ABSTRACT

KRISHNASWAMY, RAMAKRISHNAN. Mechanical and Rheological Properties of Poly-ε-Caprolactone Processed with α-Cyclodextrin. (Under the direction of Dr Alan.E.Tonelli).

Cyclodextrins (CDs) are cyclic starches containing glucose repeat units. CDs form non-covalently-bonded inclusion compounds (ICs) with various polymers, like poly (ε-caprolactone) (ar-PCL) and nylon-6 by threading the polymers through their hydrophobic cavities. PCL-α-CD-ICs are coalesced by extensive washing with water and subsequently with HCL for a short time. The aim of this work is to study the mechanical and rheological properties of the coalesced PCL(c-PCL) and try to understand the changes that result due to its processing with CD. On removal of the host α-CDs, the c-PCL that results is likely transformed into small domains (~1/10^{th} the size of the crystalline grains of the IC powder). In each domain the PCL chains have largely un-entangled extended conformations, without, however, directional correlation among the different coalesced domains.

The changes in the morphology and conformations of c-PCL are stable to melt-annealing and it does not return to the original random-coiling entangled state even when the material stays in the melt for long periods of time. This may be attributed to the differences in the volumes influenced by each chain in c- and ar-PCL samples.

As a consequence, the melt-rheology of c-PCL is markedly different from the visco-elastic behavior of the ar-PCL melt. Furthermore, a few weight percent of the c-PCL acts as an effective nucleating agent for the melt-crystallization of ar-PCL. This nuc-PCL may be melt-processed into products with enhanced properties, such as sutures, scaffolds etc.
Mechanical and Rheological Properties of Poly-ε-Caprolactone Processed with α-Cyclodextrin

by
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A thesis submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Master of Science Textile Chemistry

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APPROVED BY:

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Dr. Melissa Pasquinelli

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DEDICATION

Dedicated to God, Family and Friends.
BIOGRAPHY

Ramakrishnan Krishnaswamy was born on June 21, 1987 in India. He graduated from VJTI, University of Mumbai with a B.Tech degree in Textile Technology in 2008. Then, motivated by an interest and drive to pursue graduate education and research, and with compliments from his professors, he came to the College of Textiles, North Carolina State University on receiving a Graduate Research Assistantship from the department. There, he got interested by the research on Polymers and started work under the guidance of Dr Alan Tonelli, a distinguished professor of Polymer Science.
ACKNOWLEDGMENTS

I would like to first and foremost thank Prof Alan.E.Tonelli, under whose invaluable guidance and support I pursued my graduate research. I would like to express profound gratitude to the other members of my committee, Dr Melissa Pasquinelli and Dr Saad Khan for being of support. Thanks are also due to the members of Dr Tonelli’s research Group and friends, especially Dr Arjun Krishnan for help and guidance with melt rheology experiments. Thanks are due to Dr Hannah Gracz for NMR training and testing.

Special thanks to Ms Birgit Anderson, Ms Teresa White and Ms Judy Elston for help with sample testing.
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CHAPTER 1

INTRODUCTION

Introduction

Poly-ε- caprolactone \{\{[-\text{CH}_2\}_5-\text{C}-\text{O}-]_n\} (PCL) is a bio-degradable [1] polyester obtained from the ring opening polymerization of ε-caprolactone, using various catalysts like proton exchanged montmorillonitrile clay[2]. Hu et al analyzed the structure of PCL and demonstrated that PCL has a non-planar crystal structure [3], as first proposed by Chatani et al. [4].

The properties of PCL are strongly correlated with its semi-crystalline morphology [5], thus polymer processing-conformation-morphology correlations are interesting to study. It would seem logical to conceptualize the effect of the conformational changes of PCL on its properties, and thus the sensitivity of these changes to the processing parameters. An understanding of such processing-conformation-morphology-property correlations would be important, not just from the scientific point of view, but also from the practical processing viewpoint.

One of the novel ways of modifying the morphology and studying the resultant properties of polymers is through the formation of non-covalently bonded crystalline inclusion compounds (ICs) between guest polymers and various hosts. Tonelli et al have been studying the use of urea and cyclodextrins hosts for this purpose for over the last two decades [6].

While much work has been done to study the factors that affect the inclusion process itself and the effects of stoichiometry on polymer-IC behavior [7], less is known about the
properties of the polymers that result on coalescence from their crystalline ICs. A reasonable hypothesis, based on experimental results and models developed, would seem to suggest that the polymers coalesced from their ICs would largely retain their extended unentangled conformations, even over extended periods in the melt, as a consequence of the long time for the volume influenced by extended un-entangled coalesced polymer chains to return to the much higher levels in randomly coiled entangled melt.

There have been studies and theories by Fields et al [1] to qualitatively link molecular weight with degradation and the polarity of polymers, like polyesters, with their structurally useful properties. Re-organisation of polymer chains using host-guest complexation, followed by coalescence, and the properties that result would thus be interesting to study.

**Inclusion Phenomena**

The inclusion of various molecules in the cavity of host molecules like urea(U), thiourea (TU), perhydrotriphenylene (PHTP).cyclodextrins (CDs) etc have been studied [7, 8]. For a long time certain small molecules have been known to include in the cavities they form. Suehiro et al [9] studied urea inclusion compounds and found that the U-IC crystal structure formed with Poly-ether adopts a different crystal shape depending upon the molecular weight.

Tonelli[7] used conformational analysis to predict that these inclusion compounds with urea (See Figure 1) could be used to separate stereoregular L and D forms of polylactides from their stereoirregular D,L forms, as only the pure L or D form in the trans conformations would fit in the narrow channels and form inclusion compounds.
Figure 1: Schematic representation of the hexagonal Urea-n-hexadecane clathrate.[8]

Rusa and Tonelli[8], demonstrated that Urea shows a molecular weight selective polymer inclusion, with a preference for higher molecular weight PEG. As an example, Figure 1 shows the hexagonal channel of host Urea that includes most polymer guests in the complexation process. Apart from CD hosts, which also form soluble inclusion compounds [10], none of the other hosts have been proven to retain their cavity forming matrices (the precipitation technique used for this purpose is unique to cyclodextrin) without the presence of the long chain polymer guests nor form such soluble inclusion compounds. Also, because there are three forms of CD, with different cavity sizes, that are commercially available, make it interesting to study the effects these subtle and unique host size differences have on the morphology-property relationship of the guest polymers processed from them.

In 1990, Harada et al. first demonstrated that polymers form crystalline columnar inclusion compounds with α-CD, by demonstrating this with guest PEG oligomers, which are different
from small molecule inclusion compounds that form cage type inclusion compounds with CD[11]

**Cyclodextrins**

Cyclodextrins were first discovered by A. Villiers in 1891 and named Cellulosine, because they behaved similar to cellulose i.e resistant to hydrolysis. This crystalline product was isolated after bacterial digestion of potato starch and is regarded as the first published record of cyclodextrin[12]. Years later, Schardinger discovered two crystalline polysaccharides, while investigating food spoilage, that were named ‘crystalline dextrin α’ and ‘crystalline dextrin γ’ [13]. Freudenberg and Jacobi developed a method to purify α, β and γ-dextrin and studied the chemical composition of these molecules.[14]. A series of studies published in the 1930’s led to the confirmation of the cyclic structures of these starches. Now, it is common knowledge that cyclodextrins are annular molecules.

As shown in Figure 2, cyclodextrins have hydroxyl groups that are primary and secondary and are attached on one rim or the other [15]. The hydroxyl groups, and more importantly their positioning (outside the cavity on both rims), leads to many structural features and complexation behaviors that are unique to cyclodextrins.

The glucoperanose unit, shown in Figure 3 hinders bond rotation and leads to the truncated cone shape of the cyclodextrins. This coupled with the hydrophilic exterior/hydrophobic core and cyclodextrin’s bio-degradable, bio-absorbable nature make their utility unique for drug delivery.[15]. However there are certain issues with using cyclodextrins. For example, amongst the cyclodextrins, due to asymmetry among the odd number of glucose units and the
low solubility in water, β-CD behaves differently from α- and γ-CDs, so its oral administration/absorption is not that effective, and perenteral administration is the preferred route of drug delivery. [16]

Figure 2: Chemical structure and numbering for α-, β-, and γ-cyclodextrin (n=1 for α-CD, n=2 for β CD, n=3 for γ-CD) [17]

Figure 3: Glucopyranose unit [17]
As shown in Figure 4, the hydrophobic inner cavity and hydrophilic outer surface coupled with the variable sizes of cyclodextrins as can be seen in Table 1 below, makes them interesting biodegradable, bio-absorbable candidates for research in many applications. However, only recently[18] has the existence of larger cyclodextrins been proven. These are listed in Table 1, along with some of their properties.

Figure 4: Location of hydrophobic and hydrophilic interactions for cyclodextrin [19]
<table>
<thead>
<tr>
<th>Glycosy Units</th>
<th>Semi-systematic name</th>
<th>Generic name</th>
<th>Abbreviation</th>
<th>Molecular weight</th>
<th>Aqueous solubility [g/100 ml]</th>
<th>Surface Tension (mn/m)</th>
<th>Specific rotation [α]25</th>
<th>Half life of ring opening</th>
<th>Radius of gyration</th>
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<td>α-cyclodextrin</td>
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<td>CD13</td>
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<td>&gt;150</td>
<td>72</td>
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<td>CD</td>
<td>M.Wt.</td>
<td>TDL</td>
<td>M.L.</td>
<td>R.I.</td>
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</table>
Cyclodextrin Inclusion Compounds

The three main cyclodextrins that have been widely analyzed are α, β and γ-CD with 6, 7 and 8 α-1, 4-linked glucose units. The number of glucose units in β-CD causes it to behave differently as compared with other CD’s. As shown in Figure 5 below, the cyclodextrins exist in a cage form (powder) and, when a polymer is included in them, a columnar form. As can be seen the diameter of the inner core of α-CD is 0.5 nm, while that of γ-CD is almost twice that at 0.95 nm[18].

Cyclodextrin polymer inclusion compounds, are actually non-covalently bonded pseudo-polyrotaxanes (PPR’s), and their inclusion phenomena is influenced by many factors and has been explained in many ways. For instance Lonostro et al.[20] proposed a hypothesis for the interaction between these poly-rotaxanes that is based on the spatial dielectric anisotropy and leads to the agglomeration and precipitation of these inclusion compounds, and the Avami-Erofe’ev model is used to provide information on the mechanisms of the processes [20].

The factors that seem to affect the inclusion range from kinetic to thermodynamic stability [20]. The complexity of factors affecting the inclusion process can be evidenced not just from the study of factors [6,21] influencing the inclusion compound formation process, but also the study of competitive threading of two different polymers. Rusa et al.[22] found that the geometric compatibility of the polymer with the host cyclodextrin and the hydrophobicity of the polymer are important factors in determining the inclusion of the long chain polymers in the host CD channels. Generally the hydrophobic inner cavity of the host cyclodextrin seems to preferentially include more hydrophobic polymers. So when there is a competition between two polymers, such as PCL and PLLA, the affinity is for PCL inclusion.
Amongst the different CD’s there seems to be an increased affinity between the smaller cavity of α-cyclodextrin and PCL, as evidence of the geometric compatibility between the diameters of the cavity of the host cyclodextrin and the guest polymer.
Table 2: Basic properties of α-, β and γ-cyclodextrin

<table>
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<th>Property</th>
<th>α-CD</th>
<th>β-CD</th>
<th>γ-CD</th>
</tr>
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<tr>
<td>Number of glucopyranose units</td>
<td>6</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>9722</td>
<td>1135</td>
<td>12977</td>
</tr>
<tr>
<td>Solubility (% w/v in water, 25 °C)</td>
<td>14.55</td>
<td>1.85</td>
<td>23.22</td>
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<tr>
<td>Outer diameter (Å)</td>
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<td>15.4</td>
<td>17.55</td>
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<td>Cavity diameter (Å)</td>
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</tr>
<tr>
<td>Cavity volume (Å³)</td>
<td>1744</td>
<td>262</td>
<td>4277</td>
</tr>
</tbody>
</table>

As can be seen from Table 2 above, the inner diameter of α-cyclodextrin is half that of γ- cyclodextrin and the smaller diameter is more geometrically compatible with the size of PCL chains. Rusa et al found that when γ- cyclodextrin PCL-IC crystals are suspended in a solution containing α–CD, the PCL-α-CD IC results. Thus the Polymer --- α-CD interaction is much stronger relative to polymer—polymer interaction between the two chains that can be threaded in the inner cavity of the γ-CD. However the reverse is not true, so when a PCL-α–CD-IC is suspended in the solution containing γ-CD, transfer of chains doesn’t occur, an evidence of affinity of α-CD for PCL.[22], a factor that is validated and discussed by the experiments on the ‘coalesced polymer’ in the next chapters. As indicated in Figure 6, randomly-coiling polymer, when forced in the narrow channels of the host CDs, are converted into their fully extended,
unentangled conformations that may be largely retained for long times upon coalescence, a process in which the host is washed away. The coalesced polymer that results is expected to have micro-domains in which the polymer chains are in extended conformation, however these micro-domains of extended unentangled coalesced chains are randomly arranged. Coalesced polymers have been found to be effective nucleating agents for the melt-crystallization of same as-received bulk polymer.[25] This phenomena and the possible reasons for it are explored later.

Figure 6: Comparison of the consolidation of polymers from their solution or melts vs. coalescence from their CD-ICs [24]
The actual formation of the inclusion complex is usually done by what can be called co-precipitation, in which the CD solution is added to the polymer solution, or *vice versa*. Depending upon various factors, ranging from molecular weight of polymer, hydrophobic nature, (however this does not explain how some hydrophilic compounds/polymers include in guest CD crystals just as readily), and under suitable conditions of temperature, solvent, etc., the inclusion compound precipitation occurs. It has been suggested that the formation of soluble short cyclodextrin tubes precedes inclusion of the polymer[20]. Based on a review of the literature, relatively little investigation has been carried out on the coalesced polymers, as compared to the inclusion complex stoichiometry and factors that affect inclusion. It is therefore interesting to study the effects of the proposed conformational changes resulting from coalescence on the properties of the modified polymer.

**Inclusion Compound Characterization**

Analytical techniques, like Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), and X-Ray Diffraction are used to characterize the inclusion compound. As seen from Figure 7 the melting peaks of PCL that are characteristic of the as received polymer aren’t present in the scan of its α-CD-IC. The inclusion of the polymer chains in the CD cavity and the stability of the CD IC structure is the reason the melting endotherm disappears in the IC.

The FTIR scans (See Figure 8), which are a manifestation of the vibrational properties of the molecular structure and environment of the sample, provide evidence of the presence of both CD and the polymer. Figure 9 offers a comparison of the XRD of the Polymer CD IC and the
CD powder by itself. As discussed earlier, in the XRD results (fig 9 A) [22] of the polymer-CD IC, the characteristic columnar CD peak is seen at 20°. Fig 9b is that of the cage structure of CD powder. When combined with the DSC results of no melting peaks being observed for the guest polymers, it is evidence of the formation of polymer-CD IC.

Figure 7: DSC Scan of α-Cyclodextrin PCL 1:1 Inclusion Compound(IC)
Figure 8: FTIR Scans of α- and γ-Cyclodextrin ICs of Nylon-6 [24].
Figure 9: (A) The XRD results validate the columnar structure of CD found in the Nylon-6-α-CD- IC (B) Cage structure in CD powder [24].
CHAPTER 2
MELT RHEOLOGY OF POLYMERS

Introduction

Rheological properties of polymers are useful to determine the material behavior encountered during their processing, and have been of interest for many years. One of the most comprehensive of these studies has been of Polylactides (PLAs), viz. of melt PLAs, reported by Dorgan et.al[26]. These include the relationship of Zero Shear viscosity to molecular weight, with an emphasis on uniaxial melt characteristics of the same, and the relationship of the relaxation spectrum to molecular weight characteristics and other rheological parameters helpful in predicting the visco-elastic characteristics of PLA. For example, the strain hardening observed was concluded to be due to the dynamics of molecular relaxation.

In another study, the rheological behavior of molten PCL was both modeled and observed by Gimnez et.al. [27] In that study, the polymerization of ε- Caprolactone was carried out in the rheometer itself and a good co-relation was observed between the experimental data and the modeling results.

Rheological observations of Cyclodextrin-IC crosslinked Gels

Organogels based on β- Cyclodextrin and Propargyl functionalized PCL PPR’s have been studied by Jazkewitsch and Ritter[28]. They found that the swelling degree of the gels and their rheological behavior depend on cross-link content. As shown schematically in Figure 1.
a) and b), the re-organization of the polymer chains in the amorphous domains leads to smaller spherulite size, as seen in the polarizing microscope (POM) images.

Figure 1: Schematic representation of the proposed reorganization of polymer through formation of inclusion complex (a and b). Comparison between photographs of spherulites of 3a (c) and optic appearance of 3b-β-CD (d) obtained by polarized light microscopy (POM) [27]

Tonelli et al. found that in PVA/γ-CD hydrogels made by freeze-thaw (FT) cycling, the swelling and rheological responses can be controlled by adjusting the PVA-γ-CD molar ratio (stoichiometry) used during their formation [23]. Since both PVA and γ-CD are water soluble, the characterization of these water soluble IC’s is not possible by traditional means.
Based on the experimental results in this particular piece of work, structures for the PVA hydrogels formed in the presence of $\gamma$-CD were proposed, as shown in Figure 2. Small portions of the PVA chains may be threaded into and covered by the $\gamma$-CD and the hydrogels that result are weaker than the neat PVA hydrogels themselves.[23]

Figure 2: Schematic illustrations of the proposed structures of PVA/$\gamma$-CD dried films (upper) and swollen gels (lower) produced by F-T cycling: (1) channel structure of PVA-$\gamma$-CD IC, (2) hydrogen-bonded interactions/crystals/cross-links between PVA chains, and (3) free $\gamma$-CD molecules[23]

Shear induced Isotropic to Nematic Transition in Liquid Crystal Polymers (LCPs)

Typical visco-elastic polymers are isotropic in the melt. Studies have shown that the shear induced isotropic to liquid crystal transition is a general property of liquid-crystalline
polymers (LCPs). A slipping mechanism is corroborated by an identification of macroscopic long-range correlations of unentangled polymer melts.[29]. There have been studies to see the behavior of blends of LCPs with isotropic polymers like polycarbonates, and it was found that the $T_g$ of the PC component of the blend was elevated owing to trans-esterification, and the resultant blocky co-polymers act as a compatibiliser and improve the interfacial miscibility of the LCP Vectra and PC. Free volume characteristics of this blend were probed by positron annihilation lifetime spectroscopy (PALS) and it was found that, due to greater chain rigidity and closer packing, Vectra was found to have smaller free volume cavities. The free volume cavities of the blends were much larger than the weighted average. It was found that there was a compositional dependence of free volume cavities with blend miscibility possibly indicative of free volume created at the interfaces being offset by the reduction in free volume due to trans-esterification. The density values measured seemed to be in agreement with the free-volume fractions of the blend determined by PALS[29].

Pisitsak and Magaraphan found that when Vectra A 950 LCP and Poly (tri-methylene terephthalate) (PTT) were melt blended and subjected to capillary rheometry, the thermal stabilities of these immiscible blends were found to be enhanced[30].

**Liquid Crystal Polymers and Their Use in Composite blends**

Liquid crystal polymers may be classified as either thermotropic (liquid crystal in melt) or lyotropic (liquid crystal in solution) [31]. They find use in many high performance applications owing to their high elastic modulus, high flexural and tensile strength, dimensional stability and impact strength. Uribe[32] studied the molecular orientation and visco-elastic behavior of commercial LCPs. They showed geometry dependent flow behavior
on shear rate owing to the shear induced change of orientation of their rigid molecular segments. In this study, the flexural elastic modulus of the molded parts was found to be dependent on the sample thickness, which increases with reduction in thickness.[33]. Studies have shown that the processing temperature plays a vital role in optimizing the mechanical properties of LCP blends [34]. Studies have shown that PCL acts as a solvent (in the melt) for a lyotropic rigid rod polymer, Thus the PCL substituted terephthalic acid blend acts as a lyotropic liquid crystal blend, whereas the substituted terephthalic acid does not show liquid crystal behavior in the melt by itself [35]. Figure 3 shows the rheological measurements of the PCL at 80°C. The curve A is a plot of storage modulus vs frequency of the blend, while B represents the storage modulus vs frequency plot of the PCL. C and D represent the loss moduli vs angular frequency plot of the blend and PCL respectively.

![Rheological measurements](image)

**Kricheldorf, Wahlen, Macromolecules 1996.**

Fig 3: Rheological measurements (80°C) of neat PCL and of a blend containing 1 wt (%) of
rigid rod polymer. A: Storage Modulus of the blend $G'$. B: Storage modulus ($G'$) of PCL. C: Loss modulus ($G''$) of blend. D: Loss Modulus ($G''$) of PCL\[33\]

In a separate study it was found that because of the biphasic nature of the thermotropic liquid crystal polymer blend of a LCP with PC the complex and steady shear viscosity increased with temperature above $350^\circ$ C, and the synergistic flow behavior was explained by the alignment and superior lubrication of the thermotropic liquid crystalline polymers at the molecular level.[36].

Resia et al [37] studied the effect of thermal history on the biphasic nature and phase transitions of a thermotropic LCP and found that annealing between the liquid crystalline and isotropic phases gave rise to a double endotherm attributed to preferential segregation of the lower molecular weight molecules from the LC phase into the isotropic phase.

A study constituted to analyze the synergistic effects of using a blend of different types of carbon-fibres,\textit{vis-a-vis} in single filler composites, was tested, and it was found that the complex viscosity increased in all cases with increasing filler volume fraction. The increase was maximum for a combination of carbon black and synthetic graphite, possibly owing to the branched, high surface area structure of carbon black cross links with the graphite particles [38].
CHAPTER 3

MELT RHEOLOGY AND MECHANICAL PROPERTIES OF PCL MODIFIED WITH CYCLODEXTRINS

Introduction

PCL inclusion compounds with α-CD and their behavior, such as characteristic FTIR peaks and suppression of melting/crystallization peaks and effect of molecular weight on their yield, have been studied in the past [39]. Dong et al have been studying α-CD-PCL non-stoichiometric inclusion compounds as nucleating agents for the melt-crystallization of bulk PCL and their use in making bio-degradable composites [40-42].

However, fewer studies and attempts have been made to study the properties of the polymers that result on coalescing the ICs. Wei et al tried coalescing a small quantity of α-CD-PCL-IC enzymatically, and validated the coalescence process by the absence of CD peaks in the FTIR scans [43]. However, aside from crystallization kinetics, no other detailed analyses of the c-PCL were done.

Scaling up the α-CD-PCL-IC formation process and its coalescence has many difficulties. Brandon Williamson scaled-up and tried a host of coalescing techniques and concluded that only acid washing for a small period of time was enough to ensure α-CD removal. In this study the IC formation technique was scaled up and the coalescence technique refined further, with an attempt to make sure that a delicate balance was struck between removal of remnant α-CD and prevention of PCL degradation due to hydrolytic chain scission upon exposure to HCL [44].
Materials and methods

80,000 g/mol PCL from Sigma Aldrich was used without treatment as the as received “control” sample (ar-PCL). α-CD was procured from Cerestar and acetone from VWR. Other non-aqueous solvents and acids were obtained from sigma Aldrich and used without further treatment.

Formation of PCL-α-CD inclusion compound

As illustrated in the flow diagram below, the steps involved in the processing of PCL using α-CD involve the formation and characterization of the inclusion compound by co-

1. Formation Of PCL-CD IC

2. Coalescence Process - removal of the CD

3. Nucleating the bulk(AR-PCL) by addition of Few wt percent of Coalesced (C-PCL)

Figure 1: Flow diagram of steps involved in processing PCL with CD.
precipitation technique, the coalescence technique used to remove the $\alpha$-CD and the nucleation of the bulk by adding the coalesced polymer to it. A scaled up adaptation of the Wei et al. method [43] was used. 4 g PCL was dissolved in 500 ml acetone by stirring at 60°C overnight. 37 g of $\alpha$-CD was dissolved in 250 ml de-ionized water. The $\alpha$-CD solution was added to the PCL solution while stirring, sonicated for a few minutes and stirred at room temperature for 36 hours. The resulting precipitate was filtered, vacuum dried, as demonstrated by the schematic below, and approximately 20 g of the IC was collected. The IC was washed in water overnight and then with acid (conc. HCL) for a short time (1 min.or less), and finally washed in water and dried to get the coalesced polymer. Water washing/acid washing for a short time/water washing was done carefully, to make sure that chain scission did not happen. This was confirmed by the closely similar flow times of dilute chloroform solutions of ar- and c-PCLs observed in a viscometer.

Figure 2: Steps involved in the inclusion compound formation
Characterization Techniques and Results

Fourier Transform Infrared Spectroscopy (FTIR):

Nicolet 510 P FTIR spectrometer was used to do FTIR scanning of all materials in the range of 400 to 4000 \( cm^{-1} \) with a resolution of 4 \( cm^{-1} \) and the 64 scans conducted for all samples was analysed using OMNIC software.

Figure 3: FTIR scan of PCL-\( \alpha \)-Cyclodextrin IC

Figure 3 shows the FTIR scan of the PCL-\( \alpha \)-CD-IC. However, the sensitivity of FTIR in detecting a few percent remnant \( \alpha \)-CD is not very high, so we turned to more sensitive probing techniques, like NMR, which are discussed later. FTIR results showed that the coalesced PCL did not have any residual \( \alpha \)-CD (Figures 4 and 5). However, investigation by
solution $^1$H-NMR performed on the sample indicated small traces of remnant α-CD were present.

Figure 4: FTIR scan of C-PCL
Wide angle X-Ray Diffraction

X-Ray diffraction was done by using a Philips XLF ATPS XRD 1000 with OMNI Instruments Inc. customized Automount and Cu tube. The standard columnar IC peaks are present. When combined with the FTIR and DSC results in which no PCL melting peaks were found suggest that we have successfully managed to make the IC. The XRD scan in Figure 7 shows the columnar CD matrix precipitated in chloroform, as discussed by Rusa et al [10]. When a few weight percent of columnar CD was added as filler to the ar-PCL melt there was no significant change in the melt rheology, similar to the melt rheology of PCL with a few weight percent of CD powder added (cage structure).
Figure 6: (A) X-Ray Diffractogram (XRD) of PCL-α-CD-IC (B) XRD OF as-received cage α-CD
The DSC scan of the PCL-α-CD-IC (Figure 8) did not show any melting peaks indicating that all the chains were included in the narrow α-CD channels.
Figure 8: DSC Scan of PCL α-CD IC

**Differential Scanning Calorimetry**

The DSC curves of the material not only give the thermal characteristics and behavior, but also give information about the physical structure of the material that causes the change in thermal transitions. The melting and crystallization behavior of coalesced PCL is shown in Figure 9 and though the melting behavior is not that different from that of ar-PCL, the crystallization behavior is very different. The melt-crystallization temperature is elevated and the
Figure 9: DSC Scan of PCL coalesced from its α-CD-IC(C-PCL)
crystallization occurs over a narrower temperature range, possibly due to the elongated conformations of the hitherto constrained chains. Since the difference in crystallization temperatures of ar- and c-PCLs are so large, further investigations were carried out. Even on annealing in the melt for long periods of time, the crystallization behavior did not change. The summary of these results and possible reasons are offered later. Since the coalesced PCL crystallizes at a temperature higher than the as received PCL, c-PCL well dispersed in ar-PCL would on heating and cooling thereafter crystallize at a higher temperature than the neat ar-PCL and offer nucleation sites for its melt-crystallization. This phenomenon and the resultant change in crystallization profile of the nucleated material were also stable to annealing in the melt, as demonstrated in Figures 11 and 12, where the crystallization peak is
sharper and narrower and does not change even after staying at 90 °C for a week. All these results and our hypothesis of the free-volume change on converting the polymer to the extended chain conformation suggested melt rheology as a probe of the coalesced polymer, which is discussed subsequently.

The small reduction in melt-crystallization temperature of nuc-PCL is possibly due to reduction in crystallizability due to the few chains that are potentially constrained in the one tenth of a percent of remnant α-CD channels. However, even on annealing in the melt for a week, nuc-PCL showed a similar crystallization profile (Figure 12).

Figure 11: DSC Scan of PCL nucleated by C-PCL
Figure 12: DSC scan of ar-PCL nucleated with c-PCL after annealing at 90° C for a week

**Nuclear Magnetic Resonance:**

NMR Spectra: The $^1$H-NMR spectrum of PCL in Chloroform and DMSO were measured. The solvents were deuterated for signal locking, and the NMR spectra were run at room temperature on a 500 MHZ Bruker Avance DRX spectrometer.

The spectra in Figure 13 compare c-PCL in CDCl$_3$ and DMSO with α-CD in DMSO. They show the DMSO peak at 2.6 ppm (vs TMS), and since DMSO is hygroscopic, there is a water peak at 3.4 ppm. The α-CD peaks at 4.9 ppm and 5.6 ppm are very evident in the α-CD sample in DMSO. Since α-CD is not soluble in CDCl$_3$, the CD peaks are not present in the PCL in CDCl$_3$. When the coalesced PCL sample in DMSO was probed, small intensity peaks were seen at 5.6 and 4.9, possible evidence of remnant α-CD.
Figure 13: Solution $^1$H-NMR spectra of a) $\alpha$–CD in DMSO compared to

b) Coalesced PCL in chloroform and c) Coalesced PCL in DMSO.
Figure 14: Solution $^1$H-NMR spectra comparison of a) Ar-PCL and b) C-PCL in CDCl$_3$

The c-PCL and ar-PCL were then compared by $^1$H-NMR in CDCl$_3$ (Figure 14) and a mixture of CDCL$_3$ and DMSO (not shown here). We can see four peaks typical of PCL at 4.07, 2.34, 1.64 and 1.43ppm. There is a slight shift in PCL peaks in the coalesced PCL sample as compared to the ar-PCL in CDCl$_3$. 
Melt Rheology of c-PCL

The rheological characteristics of c- and ar-PCL films melt-pressed in a millimeter thick mould were studied on AR 2000 rheometer using the ETC plate under nitrogen atmosphere at various temperatures above the melting point. Temperature and stress sweeps were performed on the c-PCL to ascertain the window of processibility (Fig 15 and 16) and the Stress sweep was performed at 70° C, with an angular frequency of 6.284 rad/sec to ascertain the Linear Visco-Elastic region (LVE). A strain percentage of 2%, which was safely assumed to be in the LVE, was chosen for the frequency sweeps. The storage(G’) and loss(G’’ ) moduli were plotted against the oscillatory stress to find the LVE. Frequency sweep and steady shear experiments were performed thereafter.

![Graph](image.png)

Figure 15: Temperature ramp of Coalesced PCL 70 - 100° C
Figure 16: Stress sweep of C-PCL at 70° C

Frequency sweep was performed at 100° C and the visco-elastic behavior shown by the control sample of ar-PCL was used to compare with the behavior of the c-PCL. As seen in Figures 17 and 18 for ar-PCL and c-PCL melts, respectively, the loss modulus ($G''$) is higher and lower, respectively than the storage modulus ($G'$) and the difference between the two moduli decreases with increase in frequency.
Figure 17: Frequency sweep of AR-PCL 100° C

The frequency sweeps of c-PCL were different from those of the characteristic visco-elastic pattern of the melt of ar-PCL.
The PCL coalesced from its 1:1 inclusion with α-CD was found to exhibit melt rheological behavior that was significantly different from that observed for the ar-PCL melt. The storage modulus was found to be higher at lower frequencies and increased with the frequency of oscillation, while the loss modulus was found to be lower at lower frequencies, possibly due to the presence of nematic like micro-domains of the extended un-entangled PCL chains coalesced from the IC. However at higher frequencies, owing to the destruction of interactions between remnant and threaded α-CDs and also the extended conformations, chains begin to easily slip past each other more easily and the storage modulus decreased.

Figure 18: Frequency sweep of Coalesced PCL at 100⁰ C.
very high frequencies the drop in $G'$ was appreciable. Tan $\delta$, the ratio of $G''$ to $G'$ was found to increase with increase in frequency. The frequency sweeps were then performed at various temperatures (70-100\° C). Using the frequency sweep at 90\° C as the base, the frequency sweeps at other temperatures were multiplied by a shift factor (in other words the frequency sweep curve at 90 \° C was multiplied by one and at other temperatures by a number greater/smaller than that). This procedure is called time–temperature superposition (Fig 19), and is used to extrapolate the frequency sweep curves based on the common knowledge that with time and temperature there is a slight variation in the behavior of the polymer.

![Graph](image)

Figure 19: Time temperature superposition of C-PCL melt.
**Steady shear**

The steady shear experiments was performed at 100° C for both the ar- and c-PCL melts (Figure 20) and it was found that the c-PCL showed rapid shear thinning from a much higher zero shear viscosity than ar-PCL. The rapid shear thinning likely due to a combination of the expected deformation of the structure formed by remnant threaded α-CDs and the extended chains in c-PCL slipping past each other at higher frequencies, as compared to the ar-PCL melt. The latter factor possibly due to the higher melt density and possible retention of the memory of the network potentially formed by the crystalline inclusion compound formed by the remnant α-CD. The viscosity profile of c-PCL dropped to a much lower level of melt viscosity than that of the more stable ar-PCL viscosity profile.

The same PCL sample was repeatedly observed in the rheometer, with results closely similar to these initial observations. As the thermal behavior observed by DSC following long-term melt annealing of c-PCL did not change, so too the unusual rheological behavior of c-PCL was not altered by repeated rheological measurements performed on its melt. Reorganized c-PCL remains quite resistant to long term annealing and rheological stresses as well.
Figure 20: Steady shear experiments at 100° C
The Cox-Merz rule is \( n^* = G^* / iw \), where \( G^* \) is the complex modulus, and \( |n^*| = |G^*| / w \) [45], and until recently was thought to have no sound theoretical basis. However, by using the Doi-Edwards reptation model, Milner provided a theoretical basis for the rule that was partly heuristic and only applicable to polymers with a wide range of molecular weights [46].

The applicability of the rule lies in predicting steady shear behavior from the oscillatory measurements since the oscillatory measurements are more predictable and accurate compared with the high shear rates applied in the steady shear experiments. In Figure 21,
shown above, although the qualitative trend of the complex viscosity –Shear rate curve is similar to the Steady Shear viscosity /shear rate graph, there is no overlap and applicability of Cox-Merz, possibly owing to the oscillatory movements not being able to break the structural bonds caused by remnant threaded α-CD till very high frequencies, as compared to steady shear. The steady shear viscosity profile is lower than the complex viscosity and this was explained by Uribe[32], as the steady shear inducing orientation in the chains and the oscillatory shear not inducing the same orientation. In that study it was also found that the wholly aromatic LCP components was found to be different than the LCP consisting of semi-flexible domains. It was found that the rate of molecular orientation relaxation was slower for the semi-flexible than the aromatic LCPs[32].

When a few weight percent of α-CD or c-PCL were added to ar-PCL as a physical mixture, the frequency sweep qualitatively resembled that for neat ar-PCL(Figures 22 and 23), and not the c-PCL, because they either contained none or almost no remnant threaded α-CD and the molten ar-PCL chains were randomly coiling and entangled.
Figure 22: PCL nucleated with few weight percentage of $\alpha$-CD
Figure 23: Rheology of PCL nucleated with a few weight % c-PCL

**Tensile Tests**

A MTS Q-test CRE type tensile-tester was used to perform tensile tests according to ASTM D – 882-97 standards. The films were cut to 6mm width and 90 mm length dog bone shapes using a template. Tensile tests were performed using a 250 lb load cell. The cross-head speed was 50 mm/min and 5 repetitions(portions) of each PCL film were used. We actually plot a Load-Strain curve (as against a stress-strain) curve, because the stress (force/unit area) is not constant, since the area changes with elongation of the sample.
The average modulus value for the ar-PCL films was 1730 kgf/cm$^2$, whereas the average modulus value for the c-PCL was 2900 kgf/cm$^2$ and the percent strain at break for the ar-PCL was 670, while the percent strain at break for c-PCL was 7.2. (See Figures 24 and 25 and Tables 3 and 4). Thus the c-PCL has a higher modulus and a much lower elongation, was less tough, as would be expected of a more brittle material, than the ar-PCL.

Figure 24: AR-PCL Load –Strain curve
Table 3: As–Received PCL mechanical properties

<table>
<thead>
<tr>
<th>Sample I. D.</th>
<th>Peak Load kgf</th>
<th>%Strn @ Pk Ld</th>
<th>Modulus kgf/cm²</th>
<th>Breaking Factor kgf/cm</th>
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</thead>
<tbody>
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<td>AR-PCL</td>
<td>2.9</td>
<td>670</td>
<td>1730</td>
<td>4.9</td>
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</table>

Figure 25: C-PCL load-strain curve.
### Table 4: Coalesced PCL mechanical properties

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<tr>
<th>Spcmn No.</th>
<th>Peak Load @ Pk Ld kgf</th>
<th>%Strn @ Pk Ld</th>
<th>Break Load @ Break kgf</th>
<th>Elong @ Break</th>
<th>%Strn @ Break</th>
<th>Energy to Break kgf/cm²</th>
<th>Moduls kgf/cm²</th>
<th>Breaking Factor kgf/cm</th>
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<td>2.5</td>
<td>4.9</td>
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<td>2</td>
<td>0.811</td>
<td>2.94</td>
<td>1.5</td>
<td>2.9</td>
<td>2910.44</td>
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<td>8.2</td>
<td>16.5</td>
<td>3157.01</td>
<td>0.49</td>
<td></td>
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<tr>
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<td>2.29</td>
<td>4.8</td>
<td>9.7</td>
<td>2702.11</td>
<td>0.4</td>
<td></td>
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<tr>
<td>5</td>
<td>0.738</td>
<td>2.35</td>
<td>1.2</td>
<td>2.3</td>
<td>3101.17</td>
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<td></td>
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<tr>
<td>Range</td>
<td>0.504-1.739</td>
<td>2.09-4.94</td>
<td>1.2-8.2</td>
<td>2.3-16.5</td>
<td>3.03-3101.17</td>
<td>0.4-1.37</td>
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<tr>
<td>Mean</td>
<td>0.887</td>
<td>2.922</td>
<td>3.64</td>
<td>7.26</td>
<td>13.01</td>
<td>2.902.64</td>
<td>0.696</td>
<td></td>
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</table>

**Melt annealing of Coalesced PCL**

C-PCL was kept in a vacuum oven at 90° C and the DSC scans were performed at intervals of one week. Melt-crystallization temperatures were reduced at a very slow rate, possibly owing to a change in free volume occupied by the c-PCL chains initially in an un-entangled extended chain conformation. The percent crystallinity calculated from the DSC scans, assuming the 100% crystalline PCL to have a melting enthalpy of 136 j/g are summarized in Table 5.
Table 5: Crystallization temperature of the C-PCL kept in the melt for long periods of time

<table>
<thead>
<tr>
<th></th>
<th>Crystallization temperature</th>
<th>Percent Crystallinity</th>
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<tr>
<td>Coalesced PCL</td>
<td>35.58</td>
<td>42.86</td>
</tr>
<tr>
<td>Coalesced PCL (1 week in the melt)</td>
<td>33.37</td>
<td>37.89</td>
</tr>
<tr>
<td>Coalesced PCL (2 weeks in the melt)</td>
<td>32.64</td>
<td>33.36</td>
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</table>

Conclusions

We can conclude from our results that melt rheology is very sensitive to the changes in structure and conformation of PCL. For the c-PCL melt, the oscillatory frequency experiments showed a unique behavior of $G’$ being higher than $G’’$ at lower frequencies, while the relaxation times were higher and the effect was negligible at higher frequency oscillations. Shear thinning was evident in the steady shear experiments of the PCL coalesced from its $\alpha$-CD inclusion compound. The steady shear experiments showed a greater zero-shear viscosity, rapid shear thinning, and then finally a plateau viscosity (at higher frequencies) much lower than that found in the ar-PCL melt. Our basic hypotheses for this distinct behavior are that

1. At high shear rates experienced during the steady shear experiments and high frequency region of the oscillatory experiments, there is a structural deformation of the interacting remnant and threaded $\alpha$-CDs in the c-PCL melt, and
2. The subsequent slipping of PCL chains past each other is facile due to their largely extended and un-entangled conformations. This is supported by previous rheological observations performed on a small c-PCL sample that showed no remnant α-CD and evidenced no shear thinning, but a plateau viscosity much lower than ar-PCL and closely similar to that reported here for our c-PCL sample [40].

The mechanical tests showed that there was a significant (nearly 60 %) increase in modulus, similar to observations made by earlier nano-indentation studies on the mechanical properties of c-PCL film[47], likely because of the reorganization and closer packing of the chains in the non-crystalline regions, which were confirmed by density measurements [40]. Thus, it can be said that, by processing Polymers with Cyclodextrin we can significantly modify their solid state organizations, morphologies, and thus their mechanical and rheological properties.
CHAPTER 4
SUMMARY AND FUTURE WORK

The motivation for this study was to elucidate the processing-morphology-conformation-property correlations of the polymers that result from processing with cyclodextrin. Earlier studies had focused on the inclusion phenomena and found that, compared to some other polyesters, PCL had an affinity to include in α-CD [22]. So it is possible, that a small fraction of α-CD remains threaded on the c-PCL chains. These remnant α-CDs, since they are very well dispersed and are on the nano-meter scale, are able to uniformly change the behavior of the polymers, likely due to hydrogen-bonding between them, that would otherwise be impossible without any chemical modifications. Since PCL is susceptible to degradation by hydrolytic chain scission on prolonged exposure to HCL, the acid used to coalesce this polymer IC, dilute solution viscosity measurements were made and confirmed the absence of chain scission in our c-PCL sample. However, attempts to conclusively establish that we were successful in completely coalescing the IC and getting rid of all traces of α-CD proved futile, as demonstrated by 1H-NMR and steady shear experiments.

Attempts to use c-PCL as a nucleating agent for bulk melt-crystallization is similar to other such attempts in the past, that used non-stoichiometric inclusion compounds [(n-s) polymer-CD-ICs] as nucleating agent for the same polymer, the difference being that the all domains of the coalesced uncovered chains have been reorganized, as compared to the (n-s) ICs, where the chains remain anchored in the α-CD domains, but large portions remain un-
covered and unprocessed. The advantages of using c-PCL and other coalesced polymers as melt nucleants is their inherent compatibility, ease of recycling, and their “stealth” natures. The potential applications of such modified PCL is in tissue engineering scaffolds, electrospun webs, etc. that have superior mechanical properties and enhanced processability. In the future, c-PCL and non-stoichiometric inclusion compounds of PCL can be used to make nucleating agents for bulk melt-crystallization. The constrained chains in the portions not included in α-CD channels would form polymer brush-like structures anchored in the channels. Such micro-domains would remain stable to processing. These nematic-like regions should be superior in properties when used as nucleating agent for the bulk, in comparison to the use of comparable immiscible liquid crystalline/thermoplastic polymer blends, owing to better interfacial compatibility. Since PCL and α-CD are bio-absorbable and bio-degradable and are used extensively in the healthcare industry, applications of PCL nucleated with coalesced and non-stoichiometric inclusion compounds of PCL are likely to be many. The nucleated PCL can possibly be electrospun into webs and used for bio-medical applications. The same approach can also be tried on other polymers like Nylon-6, PET, poly(lactic acid), etc. based on and tailored to their application-dependant performance requirements.
References


