduction in molecular weight. From Figure 2.16, it becomes obvious that only a small amount of peroxide, 0.1%, will be the maximum amount of material needed to accomplish the task of molecular weight reduction.

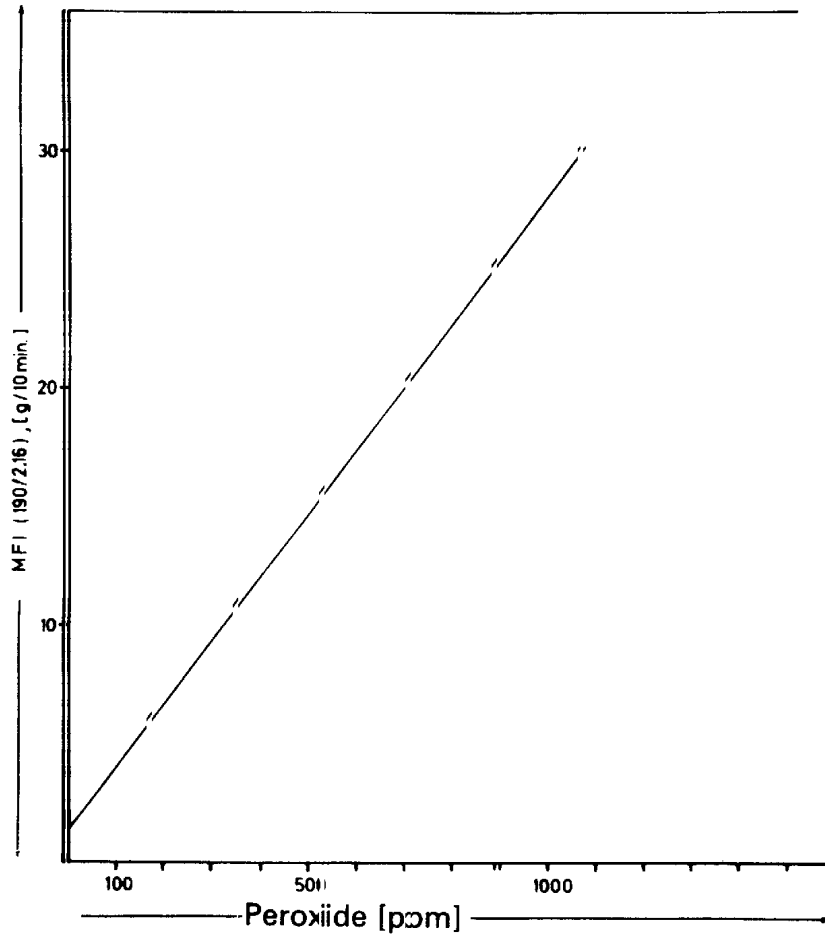


Figure 2.15 Melt Flow Index (MFI) as a function of Peroxide Concentration in the Reactive Extrusion of Polypropylene performed by Dorn. (Figure from M. Dorn, *Adv. Polym. Tech.*, **5**, 87, 1985.)

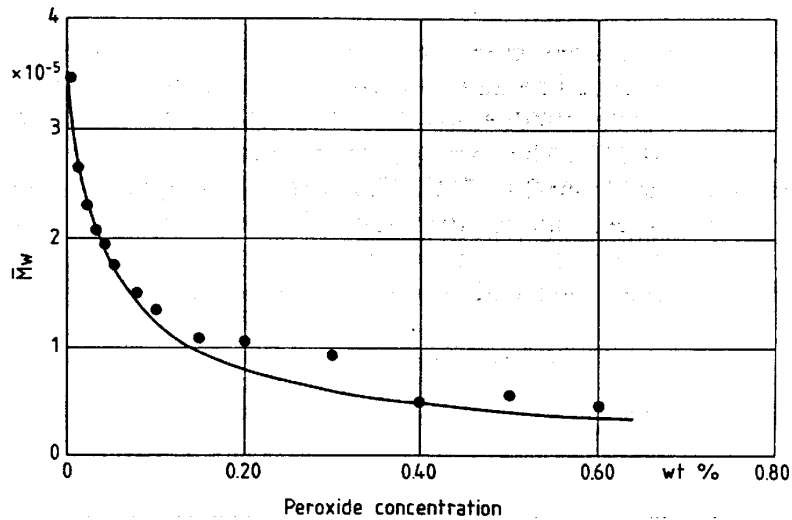
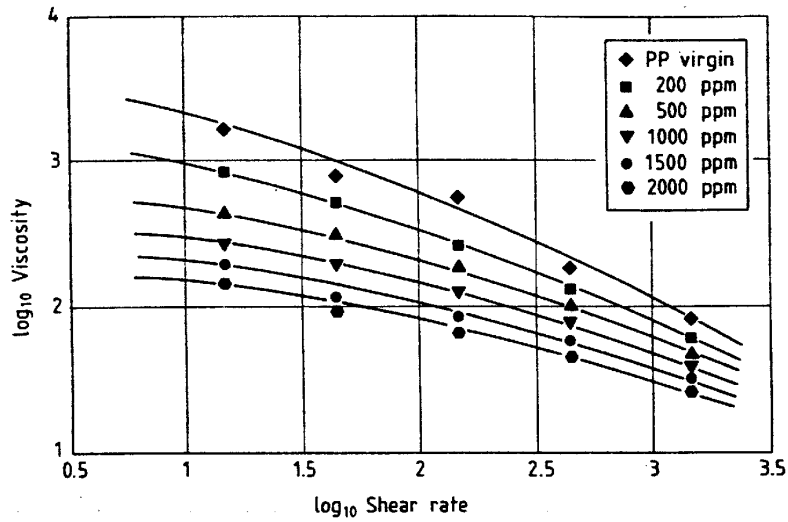


Figure 2.16 Shear Viscosity as a Function of Peroxide Concentration (top) and Molecular Weight (Mw) as a Function of Peroxide Concentration (bottom) for the Reactive Extrusion of Polypropylene. (Figures from C. Tzonganakis, J. Vlachopoulos, and A.E. Hamielec, *Intern. Polym. Process.*, III, 3, 141, 1988.)

Based on what has been shown, it appears that the degradation of polypropylene can be successfully accomplished by using reactive extrusion with organic peroxides. And furthermore, it appears that reactive extrusion can be run at very fast rates and with a little amount of organic peroxide. Researchers have shown that only the concentration of peroxide is important and not the residence time [38]. Therefore, it would seem intuitively obvious that this type of reaction could be run at very high rates. According to literature, the ability to perform reactive extrusion at very high throughputs is possible [40, 50-52]. For instance, Davison [50] was able to perform this reactive extrusion in a 12 inch diameter screw at output rates of 5 tons/hr! And, in the case of Dorn [40] and Anderson [52] et al, throughputs of 5-25 tons/hr were obtained.

In conclusion, based on the extensive work done in the area of the molecular weight modification of polypropylene by reactive extrusion with organic peroxides, it seems that this technique could be successfully used to increase the solubility of the polypropylene. By reducing the overall molecular weight of the polypropylene, and thereby increasing the free volume, the solubility of the polypropylene is increased significantly in regards to the thermodynamics of mixing. And because this type of reaction will only attack the hydrogen of tertiary carbons and because DuPont HX8000 contains none of these tertiary carbons [53], there exists a selectivity to the degradation. Therefore, it appears that the degradation of the polypropylene is a viable route to pursue in the development of a process to reclaim the liquid crystalline polymer component by dissolving the degraded polypropylene into an organic solvent.

2.5 The Reprocessing of Reclaimed or Recycled Polymer

If a process can be successfully developed to reclaim a polymeric material, than it becomes important to understand what is to be expected from this material in the area of reprocessing. The reclaimed or recycled polymeric material needs to be tested in such a way that the performance of the recovered material can be compared to the virgin resin. Unfortunately, only a few studies have been done to compare a reclaimed or recycled polymeric material with the pure resin. Fortunately, much work has been done on the recycling, and property comparison, of polyethylene terephthalate (PET) and high density polyethylene (HDPE) [54-56].

In a study by Hon et al [54], post-consumer plastic drink bottles, which consist of HDPE caps and PET bottles, were reprocessed to determine the effectiveness of this form of recycling. However, the recycled material could not be used to make further bottles because the two polymers were not isolated from each other. Instead, this recycled, compounded material was investigated for its potential use as a composite material. Because the PET is the predominant material, the influence of the HDPE needed to be determined. In Figure 2.17 (top), a plot of the stress at maximum load can be seen as a function of the weight fraction of PET in the composites. From this plot, there appears to be no appreciable difference in the values, except at 50 wt% PET, for the maximum stress. However, from Figure 2.17 (bottom), there is a large decrease in the percent strain at maximum load as the content of PET is increased.

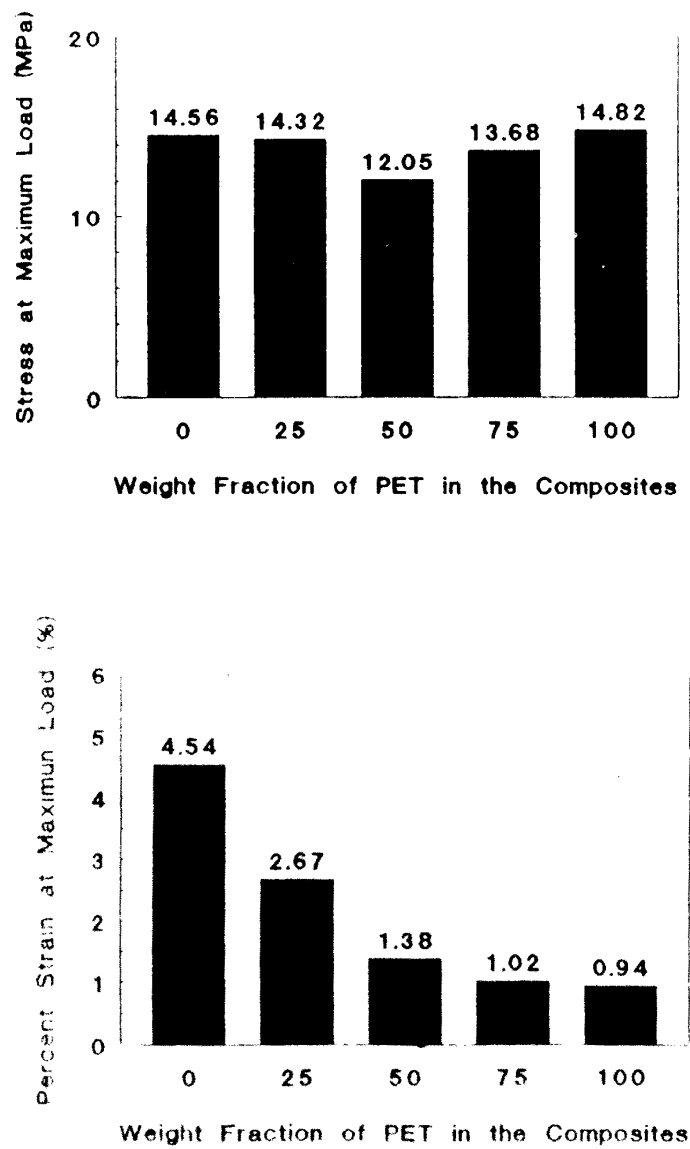


Figure 2.17 Stress at Maximum Load (top) and Percent Strain at Maximum Load (bottom) as a Function of PET Concentration for Recycled Composites. (Figures from D.N.S. Hon and C.J. Buhion, *J. Thermoplastic Comp. Mat.*, 7, 4, 1994.)

This can be attributed to the stiffness of the PET as compared to the ductile HDPE. The important point of this study is that the recycled material showed favorable properties, in tensile strength, after reprocessing. And, although the material cannot be used in a true reprocessing sense, where more bottles and caps are generated, this composite material could be used in other applications.

In another study, reclaimed polyethylene (PE) and reclaimed polystyrene (PS), were reprocessed to determine any loss in material properties. Ram et al [56] found that reclaimed PE had a tensile modulus (94.0 Kg/cm^2) that was 20% lower than that of the pure material (119.0 Kg/cm^2). And, for the polystyrene (PS), the tensile modulus for the reclaimed material (309.4 Kg/cm^2) was also ~ 20% lower than the tensile modulus for the pure resin (391.8 Kg/cm^2). These large drops in mechanical properties for both of these materials appears to be a function of degradation from the mechanical and thermal history in reprocessing. This degradation, due to reprocessing, seems to pose a concern for the successful reprocessing of reclaimed polymeric material. Therefore, it seems important to investigate whether or not the liquid crystalline component of the composites in question can stand up to a reclamation process.

Fortunately, some work has already been done to address this particular question [15, 57, 58]. In Section 2.2.2, it was shown by Sasaki et al.[15], that composites of liquid crystalline polymer and polypropylene could withstand 10 recycling cycles without any loss in tensile strength. However, Sasaki et al. [15] probably did see some substantial losses in modulus and toughness. Recently, some work has been done to show that liquid crystalline polymers can be reground and reprocessed without significant losses to mechanical properties.

Bastida et al [57] did some studies of two common thermotropic liquid crystalline polymers: 1) Vectra B950 from Quimidroga and 2) Rodrun LC-5000 from Unitaka. The basic chemical structure for the Rodrun is a copolyester of polyethylene terephthalate (PET) and p-hydroxybenzoic acid (HBA). In the case of the Vectra B950, the basic chemical structure is a copoly(ester-amide) of 2,6-hydroxynaphthoic acid, terephthalic acid, and aminophenol. These two materials were injection molded, tested, reground, injection molded, and then tested again. This process was repeated five times for five cycles.

In Figure 2.18, it can be seen that the melt flow index is increasing with increasing recycling. This can be explained by there being a loss in molecular weight with each successive recycling. From this plot, it can be seen that there was a three fold increase in melt flow index over the five recycles. This rapid loss in molecular weight can be attributed to break up of the molecular chains from the mechanical energy imposed on the material during each reprocessing cycle. Because the exact form of degradation was not known, it became important for Bastida et al. [57] to understand what effect this recycling process had on the mechanical properties of the liquid crystalline polymers.

In Figure 2.19, are plots of the Young's modulus (top) vs. number of cycles and a plot of the tensile strength (bottom) as a function of the number of recycles. In the case of the Vectra B950, there appears to be a loss in the Young's modulus as a function of the number of recycles. This loss is minimal and only represents a 15% loss in modulus over five cycles. However, for the Rodrun LC-5000, there appears to be no appreciable loss in

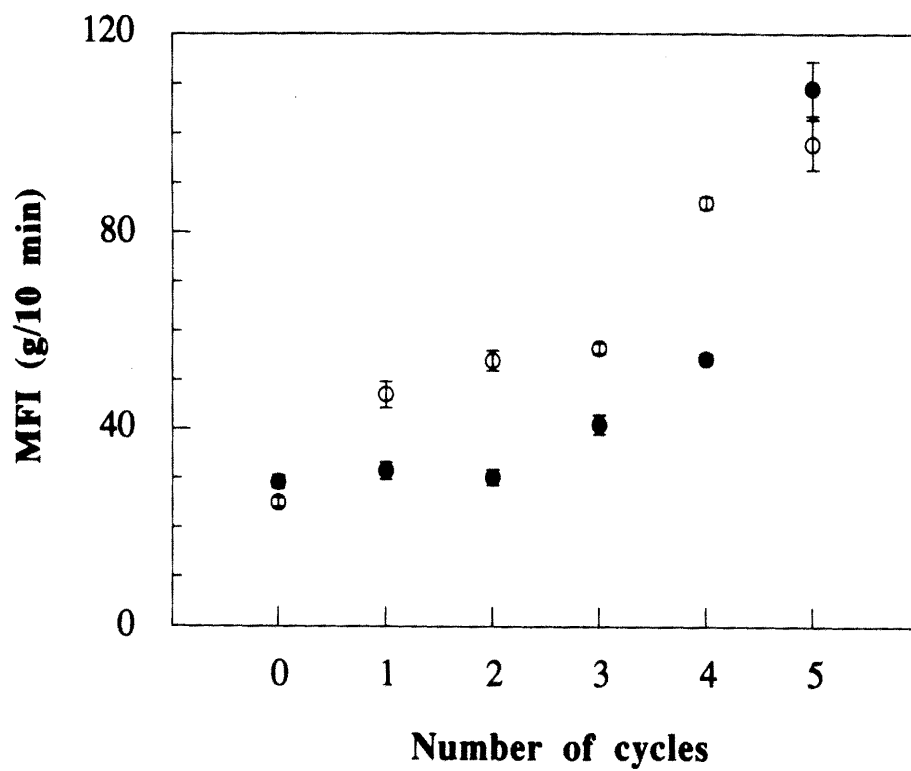


Figure 2.18 Effect of the Recycling on the Melt Flow Index (MFI) as a Function of the Number of Cycles for the two Liquid Crystalline Polymers. (Figure from S. Bastida, J.I. Eguiazabal, and J. Nazabal, *J. Appl. Polym. Sci.*, **56**, 1487, 1995.)

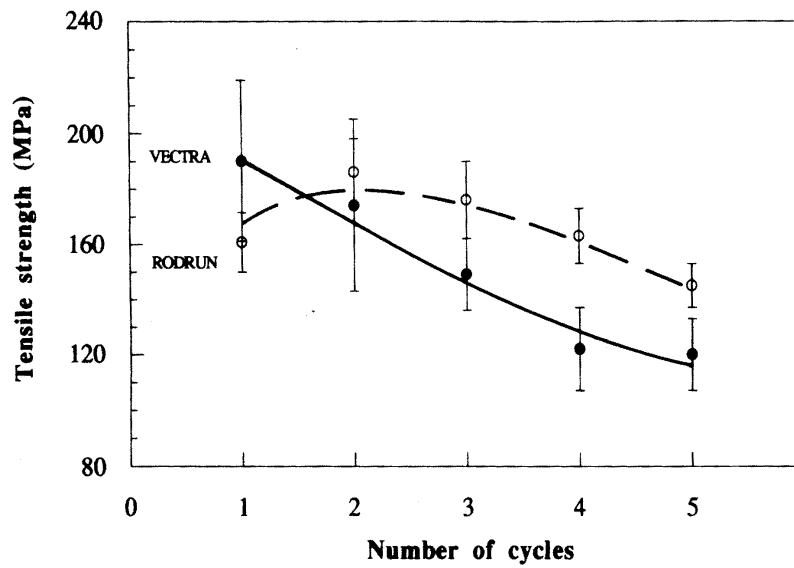
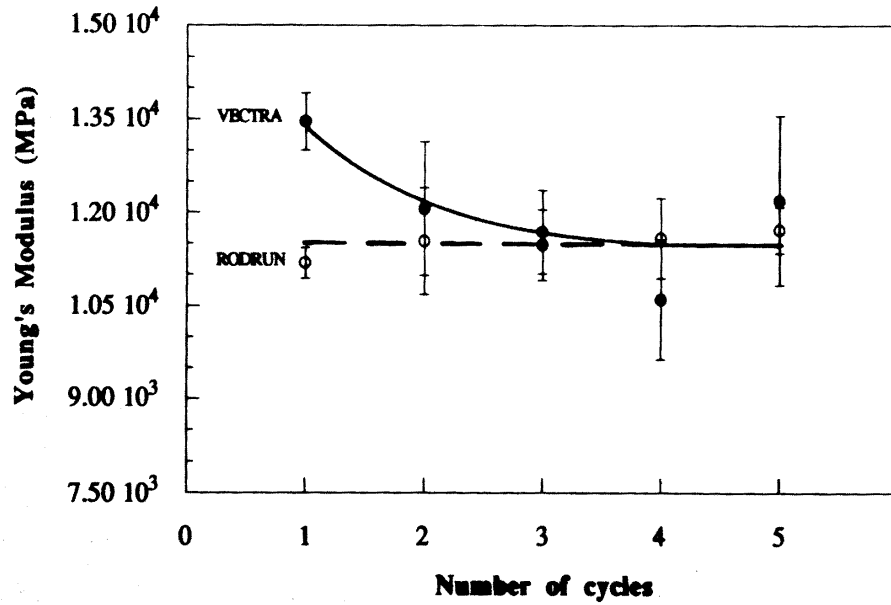


Figure 2.19 Effect of the Recycling on the Young's Modulus (top) and the Tensile Strength (bottom) as a Function of the Number of Cycles. (Figures from S. Bastida, J.I. Eguiazabal, and J. Nazabal, *J. Appl. Polym. Sci.*, **56**, 1487, 1995.)

Young's modulus over the five cycles. Interestingly enough is that both polymers show a loss in tensile strength over the five cycles. However, this is still only a 15-20% loss overall.

It appears from these results that the effect of reprocessing, on certain thermotropic liquid crystalline polymers, is one of molecular weight reduction. And, depending on the liquid crystalline polymer in question, this can lead to a 15-20 % reduction in mechanical properties over five reclamation cycles. The important point of these studies is that, though there were some losses in material properties, the overall loss is not large enough to discourage the prospect of recycling.

In conclusion, based on the information obtained on plastics recycling (Section 2.2), polymer solubility (Section 2.3), reactive extrusion (Section 2.4), and the ability of the liquid crystalline polymers to handle reprocessing (Section 2.5), there appears to be a strong potential for developing a successful reclamation process. By using reactive extrusion with organic peroxides, to selectively degrade only the polypropylene matrix, the right thermodynamic circumstances for the dissolution of the degraded polypropylene could be achieved. And if this dissolution is performed under the right circumstances, utilizing the many differences in physical characteristics between the polypropylene and the liquid crystalline polymer, a new separation technique could be designed to produce large quantities of relatively pure liquid crystal.

Furthermore, it seems intuitively obvious that the reclaimed polymer could perform as well as the virgin material in a case where the reclaimed polymer is blended in with the pure resin. The fact that there is no process currently available to successfully reclaim the liquid crystalline polymer from composites, seems to indicate that the development of such

a process would be novel in nature. And, based on the fact that there already exists much of the infrastructure for such a device, it seems that the development of such a process appears to be feasible and possible. It is therefore the recommendation of the author that effort should be put forth to develop a reclamation process for the recovery of thermotropic liquid crystalline polymer from composites generated with polypropylene and liquid crystalline polymer.

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