ABSTRACT

JOIJODE, ABHAY SHAM. Nano-structuring Polymers by Processing them with Small Molecule Hosts. (Under the direction of Dr. Alan E. Tonelli).

Nano-structuring of polymers via the host-guest inclusion phenomenon offers a novel approach to reorganize their morphologies, which affects their resultant behaviors and properties. This involves formation of a non-covalently bonded inclusion complex between the guest polymer chains and small molecule hosts which is followed by careful removal of the host molecules to obtain coalesced polymers that have a largely extended and un-entangled morphology.

The first study involves processing PMMA, PVAc, and their blends with host urea (U) to initially form inclusion complexes (ICs) followed by coalescence of the guest polymers from the U-ICs. Formation of the U-ICs was characterized using FTIR, TGA and DSC, which confirmed the inclusion of the polymer chains in the narrow crystalline urea channels. FTIR and NMR data confirmed complete removal of urea from the coalesced polymers, while their DSC data showed higher Tgs than the corresponding as-received (asr)-polymers. For the coalesced blends it was found that PMMA was preferentially included over PVAc, as inferred from FTIR & DSC results, and a Tg-Composition relationship was also established.

In the next study properties of and the effect of annealing on PVAc coalesced from its γ-CD- and urea-ICs have been analyzed. The ICs and c-PVAc were characterized using FTIR, NMR, DSC, WAXD, Nano-indentation and DMTA. The c-PVAc exhibited higher Tgs than asr-PVAc and this behavior was found to be stable even after long time annealing above Tg, which suggests that the largely extended and un-entangled chain morphology of c-PVAc is not affected by long time high temperature annealing.
In the final work, PET has been modified through a precipitation technique, and used as a homogeneous self-nucleant, because, unlike as-received PET, it is rapidly crystallizable from the melt. Thermal, mechanical, permeability, and other relevant properties of self-nucleated PET films and fibers are much improved. Repeated self-nucleation has also been demonstrated, by re-using self-nucleated PET as a nucleant.
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Nano-structuring Polymers by Processing them with Small Molecule Hosts.

by
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DEDICATION

I dedicate this work to my family and friends for their support and confidence in my capabilities.
BIOGRAPHY

Abhay Sham Joijode was born in Mumbai, India and he completed his Bachelors of Technology degree in Fiber and Textile Processing Technology at Institute of Chemical Technology (formerly UDCT), Mumbai, India. With research and career interests in polymer science, he joined the research group of Dr. Alan E. Tonelli (INVISTA Professor of Fiber & Polymer Chemistry) at North Carolina State University. He has since been an active member of this group, investigating structure property relations in polymers mainly processed with small molecule hosts like cyclodextrins and urea.

Abhay completed his Master’s degree in Textile Chemistry with a minor in Chemical Engineering in 2011 following which he started his PhD studies in the Fiber & Polymer Science Program at North Carolina State University. Working in Prof. Tonelli’s group, Abhay had the opportunity to present his research at various conferences and has received awards recognizing his work. He has mentored high school (ACS Project SEED & Photonics Explorers & Leaders) and undergraduate (Polymer & Color Chemistry & Chemical Engineering) students for their research projects & presentations. He has served as a student representative for various committees at North Carolina State University. Abhay worked as a Polymer, Colloid & Interface Science Intern at the Center for Packaging Innovation of MeadWestvaco Corporation (MWV) in the summer of 2012 where he gained valuable industry experience in developing multi-functional water based barrier coating formulations for sustainable food packaging application.
After completing his PhD education, Abhay will start working as a Researcher at the Nonwovens Cooperative Research Center (NCRC) investigating blends of synthetic and biopolymers for novel nonwovens applications.
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CHAPTER 1

1. Background – Polymer Inclusion Compounds

Macromolecules are more sensitive to processing than small molecules on account of their inherent long-chain flexible nature, which is imparted through various conformations, resulting in myriad sizes and shapes. Consequently, the behavior and properties of polymeric materials which depend on their structural organization can be readily modified through processing, as illustrated through the following example. Gel-spun Spectra poly (ethylene) (PE) fibers are extremely strong in the fiber direction and may be fabricated into light-weight armor, while molded articles, such as melt-blown PE garbage bags, are not nearly as strong, but have a much greater elasticity, even though the same polymer is used in both applications [1].

One way of processing polymers is through structuring via nano-confinement and subsequent release. This is done through formation of an inclusion complex between small molecule hosts and polymeric guests followed by careful removal of the host to obtain bulk coalesced polymer. It has been observed that polymers processed by such a technique exhibit behaviors and properties that are different from those processed from their solutions or melts. Coalesced polymers that are amorphous in nature exhibit higher glass transition temperatures and densities, while crystallizable coalesced polymers show higher crystallization temperatures than their non-coalesced analogs. This behavior can be attributed to the largely un-entangled configurations and extended chain conformations of polymers produced by nano-structuring via inclusion complexation and subsequent coalescence [1].
Research associated with polymer inclusion and coalescence phenomena is outlined schematically in Figure 1.1, using the cyclic host molecules cyclodextrins (CDs). This involves characterizing their behaviors and analyzing their properties and finally applying these morphologically novel materials. This section introduces the various hosts & guests used in our research, provides an overview of processing polymers via nano-confinement and subsequent release and the various analytical techniques used to characterize and analyze the behavior and properties of the polymers resulting from this nano-structuring process.

Figure 1.1: CD Host-Polymer Guest inclusion phenomena – processing, evaluation, and applications.
1.1 Guest Polymers

1.1.1 Poly (vinyl acetate) (PVAc)

PVAc is a commercial synthetic thermoplastic and belongs to the class of vinyl polymers. It has a molar mass of ~ 86 g/mol of repeat unit. PVAc was first synthesized by Dr. Klatte in Germany in the year 1912 but the potential for this polymer was not realized immediately. Later on Wacker Chemie developed commercial scale methods to produce vinyl acetate monomer (VAM) [CH₂=CH(OCOCH₃)], the raw material for PVAc, overcoming drawbacks in large scale manufacturing of PVAc from VAM [2].

![Synthesis of PVAc](image)

Figure 1.2: Synthesis of PVAc [2]

PVAc is usually synthesized via free radical polymerization of VAM. One method of producing VAM is starting from ethylene, which is then converted to acetaldehyde and then to acetic acid via successive oxidation steps. Acetic acid is then reacted with ethylene to
produce VAM. Polymerization of VAM can be carried out using emulsion, suspension or solution-techniques, which may result in aqueous dispersions or solid resins of PVAc. A schematic for the synthesis of PVAc has been illustrated in Figure 1.2 [2].

PVAc produced by free radical polymerization is stereochemically atactic and so is amorphous in nature, with a glass transition temperature around room temperature. It is tasteless, odorless, and non-toxic, but not biodegradable. PVAc finds major application as an adhesive in packaging and wood gluing, chewing gum bases and in emulsions as a binder for coatings [2,3]. PVAc is also used as a precursor for manufacturing poly (vinyl alcohol) (PVOH), poly (vinyl butyral) (PVB) and poly (vinyl formal) (PVF). PVOH is used in barrier coatings for food packaging applications. PVB is used in automobiles as a plastic film in laminated safety glass, while PVF finds application in wire insulation [4].

1.1.2 Poly (methyl methacrylate) (PMMA)

PMMA is a transparent rigid thermoplastic polymer and belongs to the acrylic class of polymers. It was first synthesized by Rowland Hill and John Crawford in the 1930’s and was registered under the trademark ‘Perspex’ by Imperial Chemical Industries (ICI) in England. Around the same time, Otto Röhm of Rohm and Haas AG synthesized PMMA under the trade name ‘Plexiglas’ in Germany. E.I. du Pont de Nemours & Company introduced PMMA in the USA under the trademark ‘Lucite’ [4].

PMMA is made by polymerizing methyl methacrylate (MMA) [CH2=C(CH3)CO2CH3]. In commercial production propylene and benzene are reacted to obtain cumene as a byproduct of the reaction. Cumene is oxidized and then treated with acid to form acetone
which is then converted to MMA. The presence of the pendent $\alpha$-methyl group in the repeat unit and an atactic stereosequence generally keeps the polymer chains from packing closely into a crystalline structure, resulting in amorphous PMMA [4].

At room temperature PMMA is brittle in nature and not usually used in its pure state for commercial applications. PMMA is optically clear and has good mechanical properties. It has extremely high weatherability, but with a high sensitivity to electron radiation. It is used as a replacement for glass (Plexiglas) usually in combination with an additive to reduce the brittle nature of PMMA and also in microelectronics applications [3,4].

1.2 Hosts

1.2.1 Cyclodextrins

Cyclodextrins are cyclic oligosaccharides and were discovered in 1891 [5]. Schardinger was the first to differentiate between different cyclodextrins based on the colors seen from their reaction with iodine [6]. Later, Pringsheim discovered that crystalline inclusion complexes can be formed between cyclodextrins and a range of organic compounds [7,8]. Freudenberg was the first to indicate the cyclic nature of these starches in 1930 [9]. Commercial production of cyclodextrins started in 1970 and research to investigate the practical applications of cyclodextrins has accelerated since then [10].

Commercially, cyclodextrins are produced enzymatically from starch. This involves enzymatic conversion of starch using cyclodextrin glycosyl transferase (CGTases) and $\alpha$-amylase enzymes. The production process can be of two types, namely ‘solvent’ and ‘non-solvent’ methods. In the solvent method an organic complexing agent directs the enzymatic
reaction and selectively precipitates a particular type of cyclodextrin. The non-solvent technique does not involve any complexing agent and thus yields a mixture of cyclodextrins. Figure 1.3 illustrates these processes [11].

![Cyclodextrin Production; a) Solvent & b) Non-solvent methods](image)

**Figure 1.3: Cyclodextrin Production; a) Solvent & b) Non-solvent methods [11]**

The type and amount of cyclodextrin obtained depends on various factors. The most important affecting the yield and selectivity include substrate, origin of the CGTase,
complexing agent and the reaction conditions. Purification achieved in commercial productions is up to 98%. Further purification is possible by employing techniques like ion exchange chromatography and membrane filtration [11].

Figure 1.4: Cyclodextrins [12]

Cyclodextrins possess a hydrophobic cavity and a hydrophilic surface on account of their structural arrangement. They are stable to alkalis, but degrade under acid hydrolysis. Their
stability to acid hydrolysis depends on the time of exposure, temperature and strength of the acid. They are also resistant to UV and IR [13]. Cyclodextrins are relatively less soluble than their non-cyclic analogs due to stronger intermolecular hydrogen bonding. This can be altered by substituting a hydrogen atom or other group for the hydroxyl groups in its structure. Amongst the three CDs, β-CD has the lowest water solubility and this can be attributed to the intra-molecular hydrogen bonding within its structure. Also, γ-CD is more water soluble than α-CD [14].

Cyclodextrins have many applications. They are used to form inclusion complexes (ICs) with small or macromolecules, and can be used for food packaging, where the ICs are used to preserve flavors, protect active ingredients or to mask undesired odors/tastes [15]. In pharmaceutics, ICs are used for drug preservation and delivery applications [16]. For Personal Care, Cosmetics and Toiletries products CD-ICs are used as a means to control odor, for stabilization and to convert a liquid detergent into a solid commodity [17]. The agricultural field employs CD-ICs to maximize the effects of insecticides, fungicides and other specialty chemicals [18]. CD-ICs are also used in the paint industry to modify the rheology of paints.

1.2.2 Urea

Urea is an organic molecule with the chemical formula [CO(NH₂)₂]. It is a di-amide of carbonic acid and is also known as Carbamide. Urea was first isolated by Hilaire-Marin Rouelle in 1773, while Friedrich Wöhler established its synthesis from ammonium cyanate in 1828 [4]. Commercially urea is synthesized from ammonia (NH₃) and carbon dioxide (CO₂).
This consists of four main steps, namely synthesis, purification, concentration and granulation. The process overview has been illustrated in Figure 1.5. In this method these components are reacted to yield ammonium carbamate (NH$_2$-CO-O’NH$_4^+$), which in turn is reacted further to obtain urea by loss of a water molecule. The purification stage consists of removal of water, which is formed during synthesis, and also the removal of unreacted CO$_2$ and NH$_3$. The concentration step involves evaporation of water associated with urea. The process ends with the granulation step [19].

Urea is a white crystalline material that decomposes before boiling. It is commercially used in fertilizers. It is also used to prepare urea-formaldehyde resins and inclusion complex preparations for purification purposes [4].

**Figure 1.5: Urea manufacturing process [19]**
1.3 Processing Polymers with Their Inclusion Compounds

1.3.1 Inclusion Phenomenon

Rotaxanes are molecular structures in which a cyclic molecule (host) encases another molecule (guest). This becomes a ‘polyrotaxane’ when the encapsulation assembly gets repeated, as in the case of macromolecular inclusion, wherein a single guest polymer chain gets covered up a number of cyclic host molecules. If the ends of a polyrotaxane are not terminated by bulky groups then the polyrotaxane is in equilibrium with un-included polymer and hence called a ‘poly-pseudorotaxane’. The two main types of polyrotaxanes have been illustrated in Figure 1.6. These assemblies occur at nano scale levels making it interesting to evaluate the effect of this molecular restructuring on the macroscopic properties of polymers [12].

Figure 1.6: Typical structures of polyrotaxanes [12]

Stoichiometry in cyclic host-polymer guest polyrotaxanes can be of two types. One is related to the number of polymer chains included in the cyclic channels, while the other is related to the percentage of the polymer chains covered with cyclodextrins. For the poly (ε-
caprolactone) (PCL)-γ-cyclodextrin inclusion complex, two PCL chains thread each γ-CD channel with a stoichiometry of 2:1 = PCL repeats:γ-CD. However the stoichiometry with respect to the polymer chain coverage can vary depending on the amount of γ-CD used in the inclusion complex formation process. Figure 1.7 illustrates formation of main chain type polyrotaxanes via cyclic-host and macromolecular guest inclusion where ‘m’ and ‘n’ denote number of cyclic host and polymeric guest repeat units, respectively. Depending on the ratio of ‘n’ to ‘m’ the resultant polymer chain coverage could either be stoichiometric (complete polymer chain coverage) or non-stoichiometric (partial polymer chain coverage).

![Diagram of Polyrotaxanes](image)

**Figure 1.7: Formation of Polyrotaxanes via cyclic-host and macromolecular guest inclusion**

Different organic molecules that can be used as hosts (cyclic or not) include thiourea, hydroquinone, crown ethers, etc., but CDs and U are the two small molecule hosts most widely used to form polymer inclusion complexes.

**1.3.1.1 Cyclodextrin Inclusion**

Cyclodextrins are able to include small or macromolecules in their cavities on account of their truncated cone structures. Inclusion complex formation using cyclodextrins is
predominantly carried out using $\alpha$-, $\beta$- and $\gamma$-CDs even though larger CDs are also available. For example, delta cyclodextrin ($\delta$-CD), which has nine glucopyranose units, is available commercially, but does not have a regular truncated cone shaped structure like $\alpha$-, $\beta$- and $\gamma$-CDs. Rather, its structure is collapsed and its cavity is smaller than $\gamma$-CD [20]. Small molecule guest inclusion compounds formed with cyclodextrins are used commercially with a large range of guests that include acids, ionic compounds, halogen compounds, aliphatic alcohols, aromatic compounds, monomers, dyes and drug molecules. Table 1.1 illustrates some of the examples of commercial small molecule CD-ICs applied in pharmaceutics [21].

Cyclodextrins can also form inclusion complexes with different polymers. Harada et al. were the first to report polymer-CD-ICs, when they successfully included polyethylene glycol (PEG) oligomers with different molecular weights in $\alpha$-CD [22]. Prior to this work, in-situ polymerizations using CDs had been reported by Olga et al. [23]. The research groups of Harada [12] and Tonelli [1] have since investigated various polymer-CD combinations to improve the knowledge and understanding of the phenomenon of nano-confinement.

In polymer-CD-ICs, $\alpha$- and $\gamma$-CDs are used more often than $\beta$-CD. It has been observed that $\beta$-CD does not as readily form polymer-ICs. A possible explanation for this is due to the structure of $\beta$-CD. The water inside its cavity is nearly as stable as the water around its hydrophilic outer surface, unlike in $\alpha$- and $\gamma$-CDs, where the water in their cavities is unstable and is readily replaced by a relatively more hydrophobic guest. There are four ways by which one can obtain polymer-CD-ICs. These are co-precipitation, slurry, paste and dry mixing. Each of these methods is different from the other in terms of amount of water used to dissolve CD. The co-precipitation method includes preparation of polymer and CDs solutions
followed by their mixing, which yields the ICs. In the slurry method, firstly the CDs are partially dissolved (~50% w/w). The dissolved portion of CDs forms an IC and precipitates out making way for more CDs to dissolve thereby forming more ICs. In the paste technique the amount of water used to dissolve CDs is reduced to 20-30% w/w. In the dry mixing method water is not used at all during IC formation. This is not an efficient technique as it takes a lot of time to form the CD-ICs [21].

In this research, the co-precipitation technique has been employed in the formation of polymer-CD-ICs. The mechanism of inclusion in this technique is pretty straightforward. When a saturated solution of CD is prepared the hydrophobic cavities of the dissolved CDs contain water. When a polymeric solution (prepared in a good solvent for the polymer) is added to the CD solution the comparatively hydrophobic polymer chains push out the water inside the CD cavities as they are more stable inside the hydrophobic cavity than are the water molecules. Once the IC formation reaches the saturation point, the polymer-CD-IC precipitates out.

Cyclodextrins can organize in two types of structures namely cage and columnar. Cage structure is a crystalline form adopted by uncomplexed CDs or small molecule-CD-ICs and can be further classified as herringbone-type and layer-type cage structures. The columnar arrangement also known as the channel structure, is observed in macromolecular inclusions, wherein a long guest is threaded over by many cyclodextrins with their cavities being parallel to each other and usually packed in a Head-Tail to Tail-Head fashion. Figure 1.8 illustrates these structures [24].
Polymer-CD-ICs can be characterized in numerous ways. Their ICs show characteristic peaks corresponding to both polymeric guest and the CD host in their Fourier Transform Infrared (FTIR) spectra. This indicates the presence of both components (polymer and CD) in
the IC but does not confirm if the polymer chains are inside the CD cavities or if it is just a mixture of un-included guest polymer and free CD. Having said this, it has nevertheless usually been observed that the peaks in a stoichiometric IC that correspond to the polymeric guests are usually suppressed and sometimes with different absorption frequencies in comparison to those observed in physical polymer/CD mixtures. This can be taken as an indication of inclusion of polymer chains in the CD cavities. Figure 1.9 illustrates FTIR data for the inclusion complex of poly (L-lactic acid) (PLLA) formed with α-CD.

![Figure 1.8: CD structures: a) herringbone-type cage, b) layer-type cage and c) columnar [21]](image)

Another way of characterizing polymer-CD-ICs is through their Differential Scanning Calorimetry (DSC) profiles. The characteristic transitions observed for the guest polymer,
like glass transition or melting, during a heating scan are absent in the thermographs of their corresponding stoichiometric CD-ICs. This occurs because when polymers are processed via nano-confinement each polymer chain gets threaded by CD molecules separating it from the other chains. As the polymer chains are not in contact with each other, they are unable to organize into structures that are responsible for the thermal transitions that are reflected in their DSC thermographs.

Figure 1.9: FTIR data for PLLA-α-CD-IC.

CDs undergo a change in their crystal structure from cage to columnar when their cavities include a polymeric guest. This change can be observed through their corresponding Wide
Angle X-ray Diffraction (WAXD) patterns. The WAXD pattern of an uncomplexed CD that has a cage structure is distinct from that of a polymer-CD-IC, which has a columnar structure. The cage structure shows better resolved peaks in its WAXD pattern, while the columnar structure is comparatively more featureless, exhibiting fewer peaks. Figure 1.10 illustrates the change reflected by the WAXD data for PMMA-\(\gamma\)-CD-IC [25]. Cage \(\gamma\)-CD has characteristic peaks at \(2\theta = 12.4\), 16.5, 18.8 and 23.4°. PMMA-\(\gamma\)-CD-IC crystals show a major peak at \(2\theta = 7.5\)°, which is absent for cage \(\gamma\)-CD and is characteristic for \(\gamma\)-CD in the channel structure [26].

![Figure 1.10: WAXD pattern for a) PMMA-CD-IC and b) as-received \(\gamma\)-CD [25]](image)

Nuclear Magnetic Resonance (NMR) spectroscopy is also a valuable tool to characterize polymer-CD-ICs. This can be done using \(^1\)H or \(^{13}\)C NMR in solution or the latter in the solid
state. As the environment around the hydrogen and carbon atoms is altered during IC formation, there occurs a shift in corresponding resonance peaks and this shows up in the NMR data. Also the peaks corresponding to the guest polymers, which are absent in uncomplexed CDs are also visible in the NMR spectra of their ICs [21].

Figure 1.11: Processing polymers with CDs

The different ways in which polymers can be modified using CDs has been illustrated in Figure 1.11. This can be formation of a stoichiometric inclusion complex, wherein the polymer chains are completely covered by the CD molecules. This can be followed by coalescence, i.e., complete removal of the CDs or formation of non-stoichiometric ICs that have intermediate un-included chain portions “dangling” between and/or connecting the IC
crystals. There is a lot of literature available concerning stoichiometric ICs of CDs with various guest polymers like PLLA [27], PCL [28], poly (ethylene terephthalate) (PET) [29], etc. wherein these ICs have been successfully prepared and characterized. It is also possible to intimately blend polymers, which otherwise phase separate when processed by the usual blending techniques of melt-mixing or solution blending, by simultaneously nano-structuring them through formation of their common inclusion complexes. Rusa et al. prepared a binary blend of PLLA and PCL through their common $\alpha$-CD inclusion [30], while Rusa & Uyar et al. prepared a ternary blend between PVAc, PMMA and poly carbonate (PC) to obtain novel structures [31]. Shuai et al. included a PCL-PLLA di-block copolymer in $\alpha$-CD to alter its biodegradability through mixing of the PCL and PLLA blocks following coalescence [32].

Figure 1.12: WAXD data for a) $\gamma$-CD b) 1-Propanol-$\gamma$-CD-IC c-f) PDMS-$\gamma$-CD-ICs with molecular weights 237, 770, 1250 and 62,500 g/mol respectively [34]
In another study, Rusa et al. evaluated competitive CD-IC formation, which suggested that the geometrical compatibility and hydrophobicity of the guest polymer affects the inclusion phenomenon. In this case PLLA-α-CD ICs were suspended in a PCL solution for a specific amount of time and then the IC was filtered and analyzed. It was found that PLLA chains in the IC were replaced by PCL, suggesting competitive inclusion resulting in formation of the more stable PCL-α-CD ICs [33]. Polymers that are not solid at room temperature can also be included in CD channels. One such example is poly (di-methyl siloxane) (PDMS), which was included in γ-CD. Figure 1.12 provides the WAXD data which illustrates the inclusion phenomenon (observation of a pear at 2θ ~ 7.5° as seen in columnar γ-CD-ICs) [34].

![FTIR data for PCL-α-CD-ICs, with varying PCL:α-CD ratios](image)

**Figure 1.13:** FTIR data for PCL-α-CD-ICs, with varying PCL:α-CD ratios
Non-stoichiometric ICs (ns-ICs) are obtained when excess guest polymer is used during inclusion complexation. This results in CD-ICs with partial polymer chain coverage, wherein there are “dangling”/connecting chain portions from/in between CD-IC crystals. Behavior of ns-ICs is different from the stoichiometric CD-ICs on account of the unincluded polymer chains. Figure 1.13 illustrates FTIR data for ns-ICs of PCL with α-CD in varying ratios of PCL to α-CD. As the ratio of polymer to α-CD increases the PCL carbonyl peak in the CD-IC spectrum increases (~1730 cm\(^{-1}\), corresponds to C=O in PCL).

Figure 1.14: a) Nylon 6 and b) Nylon 6 + 2% 3:1 ns-IC [35]

It has been observed that the “dangling”/connecting un-included portions of the polymer chains in ns-ICs crystallize at a higher temperature during cooling than the unmodified crystallizable guest polymer. Mohan et al demonstrated use of Nylon 6 ns-ICs as effective nucleating agents. When small amounts of Nylon 6-α-CD-ns-ICs are mixed with bulk unmodified Nylon 6, the un-included polymer chain portions in the ns-ICs crystallize first during cooling, thereby providing nucleation sites for uniform crystal growth and distribution.
for the rest of the polymer chains. Figure 1.14 shows polarized optical micrographs for bulk unmodified Nylon 6 and for Nylon 6 mixed with 2% of 3:1 Nylon 6-α-CD-ns-IC both crystallized from the melt. It is clearly evident that adding the ns-ICs results in smaller crystals that are uniformly distributed, as compared to larger crystals non-uniformly distributed in the unmodified bulk Nylon 6 [35].

For amorphous polymers, their ns-ICs show a higher glass transition temperature ($T_g$) for the unincluded chain portions than the unmodified polymer, which increase as the polymer to CD ratio is reduced. The ns-ICs can also be used to blend polymers, but the blending is not as efficient as the one obtained through formation of stoichiometric common CD-ICs. It has been observed that PVAc/PMMA-ns-γ-CD-ICs show three phases, which include phase separated PMMA-rich and PVAc-rich phases and an intermediate miscible phase whose composition can be varied depending on the PMMA/PVAc feed ratio [36].

1.3.1.2 Urea Inclusion

Bengen accidentally discovered the first urea inclusion complex (U-IC) in 1940 by isolating a crystalline aduct of 1-octanol and urea [37]. Subsequently other guest molecules have been included using urea as a small molecule host. The mechanism of inclusion with urea as host is distinct from that of CD inclusion. In U-ICs, urea molecules form a cyclic network around the guest molecules through intermolecular hydrogen bonding usually with no coordination with the guest. Figure 1.15 illustrates inclusion via U hydrogen-bonding to form a honeycomb like matrix structure [38, 39]. The suggested mechanism of urea inclusion indicates formation and growth of a ring like structure around individual polymer chains via
hydrogen bonding [40]. Polymer inclusions with urea are usually done by a co-crystallization method. Different polymers that can form ICs with urea include poly (ethylene oxide) (PEO) [41], PLLA [42], polypropylene (PP) [43], etc. Similar to polymer-CD-ICs, FTIR spectra of polymer-U-ICs show peaks corresponding to both urea and polymer. WAXD data depends on the size of the guest polymer, which in turn relates to the size of the cavities formed by urea. PCL-U-IC [44] has a hexagonal structure, in comparison to the tetragonal structure of PP-U-IC [43]. It is evident from DSC data of U-ICs that the IC crystals melt at a higher temperature than pure U [44] on account of the difference between the crystal structures of pure urea and U-ICs. U-ICs also do not show the thermal transitions of the guest molecules, because they are completely covered by U channels similar to what is observed in the DSC thermographs of polymer-CD-ICs.

Figure 1.15: Urea Inclusion – Matrix formation via hydrogen bonding [38, 39]
1.3.2 Polymers Coalesced from Their Inclusion Compounds

The CD- and U-ICs formed with polymers can be coalesced to obtain the guest polymers through careful and complete removal of the hosts. This can be done by washing with water (since both CDs and urea are water soluble) or in some instances with enzymes or acids. PCL-α-CD, for example, requires very brief treatment with hydrochloric acid for complete removal of α-CD.

Polymers coalesced from their CD- or U-ICs have behaviors and properties that are distinct from their normally processed analogs, i.e., the as-received (asr-) polymers. This includes higher crystallization temperatures for coalesced crystallizable guests [45] or higher \( T_g \)s for coalesced amorphous guest polymers [21]. Coalesced polymers also possess higher amorphous densities (even with same levels of crystallinity as that of asr-polymer) on account of the structural rearrangement to extended and largely un-entangled chains that yields better orientation and closer packing in the amorphous domains [46]. The coalesced polymers are also stable to repeated melt processing, but lose their properties if dissolved in a good solvent. PET processed by coalescence from its \( \gamma \)-CD clearly illustrates this characteristic of coalesced polymers. [47]. Crystallizable polymers coalesced from both their CD- and U-ICs are stable to long time annealing at temperatures above their melting points [28, 48]. Polymer blends coalesced from their common stoichiometric CD-ICs exhibit complete miscibility. This can be confirmed through observation of a single \( T_g \), which occurs between the \( T_g \)s of the individual guest polymers [21].

Coalesced polymers can be used as self-nucleating agents. The principle of nucleation is similar to that of ns-IC nucleants, wherein the coalesced polymer crystallizes at a higher
temperature than the asr-polymer. Thus providing sites for crystallization and resulting in uniform crystal sizes and distributions [49]. Self-nucleation offers a clean way to improve the properties of polymers and does not complicate their recycling, since addition of foreign substances is avoided. Another application is to prepare self-reinforced composites using coalesced/nucleated and asr-films or fibers. This technique solves the problem of poor interfacial adhesion in polymer composites by providing extensive mixing at the interface, because the self-nucleated reinforcing films and fibers are chemically the same, and only morphologically different and spatially distinct from the asr-polymer matrix [49, 50].

1.4 Overview of Analytical techniques for Polymer Characterization

1.4.1 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR Spectroscopy is a non-destructive polymer characterization technique that provides information about their chemical bonding and molecular structure. This analytical technique works on the principle of the vibrations of chemical bonds occurring at their characteristic frequencies. When the polymer specimen is subjected to a modulated IR beam it absorbs infrared energy at frequencies that are characteristic of that molecule and the sample’s vibrational pattern at different frequencies is transformed into an IR absorption plot as a function of wave number. The resulting FTIR spectrum is then analyzed and usually compared with a FTIR library to get a spectral match in order to identify the polymer.

The instrument consists of an IR and laser sources, interferometer, sample compartment and detector. A series of mirror assemblies directs the beam to different parts of the instrument. The instrument usually has a frequency range of 400 to 4000 cm⁻¹ and the
resolution can be varied from 0.5 to 32 cm\(^{-1}\). The sample compartment is purged to remove the effect of the presence of moisture and CO\(_2\) on the spectra. The source in the FTIR instrument is infrared energy (Globar), and passes through an aperture, which controls the energy presented to the sample. An Interferometer is an important part of the instrumental assembly. Radiation from the IR source is directed through the sample cell to a beam splitter. Half of the radiation is reflected from a fixed mirror, while the other half is reflected from a mirror which moves continuously over a distance of about 2.5 micrometers. When the two beams are recombined at the detector, an interference pattern is produced.

A Helium–Neon Laser beam is introduced into the beam leaving the interferometer and this has a few important functions. Since IR is not detected by human eye, it permits us to place the sample in the sample compartment exactly between the incident beam and the detector. It improves the accuracy of each measured frequency, and helps in synchronization of multiple scans. The beam from the sample goes to the Deuterated Triglycine Sulfate (DTGS) detector, which measures the interferogram signal. The measured signal is digitized and sent to the computer, where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation [51].

Absorption in the infrared region results from changes in the vibrational and rotational status of the molecules. A molecule will absorb infrared light only if the absorption causes a change in the dipole moment. This results in a vibrational transition in the form of bending or stretching which occurs at a characteristic frequency that is specific for a particular bond or functional group.
Infrared spectral studies were conducted with a Nicolet Nexus 470 FTIR spectrometer in the range 4000 - 400 cm\(^{-1}\), with a resolution of 4 cm\(^{-1}\) and 64 scans were collected for each sample. FTIR data were analyzed by using Omnic software.

1.4.2 **Nuclear Magnetic Resonance (NMR) Spectroscopy**

The basic property on which NMR works is the magnetic spin (I) associated with atomic nuclei, which depend on their atomic numbers and weights. Atoms with I = 0 (e.g., \(^{12}\)C) do not have a spin and thus no magnetic moment, which is essential for NMR. Atoms/isotopes with I=1/2 like \(^{13}\)C and \(^1\)H possess nuclear magnetic moments and evidence NMR spectra. For polymer analysis by \(^1\)H NMR, the samples are usually prepared in a deuterated solvent, so there are no solvent protons to interfere. Chemical shift (\(\delta\) in ppm) is an important parameter in NMR analysis. The reference for chemical shift in \(^{13}\)C or \(^1\)H NMR is tetramethylsiloxane (TMS, \(\delta=0\)). The \(\delta\) can be calculated by comparing the frequency of resonance absorptions of the chemical groups of the polymer to the resonance frequency of the reference TMS [52].

For inclusion complexation, NMR serves as an important tool to evaluate structural changes (asr- vs c-polymers), presence of remnant host molecules in coalesced polymers and to confirm formation of ICs, wherein peaks corresponding to both host and guest are observed. NMR studies were conducted using a Bruker 500 MHz NMR instrument, with data analyzed using ACD SpecManager (software version 10.02) [45].
1.4.3  Wide Angle X-ray Diffraction (WAXD)

WAXD is an important tool to study crystal structure and measure crystallinity in polymers. X-rays are electro-magnetic waves with a wavelength range ~ 0.1-100 Å. X-rays are produced when electrons ejected from a hot filament (cathode) strike a metal target (anode). For X-ray diffraction a highly monochromatic source is preferred to get a clear diffraction pattern. Semicrystalline polymers consist of amorphous and crystalline domains. X-ray diffraction from polymers occurs through apparent bending of the waves around the crystals and subsequent movement through the amorphous phase. The angle (2θ) at which the diffracted X-rays are collected can be of two types; 2θ < 5° (small angle) or 2θ > 5° (wide angle). WAXD is useful in analyzing single crystals and crystal structures, while SAXD is useful in studying the overall morphology in polymers [53].

There are four basic steps in analysis by WAXD, namely X-ray generation, diffraction, detection, and interpretation. The WAXD instrument setup starts with the source that generates X-rays and incident beam optics to align the X-rays with the sample. Next in the assembly are the sample chamber and the goniometer that helps rotate the sample. Once the X-rays pass through the sample, they are then made to go through a beam stopper which filters the unscattered radiation (to protect the detector from damage). Finally the diffracted X-rays are collected at the detector and the data is analyzed. WAXD can be performed on powders or on fibers, as well as single crystals [53].

WAXD data in the background section was obtained using a Philips XLF, ATPS X-ray diffractometer with an OMNI Instruments customized auto-mount and copper tube. The tube
produces X-rays with a wavelength of 1.54Å. The diffractograms were obtained with a 2θ range of 5-50°, and data were analyzed using TXRD 5.1 software.

1.4.4 Differential Scanning Calorimetry (DSC)

DSC is based on the principle that the response of polymers varies with changes in temperature. DSC is a quantitative analytical tool that profiles caloric heat changes from a sample pan with respect to an empty reference pan. A DSC thermogram helps in the analysis of thermal properties related to phase changes like glass transition, crystallization, and melting behavior. It measures endothermic and exothermic heat flows in the polymer samples, which is done by monitoring the power (mW) required to maintain the sample and its pan at the same temperature as the empty reference pan. Prerequisite for this instrument is the knowledge of thermal stability of the polymer sample, which can be obtained from Thermo-gravimetric analysis (TGA). TGA tells us about the percentage loss in weight of a polymer as a function of temperature. From TGA data a suitable temperature range can be chosen for DSC analysis in order to prevent sample degradation.

If a polymer sample absorbs energy when heated and becomes plastic, due to chain mobility, it will show an increase in its heat capacity. When the amorphous regions in the polymer become crystalline, they exhibit some energy release, which is the exothermic heat of crystallization. When the polymer reaches its melting temperature, it absorbs energy, resulting in an endothermic melting peak, and its molten chains become mobile and disordered resulting in an amorphous melt. All these transitions are recorded on a thermogram obtained from a differential scanning calorimeter.
DSC thermograms were obtained using a Perkin-Elmer Model 7 Differential Scanning Calorimeter (DSC). Perkin Elmer Diamond DSC is a power compensated DSC which measures the power required to keep the reference pan at the same temperature as the sample pan. The instrument consist of two aluminum pans, one containing sample and other used as a reference placed in a holder above the furnace. Temperature range for the instrument is from -50 to 700 °C and is monitored with thermocouples. For samples that may have glass transition temperatures below room temperature, there is an Intracooler 2 which can achieve temperatures down to -50 °C. A nitrogen gas cylinder is used for purging air (O₂ and H₂O) from the sample. The Pyris software analyzes the DSC plots and helps in the calculation of the transition temperatures and their associated enthalpies [54].

About 3-5 mg of sample was used in all tests. Samples were sealed in aluminum pans, and depending on the sample geometry (pellet or powder/flakes) either a volatile or non-volatile pan was used. The instrument was calibrated before each set of scans with Indium or Tin, depending on the temperature range of interest. Nitrogen was used as the purge gas to provide an inert atmosphere and to prevent sample degradation. The procedure that was employed for DSC scanning of all the samples is described as follows:

\[ \text{Hold} \rightarrow \text{Heat} \rightarrow \text{Hold} \rightarrow \text{Cool} \rightarrow \text{Hold} \rightarrow \text{Heat} \]

All DSC thermograms were analyzed using Pyris software for quantitative evaluation of glass transition, crystallization, and melting.
1.4.5 **Density Measurements**

The densities of polymer films were measured by floatation using water (W) and 40% Sodium Bromide (NaBr), which have densities of 1 and 1.4 g/cm$^3$, respectively, that are lower and higher than the density of PVAc. Small pieces of both asr- and c-PVAc films were placed in a known volume of water, vol(W) containing a magnetic stir-bar, where they sunk to the bottom of the volumetric cylinder, which was then sealed with aluminum foil. The NaBr solution was slowly added from a burette with stirring until each PVAc film was lifted and became suspended in the solvent mixture, and the volume of added NaBr solution, vol(NaBr), was noted. The PVAc densities were then obtained from:

$$\rho_{\text{exp}} = \frac{\text{vol}(W) \rho(W) + \text{vol}(\text{NaBr}) \rho(\text{NaBr})}{\text{vol}(W) + \text{vol}(\text{NaBr})}$$

1.4.6 **Thermo Gravimetric Analysis (TGA)**

The TGA technique helps us in analyzing the degradation of polymers and their IC samples by monitoring the mass of a sample as a function of temperature which can be done in the presence of air or an inert medium like nitrogen. Other applications of TGA include studying the effect of residual solvents/moisture and presence of additives on the degradation profile of samples.

The measurements were made using a Perkin Elmer Pyris 1 TGA that has a sensitive balance, usually a microbalance, a furnace surrounding the sample holder and a purge gas system. The balance is designed in such a way that changes in weight produces electric
signals proportional to weight change. The sample pan is made of platinum and can accommodate 5-10 mg of the sample. The furnace surrounds the sampler and holder and contains nitrogen gas. It is programmed for linear heating rates. The temperature range for the instrument is 25 to 950 °C [55], the heating rate can be varied between 0.1 - 200 °C/min, and the temperature is maintained using a thermocouple. The purge gas system removes residual gases and maintains a constant environment.

The software plots % weight of sample vs. temperature and it helps in analyses of weight loss and important temperatures at which degradation occurs. TGA measures the change in weight of a sample with respect to time or temperature which tells us about its thermal stability.

1.4.7 Dynamic Mechanical Thermal Analysis (DMTA)

DMTA is an analytical technique that helps us in the evaluation of viscoelastic behavior of polymeric materials. DMTA differs from traditional tensile tests in two ways. Tensile tests only analyze the elastic components and operate outside of the linear viscoelastic range. DMTA on the other hand analyzes both viscous and elastic components and works in the linear viscoelastic (LVE) range which is why it is more sensitive to structure. In this technique an oscillating stress or strain is applied to the material and the resulting behavior is analyzed. For polymers, as stress is applied there is a lag in their response. The elastic behavior of the polymer is related to the output amplitude, while the viscous behavior corresponds to the phase lag in the output. DMTA can test the samples in predominantly tensile, compressive and shear modes where the temperature of the sample can be varied at
constant frequency or vice versa. In our studies we have used TA Instruments Q800 Dynamic Mechanical Analyzer with an attached shear-sandwich clamp. In this assembly equal sized films are sheared between two fixed outer plates and a moving inner plate. A strain was selected from the LVE range and frequency was varied at a constant temperature. The instrument has a furnace to raise the temperature of polymer samples and also a nitrogen cooling unit. Data were analyzed using TA’s Universal Analysis software [56].

1.4.8 Nano-indentation

Nano-indentation is a non-destructive technique for measuring the mechanical properties of polymeric surfaces. It makes use of a probe or an indenter whose mechanical properties are known. There are different types of indenter geometries but the three sided indenters (e.g. Berkovich Indenter) are used more commonly for nano-scale evaluation.

Figure 1.16 illustrates a typical loading-displacement indentation curve which is used to back out the mechanical properties of the material. The loading curve represents the plastic behavior of the material and is related to its hardness while the unloading curve represents the elastic behavior of the material and is related to its young’s modulus. The slope of the unloading curve is the stiffness (S) of the material. For the contact area ‘A’, the hardness of the material (H) can be given by, $H = P/A$ (load/unit sample area). The effective modulus (E$_{eff}$) can be calculated knowing S and A from, $E_{eff} = E/(1 - v^2) = (n/A)^{1/2} \times (S/2)$. Nano-indentation was performed on the polymer samples using a Hysitron TriboIndenter instrument and the data were analyzed with the TriboScan software. The test mode employed was a quasi-static nano-indentation mode in order to measure the hardness and young’s
modulus of the films. All tests were performed at ambient temperature (approximately 20\degree C). Each of the sample films was indented 9 times in a 3×3 square pattern using a Berkovich diamond tip.

![Load-Displacement Curve](image)

**Figure 1.16: Load-Displacement Curve [57]**

The samples were tested in constant force mode, where a known force is applied on the surface of the film using the indenter and the resultant displacement is calculated in nanometers.

\[
\frac{1}{E_r} = \frac{(1 - \nu^2)}{E} + \frac{(1 - \nu_i^2)}{E_i}
\]
Reduced Young’s modulus (Er) and hardness values were all determined automatically by the software while the actual value (E) can be calculated from the formula shown below, where \( \nu \) is the Poisson’s ratio. The software helps in the automatic scanning of the surface of the film by adjusting the tip height based on the force feedback and mapping surface topography.

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CHAPTER 2

2. Glass-Transition Temperatures of Nano-Structured Amorphous Bulk Polymers and their Blends

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2.1 Abstract

Nano-structured amorphous bulk polymer samples were produced by processing them with small molecule hosts. Urea (U) and gamma-cyclodextrin (γ-CD) were utilized to form crystalline inclusion compounds (ICs) with low and high molecular weight as-received (asr-) poly(vinyl acetate) (PVAc), poly(methyl methacrylate) (PMMA), and their blends as included guests. Upon careful removal of the host crystalline U and γ-CD lattices, nano-structured coalesced (c-) bulk PVAc, PMMA, and PVAc/PMMA blend samples were obtained, and their glass-transition temperatures, $T_g$s, measured. In addition, non-stoichiometric (n-s)-IC samples of each were formed with γ-CD as the host. The $T_g$s of the un-threaded, un-included portions of their chains were observed as a function of their degree of inclusion. In all cases these nano-structured PVAc and PMMA samples exhibited $T_g$s elevated above those of their as-received and solution-cast samples. Based on their
comparison, several conclusions were reached concerning how their molecular weights, the organization of chains in their coalesced samples, and the degree of constraint experienced by un-included portions of their chains in \((n-s)\)-\(\gamma\)-CD-IC samples with different stoichiometries affect their chain mobilities and resultant \(T_g\)s.

![Figure 2.0: Table of Contents (TOC) Figure](image)

2.2 Introduction

As recently summarized [1], the glass-transition temperatures, \(T_g\)s, of confined amorphous polymers, such as occurring in their ultra-thin films, can be different from those observed in their bulk samples. Though complete consensus concerning the causes for the differences between the glass-transition temperatures and chain dynamics in nano-confined and bulk amorphous polymer samples has yet to be reached, it does seem clear that the heterogeneity in polymer thin films is a key to understanding their atypical properties, including their \(T_g\)s.
Somewhat related are observations of bulk guest polymer samples coalesced from their inclusion compounds (ICs) formed with small molecule hosts [2, 3], such as those with host cyclodextrins (CDs) in Figure 2.1. The polymer chains included in ICs formed with CDs and other small molecule hosts, such as urea (U), occupy narrow parallel channels, which in the case of CD-ICs range in diameter from ~0.5 – 1.0 nm. Consequently, not only are they separated from their neighboring chains, through IC confinement, but they are also highly extended. When the host small molecule lattice is carefully removed, a bulk sample of coalesced IC guest polymers is obtained.

Figure 2.1: Schematic illustration of the polymer nano-confinement in and release from their crystalline ICs formed with CD hosts

The behaviors and properties of such coalesced polymer samples have been shown to be distinct and generally improved in comparison to samples obtained by normal processing
techniques from their solutions and melts. This is likely a result of the differences between highly extended un-entangled polymer chains found in the narrow channels of their ICs and the randomly-coiling entangled polymer chains in their solutions and melts. We believe [4] that coalesced samples of amorphous polymers consist of small un-oriented regions containing extended and largely un-entangled polymer chains, because the volume of individual un-oriented crystals in the polymer-CD-IC powders are ~10 times the volume of the polymer coalesced from each.

Such nano-structured amorphous polymer samples, as obtained through confinement in and subsequent release from their ICs, have been observed [2-4] to have glass-transition temperatures, \( T_g \), substantially elevated above their normally processed samples. This is believed to result from the closer packing of extended un-entangled coalesced chains which produce samples with higher densities\(^3\). Here urea (U) and gamma-cyclodextrin (\( \gamma \)-CD) were utilized to form crystalline ICs with low [5,6] and high [7] molecular weight poly(vinyl acetate) (PVAc), poly(methyl methacrylate) (PMMA), and their blends as included guests. Upon careful removal of the host crystalline U and \( \gamma \)-CD lattices, nano-structured coalesced bulk PVAc, PMMA, and PVAc/PMMA blend samples were obtained, and their \( T_g \)s were measured.

In addition, non-stoichiometric (n-s)-IC samples of each were formed with \( \gamma \)-CD as the host, and the \( T_g \)s of the un-threaded, un-included portions of their chains were observed as a function of their degree of inclusion. In all cases these nano-structured PVAc, PMMA, and PVAc/PMMA samples exhibited \( T_g \)s elevated above those of their as-received and solution-cast samples. Based on their comparison, several conclusions were reached concerning how
their molecular weights, the organization of chains in their coalesced samples, and the degree of constraint experienced by un-included portions of their chains in (n-s)-\(\gamma\)-CD-IC samples with different stoichiometries affect their chain mobilities and resultant \(T_g\)s.

### 2.3 Methods and Materials

Atactic PMMA (Mw = 350 kDa), atactic PVAc (Mw = 167 kDa), and U were purchased from Aldrich Co. \(\gamma\)-CD was obtained from Wacker Pharmaceuticals, while dioxane was obtained from Fischer Scientific.

Inclusion complexes (ICs) of PMMA, PVAc and their blends with U were obtained by a co-crystallization process. In this method a saturated solution of urea in de-ionized (D-I) water was added drop-wise to dilute solutions (0.5% wt./vol.) of PMMA, PVAc and their blends prepared in dioxane at 50 °C. A white precipitate was observed upon addition of the U solution to the polymer solutions. After complete addition of the urea solution, the suspension was cooled to room temperature and kept overnight without stirring. The resultant U-ICs were filtered, washed with dioxane to remove uncomplexed polymer and finally dried overnight at room temperature. The polymer U-ICs were then coalesced by washing them with excess DI water for about 1 hour at 50 °C, and were finally filtered and dried overnight at room temperature.

Non-stoichiometric inclusion compounds [(n-s)-ICs] were prepared using the two solvent co-precipitation method of Uyar et al. [5] for preparation of fully covered stoichiometric inclusion compounds. \(\gamma\)-CD was dissolved in D-I water, while PMMA and PVAc were dissolved in stirred dioxane. The amount of polymer and \(\gamma\)-CD used was varied in order to
get different coverage ratios from 2:1 - 6:1. A single γ-CD can house ~ three repeat units of PMMA and PVAc, so a fully covered stoichiometric γ-CD-IC essentially contains one γ-CD for every three repeat units of the guest polymer. As an example, we doubled the relative amount of polymer (compared to the amount used for the fully covered stoichiometric IC) to form a 2:1 (n-s)-polymer-γ-CD-IC. Similarly, we used the same process to calculate the amount of polymer required to form non-stoichiometric 3:1 and 6:1 γ-CD-ICs containing excess PVAc and/or PMMA. The polymer solutions were stirred at 60 °C on a hot plate for about 5 minutes. The aqueous solution of γ-CD was added drop-wise to the polymer solution with continuous stirring, stirring was continued at this temperature for about 3 hours, and then cooled to room temperature before stirring for an additional 3 days. After this period, the precipitate was filtered and dried in a vacuum oven. In addition to the polymer blends, neat (n-s)-polymer-γ-CD-ICs were individually made with each polymer in the same ratios as used for their blends.

The ICs and coalesced polymers were characterized using Fourier Transform Infrared Spectroscopy (FTIR), Thermo-Gravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) and Nuclear Magnetic Resonance Spectroscopy (NMR). Infrared spectral studies were conducted with a Nicolet 470 FTIR spectrometer in the range 4000 - 400 cm\(^{-1}\), with a resolution of 4 cm\(^{-1}\) and 64 scans were collected for each sample. FTIR data were analyzed with Omnic software. \(^{13}\)C- and \(^{1}\)H-NMR spectra were collected on a Bruker 500 MHz NMR instrument. Spectra were obtained for dilute d\(^6\)-DMSO solutions of urea, polymers coalesced from U-ICs and the asr-polymers. TGA was performed on our samples with the help of a Perkin Elmer Pyris1 Thermo-gravimetric Analyzer. Nitrogen gas was used
to purge the furnace. Samples were heated from 25 to 800 °C at a rate of 10 °C per minute and Pyris software was used to analyze the data. Finally, DSC thermal scans were performed with a Perkin Elmer Diamond DSC-7 instrument and TA Instruments Q1000 differential scanning calorimeter. All DSC scans followed a Heat-Cool-Heat profile and the samples were held above their glass transition/melting temperatures after the first heating scan for a substantial amount of time to get rid of prior processing history. The heating and cooling rates used for U, U-ICs, physical mixture of polymer and U (same ratio as used in IC preparation) and (n-s)-γ-CD-ICs (unless mentioned otherwise) were 20 °C /min. The asr- and c-polymers and their blend samples were heated at 5 °C /min and were rapidly cooled at 50 °C/min. Nitrogen was used as the purge gas. DSC data were analyzed with Pyris software.

### 2.4 Results and Discussions

**Stoichiometric Inclusion Complexes and Coalesced Polymers:**

PMMA and PVAc processed from their stoichiometric γ-CD-ICs have been studied previously [5]. The ICs were characterized using FTIR, WAXD and DSC. FTIR results confirmed the presence of both polymer and γ-CD, while WAXD confirmed the change in crystal structure from cage to columnar due to the presence of the polymer-IC guest in the narrow columnar cavities of the γ-CD lattice. DSC thermographs for the stoichiometric γ-CD-ICs did not exhibit characteristic glass transitions seen in the pure polymers. When polymers are processed via nano-confinement each polymer chain gets threaded by CD molecules separating it from the other chains. As the polymer chains are not in contact with each other, they are unable to organize into bulk structures that are responsible for the
thermal transitions reflected in their DSC thermographs. The coalesced polymers obtained from these \( \gamma \)-CD-ICs exhibited higher Tgs on account of largely extended and un-entangled chain morphologies achieved through the nano-confinement and subsequent release processes.

In this section we discuss PVAc and PMMA processed in the above manner with U as IC host and compare the findings to those observed using their \( \gamma \)-CD-ICs. Vibrational peaks observed for the PVAc-U-IC are slightly shifted when compared to the peaks observed individually for U and PVAc, suggesting possible interactions between the two components in the IC, which is similar to that observed with other polymer-U-ICs [8-11].

Figure 2.2: FTIR spectra for (top to bottom) U, PVAc-U-IC, and asr-PVAc
Figure 2.2 displays the FTIR spectra for U, PVAc-U-IC and asr-PVAc, while the Table adjacent to the spectra shows that the peaks in PVAc-U-IC exhibit strong absorptions for bonds and functional groups present in both bulk U and PVAc. The FTIR spectrum for PVAc-U-IC shows peaks for amino and carboxylic groups observed in U and also exhibits peaks from carboxylic and methyl groups from the acetate groups present in PVAc, thus confirming the existence of both in the IC. The change in the crystal structure resulting from the polymer inclusion process can be evaluated from some of the peak shifts observed in its FTIR spectrum. For example, the carbonyl (C=O) stretching vibration in U has shifted from 1675 to 1681 cm$^{-1}$, while the amino (N-H) bending vibration at 1590 cm$^{-1}$ has shifted to 1596 cm$^{-1}$. FTIR results indicate the presence of both PVAc and U in the complex, but only suggest and do not confirm if guest PVAc chains are included in the continuous columnar cavities of the host U or if it is simply a physical mixture.

Figure 2.3: FTIR spectra for coalesced polymers
The FTIR spectra of c-polymers obtained from their U-ICs (Figure 2.3) are virtually identical to those of their asr-polymers, thus suggesting that there is no difference in the chemistry of asr- and c-polymer samples, and that inclusion complex formation and coalescence are merely physical processes. Also, the slight shift in the peak positions of c-polymers with respect to their asr-samples can be attributed to the change in their conformations resulting from the inclusion and coalescence processes. The c-PVAc FTIR spectrum does not show any observable traces of U. To confirm this observation, c-PVAc was analyzed using $^{13}$C-NMR, which is more sensitive than FTIR for detecting traces of U as seen in Figure 2.4. The carbonyl carbon resonance in c-PVAc was observed at $\sim$ 170 ppm [12]. The carbonyl (C=O) peak in urea is located at $\sim$ 161 ppm [13] and was absent in the c-PVAc spectrum, thus confirming the fact that the coalescence process completely removed urea from the inclusion complex.

Figure 2.4: $^{13}$C-NMR spectra (below) for urea and c-PVAc
TGA data helps in understanding the decomposition profile of a sample, and can provide another means to confirm the presence of both polymer and U in their ICs. The decomposition of U into ammonia and cyanic acid followed by formation of an intermediate biuret (which decomposes into the final residues) is well known and can be represented as follows:

\[
\text{NH}_2\text{CONH}_2 \rightarrow \text{NH}_3 + \text{HNCO} \rightarrow \text{H}_2\text{N–CO–NH–CO–NH}_2 \rightarrow \text{Decomposition of Residues}
\]

The inert decomposition observed for U was comparable to that described in the literature [14, 15]. It has been previously shown that in U-ICs, the degradation transitions are slightly
shifted when compared to pure U due to the presence of the additional included guest component [16]. Similarly the decomposition transitions for PVAc-U-IC were shifted when compared to U and this difference is also evident in the derivative plots of the TGA curves in Figure 2.5. Careful observation of the TGA curves between the temperature range of 300 to 550 °C shows the presence of an additional thermal transition for PVAc-U-IC. The thermal transition at ~400 °C can be attributed to the decomposition of the deacetylation products of PVAc [17], thus confirming the presence of both components in the IC.

Figure 2.6: DSC observed glass transitions for U, P-U-ICs, and their physical mixtures

Figure 2.6 shows the DSC heating scans for urea, P-U-ICs and the physical mixtures of the polymers and U. When the P-U-ICs were heated beyond the melting temperature of U, they showed a slightly higher melting point than pure U and the physical mixture of U and asr-polymers. This is due to a change in the structure of U molecules in the IC, as observed in other polymer-U-ICs. Our PVAc- and PMMA-U-ICs do not evidence a glass transition, thus
suggesting complete inclusion of the polymer-IC guest, while their physical mixtures show T₉s indicating there is no interaction between them.

Figure 2.7 shows the heating scans for asr- and c-polymers, and there it is seen that both c-polymers have higher T₉s. These observations are closely similar to the behavior of coalesced PVAc and PMMA obtained from their γ-CD-ICs [5] and can be attributed to the better packing of chains in the largely un-entangled extended chain morphologies, resulting from their processing with urea. Solution-cast PVAc does not show any increase in its T₉, thus confirming the fact that the improvement in the T₉ of coalesced polymers is a result of the IC formation and coalescence processes. PVAc with molecular weights of 13 and 167 kDa that were coalesced from their γ-CD- and U-ICs, respectively, showed T₉s of 36 and 41 °C (see Figure 2.8). This difference in T₉s seems rather small considering the over one-order of magnitude difference in their molecular weights.

It should also be mentioned that the T₉s observed for PMMA are 83 and 97 °C [5] and 110 and 124 °C, respectively, for samples with molecular weights of 15 and 350 kDa that were, respectively, coalesced from their γ-CD- and U-ICs. Since 15 and 350 kDa are considerably below and above the entanglement molecular weight of PMMA respectively [18], it is not surprising that the T₉s observed for their asr-samples differ by 27 °C. However, it seems somewhat surprising that their coalesced samples also have T₉s that differ by 27 °C. Assuming the agreement of the T₉ differences between asr- and c-PMMA samples with very divergent molecular weights are not fortuitous, it may indicate that the molecular weight dependence of polymer glass-transition temperatures is not as sensitive to whether or not they are entangled, but rather to the concentration of their chain-ends [19]. This suggestion is
made because c-polymer samples are believed to be comprised of largely extended and un
entangled chains, while the chains in asr-samples are randomly-coiling and entangled (See
Figure 2.1).

Figure 2.7: Glass transitions in asr-polymers and those coalesced from their U-ICs
Non-Stoichiometric Inclusion Complexes:

For the neat (n-s)-γ-CD-ICs we observe shifts in the T_gs of the un-included portions of PMMA and PVAc chains to higher temperature compared to those of both their as-received and coalesced neat samples. For the neat (n-s)-PVAc-γ-CD-ICs in Figure 2.8 and Table 2.1, we observe higher glass transition temperatures as we progressively increase the quantity of γ-CD added to the preparation mixture. In other words, as the average lengths of the un-included PVAc chains decrease their T_gs increase, consistent with the expected increasing constraint placed on shorter un-included PVAc chain portions emerging from their (n-s)-γ-CD-ICs. For example, the T_g observed for the 6:1 (n-s)-PVAc-γ-CD-IC with the longest un-included chain portions is close to that of c-PVAC obtained from its neat γ-CD-IC.

Table 2.1: T_gs of (n-s)-PVAc-γ-CD-ICs

<table>
<thead>
<tr>
<th>Sample</th>
<th>PVAc (g)</th>
<th>γ-CD (g)</th>
<th>T_g (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>asr-PVAc</td>
<td>-</td>
<td>-</td>
<td>28</td>
</tr>
<tr>
<td>2:1</td>
<td>0.369</td>
<td>0.928</td>
<td>49</td>
</tr>
<tr>
<td>3:1</td>
<td>0.369</td>
<td>0.615</td>
<td>49</td>
</tr>
<tr>
<td>6:1</td>
<td>1.107</td>
<td>0.928</td>
<td>44</td>
</tr>
</tbody>
</table>

For PMMA, we again observed a higher glass transition temperature for the 2:1 (n-s)-γ-CD-ICs in comparison to neat asr- and c-PMMAs. This can be attributed to the increased
constraint placed on the un-included “dangling” chain portions by the ordering of the remaining included polymer chain portions that are forced to arrange themselves within the γ-CD cavities [20].

Figure 2.8: Heating DSC scans of asr-PVAc and -PMMA and their (n-s)-γ-CD-ICs
It has been shown that the PVAc coalesced from their stoichiometric $\gamma$-CD-ICs has a largely extended chain configuration with distinct properties that are distinct from those of its as received analog which has a random coiled morphology. We felt it would interesting to investigate PVAc coalesced from their ns-$\gamma$-CD-IC that has dangling chains which exhibit higher $T_g$. For this, we prepared a 2-1-ns-PVAc-$\gamma$-CD-IC, coalesced it and analysed its thermal behavior (See Figure 2.10).

Figure 2.9: Channel structure of a polymer-$\gamma$-CD-IC. 0.4 polymer chains/nm$^2$ of $\gamma$-CD-IC crystal surface in the case of PVAc and PMMA, [21] which are singly included in each channel $\Rightarrow$ protruding polymer chains form Dense Polymer Brushes ~ half the density of chains in bulk polymer crystals [22]

It was observed that the PVAc coalesced from its 2-1-ns-PVAc-$\gamma$-CD-IC shows a $T_g$ higher than the asr-PVAc and comparable to c-PVAc from its stoichiometric $\gamma$-CD-IC. This
is not unexpected since the dangling chains in the ns-ICs have a high $T_g$ and this behavior stays even after the coalescence process.

Figure 2.10: DSC scans of 2-1-ns- $\gamma$-CD-IC (top) and PVAc coalesced from it (bottom)
Blending two or more polymers offers a way to obtain a single functional material with properties that possess, or hopefully even surpass, the desired properties of its constituent polymers. Blending can be achieved by various techniques, but the most popular is casting from their common solvents. Miscibility in solution-cast polymer blends depends on many factors, such as type of solvent, evaporation rate, composition of the casting solution, etc. Studies done previously on PMMA/PVAc blends found that they are generally not miscible [6]. Miscibility can be achieved by treatment with some solvents [23], but these blends phase separate when processed at temperatures above their \( T_g \)s [6].

**Table 2.2: Hansen Solubility Parameters for PMMA and PVAc [24]**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( \delta_d )</th>
<th>( \delta_p )</th>
<th>( \delta_{hb} )</th>
<th>( \delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>15.6</td>
<td>10.5</td>
<td>5.2</td>
<td>19.5</td>
</tr>
<tr>
<td>PVAc</td>
<td>15.7</td>
<td>11.4</td>
<td>7.8</td>
<td>20.9</td>
</tr>
</tbody>
</table>

Interactions between PMMA and PVAc can be analyzed by estimating their solubility parameters (\( \delta \)). \( \delta \) provides a numerical estimate for interaction between polymer & solvents or between polymers. Each group present in the repeat unit of the polymer has a volume and energy associated with it using which we can calculate the molar volume and \( \delta \). Hansen solubility parameter incorporates the various interactions such as dispersion, polar and
hydrogen bonds while estimating $\delta$ as shown in the following equation, and the $\delta$ values for PMMA and PVAc have been summarized in Table 2.2. $\delta$ values and structure for PMMA and PVAc are quite similar and this suggests potential for polymer blend miscibility mainly through hydrogen bonding as illustrated in Figure 2.10. In this study we have used $\gamma$-CD and U inclusion for blending PMMA and PVAc.

$$\delta^2 = \delta^2_d + \delta^2_p + \delta^2_{hb}$$

where,

d ~ dispersion forces,

p ~ polar interactions,

hb ~ hydrogen bonds.

PMMA/PVAc intimately mixed blends have been previously obtained by formation and coalescence of their common $\gamma$-CD-ICs [6]. This was done using lower molecular weight PVAc ($\sim$ 13 kDa) and PMMA ($\sim$ 15 kDa). It was observed that blends coalesced from their common $\gamma$-CD-ICs showed some miscibility above the Tg of PVAc, where PVAc chains can diffuse in to PMMA domains.

Figure 2.11: Suggested hydrogen bonding in PMMA/PVAc blends
PMMA/PVAc can also be partially blended using γ-CD as a compatibilizer through formation of their common non-stoichiometric (n-s)-γ-CD-ICs. In such a study we prepared (n-s)-γ-CD-ICs with a 3:1 ratio of the polymer pair (1:1 & 1:2, PMMA:PVAc) to γ-CD. In order to experimentally verify the ratio of polymer to cyclodextrin in these (n-s)-γ-CD-ICs of PMMA/PVAc, and the relative ratio of the PVAc and PMMA in the blend, we employed $^1$H-NMR (See Figure 2.12). The analysis was done on the 3:1 γ-CD (n-s)-IC of PMMA/PVAc (1:2) using d$_6$-DMSO, as the solvent. Partial integration was carried out on the peaks corresponding to the PMMA (CH$_2$), PVAc (CH), and γ-CD ($^1$H) protons at ~4.4, ~5.6, and ~4.9 ppm, respectively. Keeping in mind the number of protons contributing to each, PMMA (2), PVAc (1), and γ-CD(8) peak, and that one γ-CD includes 3 repeat units of either PVAc or PMMA, we determined the relative ratio of included polymer (PMMA + PVAc) to cyclodextrin in their common (n-s)-γ-CD-ICs. The ratio of PVAc:PMMA in the (n-s)-blend-γ-CD-IC can also be obtained.

Figure 2.12: $^1$H NMR (500MHz) data for 3:1(n-s)-PMMA/PVAc(1:2)-γ-CD-IC in d$_6$-DMSO
Theoretically, we expect the ratio of total polymer to the cycloexextrin in the 3:1-(n-s)-γ-CD-IC to be 3.375, based on the calculation of 3x the number of polymer protons that are included in a fully-covered 1:1 IC. The $^1$H-NMR analysis yielded an experimental value of 3.4±0.4, which is close to the expected value. The observed molar ratio of PVAc:PMMA in the blend was found to be 2.1±0.2, also very close to the expected value of 2.

DSC results for the (n-s)-PVAc/PMMA-γ-CD-IC blends have been summarized in Table 2.3. In the 1:1 PMMA/PVAc initial mixture we observe the glass transition temperatures of PVAc and PMMA at 48 and 143 °C, respectively, as seen in Figure 2.13. This is similar to the $T_g$s obtained for the neat (n-s)-ICs of PVAc and PMMA in the previous section. This indicates that the 3:1 (n-s)-PMMA/PVAc(1:1)-γ-CD-IC contains distinct γ-CD-IC crystals including exclusively each of the neat guest polymers. We can also see in Table 2.3, that unlike the $T_g$’s of the neat (n-s)-γ-CD-ICs, which simply shifted to higher temperatures, in the case of the 3:1 (n-s)-PVAc/PMMA-γ-CD-IC, with 2:1 PVAc;PMMA stoichiometry, they move closer to each other, indicating a certain degree of mixing between the “dangling” PVAc and PMMA chain portions.

<table>
<thead>
<tr>
<th>(n-s)-IC Sample (Polymer:γ-CD)</th>
<th>PMMA/PVAc (Molar Ratio)</th>
<th>$T_{g1}$ (°C)</th>
<th>$T_{g2}$ (°C)</th>
<th>$T_{g3}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:1 1:1</td>
<td></td>
<td>48</td>
<td>-</td>
<td>142</td>
</tr>
<tr>
<td>3:1 1:2</td>
<td></td>
<td>68</td>
<td>113</td>
<td>137</td>
</tr>
</tbody>
</table>

Table 2.3: $T_g$s of PMMA/PVAc Blends in Their Common (n-s)-γ-CD-IC
Although the mixing was not complete, as confirmed by a $T_g$ close to that of the neat 3:1 (n-s)-PMMA-$\gamma$-CD-IC, the difference in the other two $T_g$s observed in relation to both the as-received and coalesced polymers is an indication of the presence of PMMA in PVAc-rich domains and vice versa. Thus, we get hardening (higher $T_g$) of the PVAc component caused by the presence of PMMA, and softening (lower $T_g$) of the PMMA from the presence of PVAc, resulting in a decrease of its glass transition temperature, compared to both asr- and c-PMMAs. Rather more interesting is the observation of an intermediate $T_g$ at 113 °C, which is consistent with a well-mixed phase containing similar amounts of un-included portions of PVAc and PMMA chains.

![Figure 2.13: Heating DSC scans of (n-s)-PVAc/PMMA-$\gamma$-CD-ICs](image)

**Figure 2.13: Heating DSC scans of (n-s)-PVAc/PMMA-$\gamma$-CD-ICs**
Another way to blend these polymers is through formation and coalescence of their common U-ICs. FTIR data for a 50/50 PMMA/PVAc (mol%) blend coalesced from their common U-IC are presented in Figure 2.13. PMMA peaks are observed to be more intense in the spectrum, suggesting preferential inclusion of PMMA over PVAc, but this cannot be confirmed from FTIR alone, because of the overlapping of peaks observed from their similar chemical structures. For example, the C=O stretch is observed in asr-PMMA at 1741 cm\(^{-1}\), in asr-PVAc at 1733 cm\(^{-1}\), and in their 50-50 coalesced blend at 1739 cm\(^{-1}\). Two distinct C-O-C stretching peaks can be differentiated for both polymers and are pointed out in Figure 2.14.

<table>
<thead>
<tr>
<th>Peaks (cm(^{-1}))</th>
<th>Functional Groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>1237</td>
<td>C-O-C stretch in PVAc</td>
</tr>
<tr>
<td>1147</td>
<td>C-O-C stretch in PMMA</td>
</tr>
</tbody>
</table>

**Figure 2.14: FTIR data for a 50/50 PMMA/PVAc blend coalesced from its U-IC**
DSC data for PMMA/PVAc blends coalesced from their common U-ICs with varying initial PMMA:PVAc (70/30, 50/50 and 30/70) mol% are illustrated in Figure 2.15. All heating scans exhibit three $T_g$s. The higher and lower $T_g$s ($T_{g1}$ & $T_{g2}$) correspond to those of neat PMMA and PVAc, respectively, coalesced from their U-ICs. This indicates that the polymer chains in the coalesced blends are largely aligned similar to the coalesced homopolymers processed with U. In between these two, there is an intermediate $T_g$ which corresponds to the miscible phase ($T_{g\text{-miscible}}$). From the DSC scans it can be concluded that $T_{g\text{-miscible}}$ moves towards the $T_g$ of PVAc with increasing initial PVAc content. The composition of the phase corresponding to $T_{g\text{-miscible}}$ was estimated using the Fox Equation [25] and has been presented in Figure 2.16. This analysis confirms preferential inclusion of PMMA over PVAc and indicates that in order to get an ~ equimolar mixture of a coalesced
PMMA/PVAc blend an initial PVAc/PMMA composition of 70/30 –, or close to 2:1, in the feed is required.

\[
\left( T_{g\text{-miscible phase}} \right)^{-1} = W_{PVAc}/T_{gPVAc} + W_{PMMA}/T_{gPMMA}
\]

![Tg-miscible vs. Composition](image)

**Figure 2.16: Tg vs. Composition for PMMA/PVAc blends coalesced from their common U-ICs**

<table>
<thead>
<tr>
<th>Feed PVAc/PMMA (mol%)</th>
<th>Blend Tg-miscible (K)</th>
<th>PVAc (mol%)</th>
<th>PMMA (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30/70</td>
<td>378</td>
<td>21</td>
<td>79</td>
</tr>
<tr>
<td>50/50</td>
<td>369</td>
<td>31</td>
<td>69</td>
</tr>
<tr>
<td>70/30</td>
<td>357</td>
<td>46</td>
<td>54</td>
</tr>
</tbody>
</table>

**2.5 Summary**

We have presented a unique way of restructuring PVAc, PMMA and their blends by processing them with U and γ-CD. The formation of U-ICs was established using FTIR,
TGA and DSC analysis. Complete removal of U to obtain coalesced polymers was confirmed from the $^{13}$C-NMR results. It was found that the coalesced polymers obtained from U-ICs had behaviors and properties closely similar to those obtained from their $\gamma$-CD-ICs, which in both cases exhibited higher $T_g$s than their asr-samples on account of largely extended and un-entangled chain morphologies. This is likely a result of the similarity in IC channel diameters in the PVAc- and PMMA-U- and $\gamma$-CD-ICs, and confirms the conclusion that the unusual behaviors of polymers coalesced from their CD-ICs are not the result of remnant CDs threaded on their chains. Comparison of the $T_g$s of asr- and c-samples of PMMA, with molecular weights below (15 kDa) and above (350 kDa) the entanglement molecular weight of PMMA [18], suggest that the molecular weight dependence of polymer glass-transition temperatures is not as sensitive to whether or not they are entangled as they are to the concentration of their chain-ends [19]. The (n-s)-$\gamma$-CD-ICs of PMMA and PVAc obtained with varying ratios of total polymer to $\gamma$-CD show $T_g$s of the un-included chain portions that are higher than both their asr- and c-samples. The DSC results also indicate that their $T_g$s increase with increasing amount of $\gamma$-CD in the (n-s)-ICs, resulting from the greater constraint placed on shorter un-included chain portions. It can be concluded that the motional constraints placed on the un-included chain portions in (n-s)-$\gamma$-CD-ICs by their connection to chain portions included in the crystalline $\gamma$-CD channels is greater than that experienced by the largely extended and un-entangled polymer chains coalesced from their stoichiometric ICs. PMMA/PVAc blends obtained through formation and coalescence of their common $\gamma$-CD-ICs have been previously shown to possess some degree of miscibility. Here these polymers were blended through formation of their common (n-s)-$\gamma$-CD-ICs. The miscibility
in these blends was altered by changing their initial polymer:γ-CD ratios, and preferential inclusion of PMMA over PVAc was observed. PMMA/PVAc blends were also formed through formation and coalescence of their common U-ICs. FTIR data established the presence of both polymers and also suggested preferential inclusion of PMMA over PVAc. This was confirmed by analyzing the DSC results using the Fox Equation. DSC results indicated largely separated PMMA and PVAc-rich domains in the blend, with an additional miscible phase confirmed through observation of an intermediate T_g.

2.6 References

CHAPTER 3

3. Annealing Studies and Properties of Poly (vinyl acetate) (PVAc) Coalesced from its Inclusion Complex with Gamma-Cyclodextrin (γ-CD) and Urea (U)

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* This chapter is in preparation for publishing in a peer-reviewed journal

3.1 Abstract

In this study we have carefully examined the organization of chains in and resultant properties of bulk samples of an amorphous polymer, poly (vinyl acetate) (PVAc), that was coalesced from its γ-CD-IC and U-IC crystals (c-PVAc), with particular emphasis placed on the effects of long-time annealing above \( T_g \). By comparison to as-received PVAc (asr-PVAc) samples, c-PVAc exhibits a higher \( T_g \) and density, which both remain higher even after prolonged annealing (two weeks or more at 70 °C) above its \( T_g \). Moduli of PVAc samples measured above their \( T_g \)s indicate improved mechanical behavior for c-PVAc. We discuss, offer, and solicit possible reasons why c-PVAc, and, by extension, other polymers coalesced from their CD-ICs and U-ICs, retain their unique as-coalesced organizations and behaviors even after extensive annealing above their \( T_g \)s and \( T_m \)s, where their constituent chains are mobile.
3.2 Introduction

The cyclic starches, cyclodextrins (CDs), which are able to thread over polymer chains to form non-covalent inclusion complexes (ICs), have been observed to restructure polymer materials at the molecular level (See Figure 3.1) [1]. When the separated and highly extended guest chains in polymer-CD-ICs are coalesced into a solid bulk sample by carefully removing the host CDs, they remain largely extended and un-entangled. This results in behaviors and properties that are quite distinct from those shown by bulk polymer samples solidified from their melts or solutions, and which remain distinct even after annealing the coalesced samples for long times (hours, days, weeks) above their T_g's and T_m's [2,3]. As a result, we may melt-process polymer samples coalesced from their CD-ICs to produce materials with unique structures and unusual properties.

It has been demonstrated [1-5] that in the melt the transition of polymer samples coalesced from their CD-IC crystals, with initially largely extended un-entangled chains, to the normal randomly-coiled entangled melt (See Figures 3.1 and 3.2) is extremely sluggish
(several days or more) [2,3]. However, most studies of guest polymers coalesced from their CD-ICs upon removal of the host CDs have been conducted on polymers able to crystallize, resulting in as-coalesced morphologies that are semi-crystalline and require observations to be made at high temperatures above their $T_m$s in order to examine their melts. Here we focus on a completely amorphous polymer with a low $T_g$, poly (vinyl acetate) (PVAc), to further examine the organization and behavior of polymers coalesced from their ICs formed with host CDs, and to assess their stability to extended annealing above $T_g$.

Figure 3.1: Formation of and coalescence of a polymer sample from its crystalline cyclodextrin inclusion complex

In addition, similar observations are performed upon PVAc samples coalesced from its IC formed with host urea, which cannot thread over the PVAc during inclusion, and is therefore more easily removed.
Please note that, though the guest polymer chains in each crystal of the CD-IC powder are expected to be coalesced somewhat as indicated, we do not mean to imply that this results in the initial overall macroscopic orientation of all extended and un-entangled chains. Rather, we suggest that the initial macroscopic organization of polymer chains in the melt might resemble something like a collection of small “nematic-like” regions randomly arranged without a preferred orientation of their directors. [See D. E. Beers and J. E. Ramirez [6] for a discussion of Vectra, a liquid-crystalline polyester/polyarylate copolymer, that evidences an anisotropic melt much like that suggested above for coalesced polymers.]

3.3 Experimental Section

Formation and Coalescence of PVAc-γ-CD- and PVAc-U-ICs to obtain c-PVAc

Atactic poly(vinyl acetate) (asr-PVAc), with MW = 167 kDa, dioxane solvent and urea were purchased from Aldrich Co and Fischer Scientific respectively, while gamma
cyclodextrin (γ-CD) was obtained from Wacker Chemie. The water used in this study was
deionized (DI-H2O). The procedures for preparation of PVAc-γ-CD IC (stoichiometric and
non-stoichiometric) and the resulting c-PVAc used by Uyar et al. [6,7] were followed, and
the experiment was scaled up to get a higher yield of c-PVAc. Similarly the formation and
coalescence of PVAc from its urea inclusion complex used by Joijode et al. [8] was followed.

**Annealing studies of as-received and coalesced PVAc**

Asr- and c-PVAc films were pressed and then annealed at 70 °C for different time periods
in a vacuum oven, and the effect of annealing on their glass transition temperatures and
densities were evaluated using DSC and a simple floatation method (See below). Similar
DSC and density observations were also carried out, before and after annealing for long
times at 70 °C, for a 50/50 asr-PVAC/c-PVAC physical mixture obtained by grinding
together the asr- and c-PVAc films.

**FTIR**

Infrared spectral studies were conducted with a Nicolet 470 FTIR spectrometer in the
range 4000 - 600 cm⁻¹, with a resolution of 4 cm⁻¹. FTIR data were analyzed by using Omnic
software. 64 scans were collected for each powder sample.

**NMR**

¹H-NMR spectra were collected on a Bruker 700 MHz NMR instrument. The spectra
were obtained for dilute solutions of γ-CD, urea and neat asr- and c-PVAc's dissolved in
d₆-DMSO.
**DSC**

Differential scanning calorimetric (DSC) thermal scans were performed with a Perkin Elmer Diamond DSC-7 instrument. Heating scans were started at 0 °C, and each sample was heated to 70 °C at a heating rate of 5 °C/minute. Next the samples were held at 70 °C for 10 minutes, rapidly cooled at 50 °C/minute to get rid of prior processing history and this was followed by a second heating cycle. Nitrogen was used as the purge gas. DSC data were analyzed with Pyris software.

**Density Measurements**

The densities of asr- and c-PVAc samples were measured by floatation using water and a solution of NaBr in water, which have densities of 1.0 and 1.4 g/cm³, respectively, that are lower and higher than that of PVAc. Small pieces of both PVAc films pressed at 70 °C, were placed in a known volume of water, vol(H₂O) containing a magnetic stir-bar, where they sank to the bottom. The NaBr/H₂O solution was slowly added with stirring from a burette until each PVAc film was in turn elevated from the bottom and suspended in the aqueous solution, and the volume of added NaBr/H₂O, vol(NaBr/H₂O), was noted. The PVAc densities were then obtained from:

\[
\rho = \frac{\text{vol}(\text{H}_2\text{O})\rho(\text{H}_2\text{O}) + \text{vol}(\text{NaBr/\text{H}_2\text{O}})\rho(\text{NaBr/\text{H}_2\text{O}})}{\text{vol}(\text{H}_2\text{O}) + \text{vol}(\text{NaBr/\text{H}_2\text{O}})}
\]
The densities of both asr- and c-PVAc films were obtained below and above their glass transition temperatures, and before and after annealing. In addition, the density of a film pressed from a 50/50 asr-PVAc/c-PVAc physical mixture was also measured below and above its $T_g$ and before and after annealing.

**Dynamic Mechanical Analysis (DMA)**

DMA was performed using a TA Instruments Q800 Dynamic Mechanical Analyzer with an attached shear-sandwich clamp. The samples were held at 70 °C and at 0.1% strain, which is in the linear viscoelastic region (LVE), and then subjected to a frequency sweep from 0.01-10 Hz. The data were analyzed using TA’s Universal Analysis software.

**Solution Viscometry**

Single concentration flow times for dilute PVAc solutions were obtained using an Ubbelohde viscometer. Samples of PVAc before and after annealing were dissolved in dioxane to obtain 0.2 g/dL solutions, and their flow times at 25 °C were compared to see if annealing caused any reduction in their molecular weight.

**3.4 Results & Discussion**

**Inclusion Complexes & Coalesced Polymers**

FTIR spectra of PVAc-$\gamma$-CD-IC and PVAc-U-IC show peaks characteristic for asr-PVAc, $\gamma$-CD, and urea. This suggests presence of both polymer and small molecule host in the ICs but does not confirm whether the polymer chains are included in the narrow channels of the
small molecule hosts or if they just physically mixed. Thus, success of the polymer inclusion process was further confirmed by DSC observation of both PVAc-ICs. The thermal scans for these ICs do not exhibit a glass transition due to isolation of individual polymer chains by the narrow channels [8]. Figure 3.3 illustrates these observations. In addition, the FTIR spectra of both c-PVAc samples are virtually identical to that of asr-PVAc, suggesting that little if any $\gamma$-CD or urea remains in their c-PVAc samples. The effectiveness of the coalescence process was confirmed by $^1$H-NMR examination of the c-PVAc dissolved in $d_6$-DMSO, which are presented in Figure 3.4, and by previous mass-spectrometric observations performed on PVAc coalesced from its $\gamma$-CD-IC [2]. In Figure 3.4, the protons corresponding to urea and PVAc (on methine carbon) have been identified at 5.7 ppm and 4.7 ppm respectively [9, 10]. The $^1$H-NMR spectrum of urea shows a peak at around 5.7 ppm [9] corresponding to the urea protons which is not seen in the $^1$H-NMR spectrum of c-PVAc. Similarly, it was observed in the spectrum that the c-PVAc obtained from its $\gamma$-CD-IC does not show peaks for the anomeric protons (protons protruding from the $\gamma$-CD ring) at around 5.5 ppm. This confirms absence of any remnant $\gamma$-CD or urea in the c-PVAc samples that could if at all affect their properties.
Figure 3.3: FTIR spectra for PVAc-γ-CD-IC (above) and DSC scans for PVAc-ICs (below)
Since PVAc is an amorphous polymer, it exhibits a glass transition temperature, which is found to be different [1] for asr- and c-PVAc samples (See Figure 3.5). The difference in their $T_g$s is substantial, and a possible explanation for this observation is due to the fact that c-PVAc maybe structurally more organized due presumably to its largely extended and un-entangled chain morphology [2]. It should also be mentioned that the mobilities of c-PVAc chains above $T_g$ are apparently restricted in comparison to those of asr-PVAc, as indicated by the observation that the $\Delta C_p(T_g)$ for asr-PVAc is higher than that observed for c-PVAc.
Figure 3.5: DSC Scans for asr-PVAc, c-PVAc from $\gamma$-CD and from urea

Table 3.1: Measured Densities for as-received and coalesced PVAc

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density at 25 °C (g/cm$^3$) (below $T_g$)</th>
<th>Density at 58 °C (g/cm$^3$) (above $T_g$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>asr-PVAc</td>
<td>1.093</td>
<td>1.040</td>
</tr>
<tr>
<td>c-PVAc ($\gamma$-CD)</td>
<td>1.156</td>
<td>1.077</td>
</tr>
<tr>
<td>c-PVAc (urea)</td>
<td>1.154</td>
<td>1.076</td>
</tr>
</tbody>
</table>
obtained from both γ-CD and urea. Table 3.1 summarizes the density measurements, where it is seen that PVAc coalesced from either γ-CD or urea is denser than asr-PVAc, both below and above their T_g's. This increase in density is likely also due to the more organized and closer packing of chains in c-PVAc, as suggested in Figure 3.2.

DSC observations (differences in T_g's and ΔC_p's at T_g) and density measurements suggest that there is some non-random organization of the polymer chains in c-PVAc, and this was further investigated by Dynamic Mechanical Thermal Analysis to translate these observations into terms of mechanical properties. The asr- and c-PVAc samples were subjected to a constant strain with increasing frequency (f) at a temperature (70 °C) much higher than their respective T_g's. This helps us to understand and compare the thermo-mechanical behavior of the asr- and c-PVAc samples at a higher processing temperature. At 70 °C, the polymers are more viscous than elastic and hence, their viscous moduli have been observed and reported as a function of varying frequency. When a polymer sample is subjected to varying frequency (at a constant temperature) its modulus changes as a function of the instantaneous frequency. At higher frequencies, which translate into shorter times, the polymer has less time to respond to the change in frequency. Thus, it exhibits a higher modulus as compared to its modulus at a lower frequency (longer time as t ~ 1/f), where the polymer chains have enough time to respond to the change in frequency (hence the trend in G” vs f). From the results in Figure 3.6, it is clear that c-PVAc has a higher viscous loss modulus G” than asr-PVAc even above their T_g's, which can be attributed to its higher density with more closely packed and because 70 °C – T_g ~ 30 for c-PVAc and ~40 °C for asr-PVAc.
Annealing of PVAc Samples

From DSC and density observations it is clear that c-PVAc is organized and behaves distinctly from asr-PVAc. As a consequence, we conducted annealing studies in order to estimate the time taken for c-PVAc to revert back from its presumed extended un-entangled chain morphology to the randomly-coiling entangled chain morphology of asr-PVAc (See Figure 3.2). The $T_g$s observed for asr-PVAc before and after annealing at 70 °C for 14 days were 29.1 and 29.4 °C, respectively, i.e., essentially the same. The $T_g$s observed for c-PVAc ($\gamma$-CD) after annealing at 70 °C for different times are presented in Table 3.2 (Also see figure 3.7). They remain around 41 °C, so c-PVAc chains apparently remain largely extended and
un-entangled even after annealing above their $T_g$, without apparently returning to entangled random coils as in asr-PVAc.

**Table 3.2: $T_g$s of c-PVAc from its $\gamma$-CD-IC annealed at 70\(^{\circ}\)C for different time periods**

<table>
<thead>
<tr>
<th>Annealing time (days)</th>
<th>$T_g$ ((^{\circ})C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>41.5</td>
</tr>
<tr>
<td>2</td>
<td>41.7</td>
</tr>
<tr>
<td>8</td>
<td>41.5</td>
</tr>
<tr>
<td>14</td>
<td>41.2</td>
</tr>
</tbody>
</table>

It should also be noted that single concentration (0.2g/dL) flow times for asr- and c-PVAc measured in dioxane before and after annealing were both ~ 400 seconds, suggesting that long-time annealing above $T_g$ (70\(^{\circ}\)C) has not caused any PVAc degradation.

Figure 3.8 presents the DSC results for a 50/50 asr-PVAC/c-PVAC ($\gamma$-CD) mixture before and after long-time annealing above $T_g$ at 70 \(^{\circ}\)C. Note that the initial heating scan reveals distinct $T_g$s for asr- and c-PVAc, as expected for their physical mixture. However, after annealing for 14 days, apparently the 50/50 asr-PVAC/c-PVAC mixture is now a well-mixed blend, because a single $T_g$ between those of asr-PVAc (29 \(^{\circ}\)C) and c-PVAc (41 \(^{\circ}\)C), but much closer to that of c-PVAc, is observed around 38 \(^{\circ}\)C. After four weeks of annealing
at 70 °C, the 50/50 asr-PVAc/c-PVAc blend has a $T_g$ (DSC not shown) and density (Table 3.3) nearly identical to that of neat c-PVAc($\gamma$-CD). The observation of a single $T_g$ for the 50/50 asr-PVAc/c-PVAc($\gamma$-CD) physical mixture annealed a long time above their $T_g$s into a well-mixed blend is not surprising. However, the observation that the single $T_g$ observed for their apparently well-mixed blend is close to that of c-PVAc, rather than asr-PVAc, is surprising. In other words, the blend is likely not characterized by completely entangled randomly-coiling PVAc chains, but rather by an organization of PVAc chains more similar to that of the initially coalesced neat c-PVAc($\gamma$-CD) (See Figure 3.2).

Figure 3.7: c-PVAc from U-IC annealed for different time periods
Figure 3.8: DSC scans of an initial 50/50 physical mixture of asr-PVAc/c-PVAc before (top) and after (bottom) annealing for 14 days at 70 °C.
Rastogi et al. [12] recently observed that slow and carefully controlled melting of ultra-high molecular weight, metallocene catalyzed, single-chain crystalline polyethylenes (UHMW-PEs), as illustrated by the drawing at the left in Figure 3.9, can produce heterogeneous melts, with more and less entangled regions. They observed that it took more than a day of heating at 180 °C to produce a fully entangled melt of randomly-coiling PE chains. On the other hand, melts of those polymers initially coalesced from their CD-IC crystals, such as those reported here for c-PVAc, with presumably extended and largely un-entangled chains, apparently take much longer to return to their randomly-coiling entangled melt state.

Table 3.3: Densities of asr-PVAc, c-PVAc (γ-CD), and their 50/50 blend after annealing at 70° C for 4 weeks

<table>
<thead>
<tr>
<th></th>
<th>Density (g/cm³) at 58 °C (above T_g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>asr-PVAc</td>
<td>1.044</td>
</tr>
<tr>
<td>c-PVAc</td>
<td>1.077</td>
</tr>
<tr>
<td>Blend</td>
<td>1.076</td>
</tr>
</tbody>
</table>

*T_g of asr-PVAc film is ~29° C and for the c-PVAc(γ-CD) and the 50/50 blend films are both ~41° C.
Quoting Rastogi et al. “...crystals composed of single chains are feasible, where the chains are fully separated from each other. If such separation can be maintained in the melt a new melt state can be formed. Here we show that through slow and carefully controlled melting such polymer crystals form a heterogeneous melt with more entangled regions, where the chains are mixed, and less entangled ones, composed of individually separated chains. Chain reptation, required for the homogenization of the entanglement distribution, is found to be considerably hindered. The long-lived heterogeneous melt shows decreased melt viscosity and provides enhanced drawability on crystallization.”

Figure 3.9: Idealized comparison of regularly-folded single-chain lamellar crystals (left), irregularly-folded multi-chain “switchboard” lamellar crystals (center), and “fringed-micelle” semi-crystalline morphology (right)

In contrast, the usual morphology of semi-crystalline polymers with intimately mixed chains, as illustrated by the central drawing in Figure 3.9, is rapidly converted upon heating into a homo-geneous entangled melt of randomly-coiling chains. Chain reptation is required
to produce homogeneous melts from both semi-crystalline morphologies. However, in the case of the slow heating of metallocene-catalyzed UHMW-PE nascent single-chain crystals, the initial rapid entanglements formed between portions of PE chains melting and detaching from the ends of different single-crystals serve to retard the further entanglement of the central portions of the PE chains, leading to a heterogeneous melt whose ultimate homogenization is thus retarded.

More recently, McLeish [13] has suggested “In the case of these heterogeneous melts, however, chains leaving and entering the original ‘‘cells’’ (single-crystal interiors) must result in strong elastic deformations of the entangled material of the cell walls (detached chain-ends). This will result in a free-energy barrier to chain motion. …. single-chain (non-cooperative) reptation may be strongly suppressed by elastic deformation of the partitioning regions (initially detached and entangled chain-ends, see Figure 3.10).”

Assuming the morphology of polymers initially coalesced from their CD-IC crystals resembles that of the right hand drawing in Figure 3.9, but without tie-chains connecting the randomly arranged regions of extended and un-entangled chains, can we (or you) suggest why its transformation to a randomly-coiling entangled melt takes so long?

It seems likely that the chain-ends emerging from each individually coalesced sample region, resulting from the individual polymer-CD-IC crystals from which they were coalesced, should be able to rapidly entangle. Once this occurs, however, it would appear difficult to entangle the central portions of the essentially parallel and extended coalesced chains, as in the case of the heterogeneous melts produced from nascent UHMW-PE single-chain crystalline samples. Then why does it take so much longer for the melt of an initially
coalesced polymer to become fully randomly-coiled and entangled, even though their chains are more than an order of magnitude shorter than those of the UHMW-PEs?

Figure 3.10: McLeish [13] model for the heterogeneous melt structure produced by the slow heating low-temperature melting of the outer portions of the original single-chain UHMW-PE crystals (left) to form entangled normal melt regions. These partition the remaining crystal cores into “cells” (right). On further melting, the inner regions of these cells contain un-entangled melt.

The reason may have its basis in the topological distinction(s) between their initial semi-crystalline and/or as-coalesced morphologies, as indicated in the right and left hand drawings in Figures 3.9 and 3.10. As the nascent single-chain UHME-PE crystals melt by detachment from the ends of the single crystals and their chain-ends entangle, the un-entangled central portion of each PE chain remains more mobile [12], though their reptative motion is restricted by the entanglement of their previously detached chain-ends. In addition to a
reptation hindered by entanglement of their chain-ends, the un-entangled central chain portions in the coalesced polymer melt are initially more extended and closely packed with a density higher than that of its homogeneous melt. This likely reduces their mobility and may lead to a significant enhancement of the elastic strain placed on the already entangled chain-ends, thereby further retarding their full entanglement.

The distinctions between the inter-chain packing densities and mobilities of the initially un-entangled chain portions of coalesced polymers and those of the un-entangled and mobile central portions of UHMW-PE chains individually detached from their single-chain crystals may account for the increased sluggishness of the transition to a fully entangled randomly-coiled melt exhibited by polymers coalesced from their CD-ICs.

3.5 Acknowledgements

We are grateful to the College of Textiles at North Carolina State University for their financial support. We would also like to thank Dr. Russell Gorga for his valuable help with DMTA measurements.

3.6 References

CHAPTER 4

4. Improving the Behavior and Properties of Poly (ethylene terephthalate) (PET) Through Self-Nucleation

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Citation: Macromolecular Materials and Engineering, 298, 1190–1200 (2013)

4.1 Abstract

Bulk as-received poly (ethylene terephthalate) (asr-PET) has been observed to reorganize both morphologically and conformationally, either by formation of a crystalline inclusion compound (IC) between guest PET and host $\gamma$-cyclodextrin ($\gamma$-CD), followed by removal of the host $\gamma$-CD and coalescence of the guest PET (c-PET), or by precipitation (p-PET) from its solution in trifluoroacetic acid upon gradual addition to a large excess of rapidly stirred acetone. c-PET and p-PET show very similar behaviors, but p-PET can be more easily produced in larger quantities. DSC and density observations of p-PET imply structures/morphologies and chain conformations and packing in the non-crystalline sample regions different from those of asr-PET obtained by standard processing techniques. In comparison to slowly crystallizing/easily melt-quenched asr-PET, p-PET repeatedly crystallizes rapidly from the melt. Upon subsequent heating, its non-crystalline domains do
not show a glass transition or undergo crystallization, but only a melting endotherm that is virtually identical in magnitude to the crystallization exotherm observed during its prior rapid cooling from the melt. These observations suggest that p-PET readily attains higher crystallinity even when repeatedly cooled rapidly from the melt. Apparently the extended conformations of largely un-entangled chains in p-PET do not become coiled and entangled even after spending substantial time in the melt.

As a consequence, we have demonstrated that p-PET can be used in small quantities (a few %) as an effective self-nucleating agent to control the bulk semi-crystalline morphology of melt-processed asr-PET, and the resulting properties of nucleated PET (nuc-PET) have been assessed. For instance, comparison of asr- and nuc-PET films, each with ~10% crystallinity, reveal that the nuc-PET film has significantly increased hardness and Young’s modulus and is also much less permeable to CO₂ than the asr-PET film. Undrawn nuc-PET fibers also exhibited significantly higher tenacities and moduli than undrawn asr-PET fibers. Self-nucleated PET not only possesses improved properties, but contains no incompatible additives, and so may be readily recycled.

![Figure 4.0: Table of Contents (TOC) Figure](image-url)
4.2 Introduction

PET is a semi-crystalline polymer composed of crystalline and amorphous regions, and is a versatile engineering plastic material with excellent thermal and chemical resistance and mechanical performance. PET has been studied extensively due to its commercial importance and chemically flexible nature [1]. PET is extensively used in fiber form for apparel, as film for packaging, in bottles for beverages, and is also molded into engineering components. Because of its high melting ($T_m \sim 250 \, ^\circ C$) and glass transition temperatures ($T_g \sim 80 \, ^\circ C$), PET retains its good mechanical properties at temperatures up to 175-180 $^\circ C$. With regard to this last statement, it should be noted that it applies only if the PET materials have been annealed above $T_g$ to achieve their maximum crystallinity.

Because PET is a slow crystallizing polymer with a $T_g$ above room temperature, its crystallinity can be easily varied from nearly completely amorphous to fairly crystalline. It can be highly transparent and colorless, but thicker samples are usually opaque and off white. PET is a hard, stiff, strong, dimensionally stable material that absorbs very little water. It has good gas barrier properties and has good chemical resistance except to alkalis, which hydrolyze it [2].

The main aim of this research is to improve the properties of PET by using a simple precipitation method [3,4]. We are trying to generate a PET with novel morphologies and unique properties that will be easy to process with retention of all desirable qualities. The initial motivation for this research was the improvement in the properties of PET observed by processing the polymer with cyclodextrins [3-5]. We have previously observed [6] that when polymers are made to form inclusion compounds (ICs) with cyclodextrins (CDs), and are
then coalesced by removing the CD hosts, the resulting CD-processed polymers are found to behave differently than the as-received polymers, and this is particularly striking for PET (See Figures 4.1 and 4.2).

![Figure 4.1: Schematic representation of α-, β-, γ-cyclodextrins](image)

As described previously, γ-CDs are capable of forming an inclusion compound with PET. [3] Modeling of PET conformations able to thread through CDs suggested that the gauche±trans gauche+ ethylene glycol conformations illustrated in Figure 3 have a narrower cross section than the all trans crystalline PET conformation also illustrated there [7]. Analyses of the FTIR [3] and solid-state $^{13}$C-NMR [5] spectra of PET coalesced from its γ-CD-IC (c-
PET) are consistent with the narrower gauche± trans gauche± conformations for the non-crystalline portions of the coalesced sample. Unlike normal as-received PET (asr-PET), c-PET was observed to be repeatedly rapidly crystallizable from its melt. During the course of forming the PET-γ-CD-IC, [3] several control experiments were conducted. It was observed that PET rapidly precipitated (p-PET) from a trifluoroacetic acid/chloroform solution upon slow addition to rapidly stirred acetone (See Supplementary Material) evidenced behavior closely similar to that of c-PET [4,5].

![Figure 4.2: Formation of and coalescence from polymer-cyclodextrin inclusion complexes](image)

Based on the ability of p-PET to repeatedly rapidly crystallize from its melt, here we describe its use to nucleate the melt-crystallization of asr-PET. By controlling the melt-crystallization and resultant semi-crystalline morphology of PET in this manner we hoped to
achieve significant improvements in the material properties of PET. As described below, this hope was indeed successfully realized.

![Figure 4.3: Crystalline all trans (t) [top] and γ-CD-included g±tg \(\overline{\gamma}\) (bottom) conformations of PET](image)

4.3 Experimental Section

Materials

Virgin Poly (ethylene terephthalate) (Mₜ ~ 18,000, asr-PET) and 30% Glass Reinforced PET (GR PET), trifluoro acetic acid (TFA), acetone, and talc were obtained from Sigma-Aldrich, while gamma cyclodextrin (γ-CD) was obtained from Cerestar (Hammond, IN).

Methods

PET Precipitation and Nucleation

PET was structurally modified by the precipitation technique indicated schematically in the Supplementary Material. About 3g of asr-PET were dissolved in 50 ml of TFA, and the
polymer solution was heated to 50 °C with rapid stirring until the polymer completely dissolved (approximately 30 minutes). Then the heated polymer solution was gradually added drop wise to 150 ml of acetone in a 400ml beaker, while the mixture was stirred at a high rate (~600 rpm). A white precipitate of the polymer (p-PET) was obtained at the end of the addition of the PET/TFA solution, and was then washed with acetone, filtered under vacuum, and dried in a vacuum oven overnight at 40 °C to obtain dry p-PET. Flow times measured for 0.2 g/dL TFA solutions of asr- and p-PETs in a Fenske viscometer were closely similar, suggesting that the precipitation process did not cause any serious PET degradation. Finally, both asr-PET and p-PET were characterized for their resultant behaviors.

Asr-PET was nucleated with p-PET by a solvent casting method. In this technique asr-PET was initially dissolved in TFA. Then 5% p-PET (weight basis with respect to asr-PET) was added to the solution after about two thirds of the solvent had been evaporated. It was observed that p-PET did not dissolve in this concentrated polymer solution. A film of nucleated PET (nuc-PET) was obtained after complete solvent evaporation. To observe and evaluate the nucleating ability of p-PET with respect to traditional nucleating agents, asr-PET was also nucleated with 5% γ-CD (bio-nucleating agent), 5% talc (traditional nucleating agent) and PET with 30% glass reinforcement (GR PET). The percentage crystallinity in each case was calculated from their respective DSC thermograms, and the nucleation ability of each nucleating agent was evaluated by comparison to the percentage crystallinity in the un-nucleated polymers.
**Film Preparation**

PET films were prepared by a melt pressing method. The polymer was heated to 260 °C in a Carver Melt Press and a pressure of 1000 psi was applied as soon as the polymer was completely molten. Holding time for the polymer in its molten state depended on its geometry (pellets/flakes). Once the film was pressed, it was immediately quenched into ice water in order to minimize crystallization; thus, maintaining the same level of crystallinity (~10%) in both asr-PET and self-nucleated nuc-PET samples, which was confirmed by DSC. Both PET films were ~100 μm thick, as determined with a hand-held digital Vernier caliper.

**Fourier Transform Infrared (FTIR) Spectroscopy**

Infrared spectral studies were conducted with a Nicolet Nexus 470 FTIR spectrometer in the range 4000 - 400 cm⁻¹, with a resolution of 4 cm⁻¹ and 64 scans were collected for each sample. FTIR data were analyzed by using Omnic software.

**Differential Scanning Calorimetry (DSC)**

DSC thermograms for all PET samples were obtained using a Perkin-Elmer Model 7 Differential Scanning Calorimeter. 3-5 mg samples were sealed in aluminum pans. Depending on the sample geometry (pellet or powder/flakes), either a volatile or non-volatile pan was used for sampling. The instrument was calibrated before each set of scans with Indium or Tin, depending on the temperature range of interest. Nitrogen was used as the purge gas to provide an inert atmosphere and to prevent sample degradation. The procedure that was employed for DSC scanning of all the PET samples was as follows:
- Hold at 25 °C for 1 minute
- Heat from 25 to 280 °C at 20 °C/minute
- Hold the in the melt for 10 minutes
- Cool from 280 to 25 °C at 50 °C/minute
- Hold at 25 °C for 1 minute
- Heat from 25 to 280 °C at 20 °C/minute

All DSC thermograms were analyzed using Pyris software for quantitative evaluation of glass transition, crystallization, and melting temperatures and their associated heat capacities and enthalpies.

**X-ray Diffraction**

Wide-angle X-ray diffraction (WAXD) of powdered samples were performed with a Siemens type-F X-ray diffractometer, using a Ni-filtered Cu K_α radiation source (λ = 1.54 Å). Diffraction intensities were measured every 0.1° from 2θ = 5 to 30°.

**Polarized Optical Microscopy (POM)**

Polarized Optical Microscopy (POM) was used to observe the crystal size and distribution in the quenched PET films. This technique involves observation of the sample with polarized light, so that the resultant magnified image is visible to the human eye. Micrographs of asr- and p-PET films were obtained using a Nikon Eclipse 50i POL Optical Microscope at 100x zoom and the images were captured by a CCID-IRIS/RGB color video camera made by Sony Corp.
Density Measurements

The densities of asr- and nuc-PET films were measured by floatation using toluene (T) and carbon tetrachloride (CT) solvents, which have densities of 0.8668 and 1.594 g/cm³, respectively, that are lower and higher than the density of PET. Small pieces of both asr- and p-PET films were placed in a known volume of carbon tetrachloride, vol(CT), containing a magnetic stir-bar, where they floated, and sealed with aluminum foil. The toluene solvent was slowly added from a burette with stirring until each PET film sank and became suspended in the solvent mixture, and the volume of added toluene, vol(T), was noted. The PET densities were then obtained from:

$$\rho_{exp} = \frac{\text{vol}(T)\times \rho(T) + \text{vol}(CT)\times \rho(CT)}{\text{vol}(T) + \text{vol}(CT)}$$

CO₂ Permeability of PET Films

CO₂ sorption measurements were performed with an ISOSORP®GAS High Pressure Gravimetric Analyzer with an attached Rubotherm Magnetic Suspension Balance assembly. The most important part of this equipment is the magnetic suspension balance, which facilitates accurate weight measurement of the samples. The instrument broadly consists of the Rubotherm magnetic suspension balance connected to the gas tank and vacuum system through a series of valves. The instrument is operated using the MesPro software, which enabled us to perform blank runs and collection of actual gas permeability data. A simple
schematic diagram for the Rubotherm magnetic suspension balance is presented in the Supplementary Material.

V-shaped film samples were placed in the sample basket, which is mounted on a hook connected to the suspension balance. The sample cell was then closed, the gas line connected to the Helium tank, and a vacuum pulled through the system for about 6 hours. After this period, a blank run was performed using Helium gas to accurately measure the mass and volume of the sample. The gas line was then connected to the CO₂ tank and the assembly was subjected to vacuum for another 6 hours. A CO₂ run was then performed on the sample at approximately 21 °C and at a pressure of 2 bars (i.e. 0.2 MPa), and a mass difference curve as a function of time was obtained. A blank run was also performed on the empty basket in order to accurately determine its mass. MesPro software was used to control the blank and CO₂ runs.

**Nano-Indentation**

Nano-Indentation is a non-destructive technique for measuring the mechanical properties of polymeric surfaces. It makes use of a probe, or an indenter, whose mechanical properties are known. The test mode employed was quasi-static in order to measure the hardness and Young’s modulus of the films [8,9].

Nano-Indentation was performed on the PET samples using a Hysitron TriboIndenter instrument and the data were analyzed with the TriboScan software. All tests were performed at ambient temperature (approximately 25 °C). Each of the sample films was indented 7 times in a square pattern using a Berkovich diamond tip and this test was repeated 5 times.
The samples were tested in constant force mode, where a known force is applied on the surface of the film using the indenter and the resultant displacement is calculated in nanometers. Reduced Young’s modulus and hardness values were all determined automatically by the software. The software helps in the automatic scanning of the surface of the film by adjusting the tip height based on the force feedback and mapping of the film surface topography.

Formation and Physical Testing of asr-and nuc-PET Fibers

Undrawn PET fibers were prepared by melt-spinning from an Atlas Lab Mixing Extruder (Model # LME 1). The set point temperature for the header and rotor was 255 °C. The melt-spun undrawn fibers were collected on a rotating Dayton Collector. Optical Microscope images were captured to detect any defects in the fibers.

An Instron Tensile Strength tester was used to analyze the tensile properties of the undrawn PET fibers, using the ASTM D2256 standard for fibers with a sample size of 10 fibers. All samples were tested at 20 °C and 65 % RH. Sample and test specifications include a gauge length of 1 inch, with a 5 lb. load cell and a cross head speed of 90 mm/min. The fibers were gripped with masking tape at their ends in order to avoid filament slippage. Modulus and tenacity values were directly calculated by the software.
4.4 Results and Discussion

FTIR

Though not presented here, the FTIR spectra of asr- and p-PETs are similar except for greater resolution in the p-PET spectrum [4] (See Supplementary Material). Improved resolution was also seen for c-PET [3] and attributed to its high crystallinity and non-crystalline regions consisting of chains pre-dominantly in the gauche± trans gauche± conformations (See Figure 3), which guest PET chains in the channels of its precursor γ-CD-IC crystals are believed to adopt [3-5,7]. PET cast from TFA/chloroform solution exhibited an FTIR spectrum closely similar to that of asr-PET [3].

As noted previously [3], FTIR has indicated a high concentration of gauche and trans bond conformations in coalesced (from its γ-CD-IC) and solution-cast PET samples, respectively. Because the coalesced PET sample was more crystalline than the solution-cast sample of PET, the higher concentration of trans bond conformations in the latter sample did not reflect the conformational character of the -CH2—CH2- bond alone, but was instead mainly due to the concentration of trans -O—CH2- and -CH2—O- bond conformers, which is higher in the solution-cast PET and lower in the coalesced sample. Solid-state 13C-NMR also confirmed that the -CH2—CH2- bonds in c- and p-PETs were predominantly trans, including those in their non-crystalline regions, [5] consistent with expectations [7] of the conformations of PET chains in the non-crystalline portions of these samples. As a result, it was proposed there that the conformationally sensitive vibrational bands observed in PET be reinterpreted to reflect primarily the conformations of -O—CH2- and -CH2—O- bonds and not that of the -CH2—CH2- bonds in the ethylene glycol unit.
Thermal Behavior of As-received-, Precipitated-, and Self-nucleated-PETs

Figures 4-6 present the first-cooling and second-heating DSC scans for asr-, p-, and nuc-PETs that were observed at -50 and 20 °C/min, respectively. It is clear that asr-PET is barely able to develop any crystallinity upon cooling from the melt, and becomes semi-crystalline largely during the subsequent heating above its glass-transition. Though the DSC scans presented in Figure 4 for asr-PET are those of the untreated PET pellets, virtually identical scans are obtained for asr-PET samples cast from TFA solution. Thus, after 10 minutes in the melt, both untreated and solvent-cast asr-PET melts crystallize similarly, indicating their different prior processing histories have been fully erased.

Because untreated and TFA-cast PETs behave similarly (dilute solution viscosities, FTIR, 1st-cooling 2nd-heating DSC scans), we conclude that quiescent TFA processing has neither degraded nor produced nucleants in PET, and the PET cast from TFA produces a closely similar slow crystallizing melt like untreated asr-PET.

![Figure 4.4: 1st cooling and 2nd heating DSC scans for asr-PET](image)

Figure 4.4: 1st cooling and 2nd heating DSC scans for asr-PET
Figure 4.5: 1\textsuperscript{st} cooling and 2\textsuperscript{nd} heating DSC scans for p-PET.

Figure 4.6: 1\textsuperscript{st} cooling and 2\textsuperscript{nd} heating DSC scans for Self-Nucleated PET (95% as-PET/5% p-PET).

In marked contrast, p- and nuc-PETs develop their final full level of crystallinity during cooling from their melts. Precipitation and self-nucleation of PET has rendered the slow
crystallizing asr-PET into a rapid crystallizer (nuc-PET), with a rate roughly three orders of magnitude greater than the asr-PET melt [5]. It should be noted that heating at 10° C/min and cooling at various rates faster and slower than the -50° C/min rate used here produced similar results [3,5].

Though not shown here, the DSC scans of p- and nuc-PET remain unchanged by repeated cycling between their melts and semi-crystalline solids [3,4]. As a consequence, p- and nuc-PETs should now be able to retain their mechanical properties at temperatures approaching T_m, because they are able to develop their full semi-crystalline morphologies upon cooling from their melts. Similar behavior has been observed [8-13] for poly (ε-caprolactone), nylon-6, and poly (L-lactic acid) samples self-nucleated with small amounts of the identical polymers coalesced from their CD-ICs.

We have previously suggested [3-5] that the chains of c- and p-PETs in their non-crystalline regions largely adopt the extended gauche± trans gauche⁻ conformation, with trans –CH2 – CH2 – bonds, as in their crystals. Normally in the melt, the -CH2–CH2- bond is predominantly gauche±, [14,15] and so must rotate to trans during crystallization. This conformational transition is not possible without sweeping out a large volume. On the other hand, crystallization of c- or p-PETs into the all-trans conformation proceeds rapidly from preponderantly gauche± -O–CH2-, trans -CH2–CH2- and gauche⁻ -CH2–O- bond conformers through facile counter rotations about the -O–CH2- and -CH2–O- bonds, requiring only a very modest amount of swept-out volume [3,7]. Thus, it may not be surprising that asr-PET crystallizes slowly from its melt, while c- and p-PETS crystallize rapidly.
It should be noted that when only 2 wt% p-PET is added to asr-PET this nuc-PET shows DSC behavior similar to that seen in Figure 6 for asr-PET nucleated with 5 wt% p-PET. The only difference is the observation of a glass-transition in both the cooling and subsequent heating scans.

When we mix a small amount of p-PET with asr-PET and subject the polymer mixture to melting conditions, asr-PET loses its processing history and goes back to random coil configurations, whereas presumably p-PET retains its largely unentangled extended chain conformations, as suggested in Figure 2. On cooling this mixture from its melt at a rate where asr-PET hardly crystallizes, p-PET rapidly crystallizes and the domains where p-PET is present in the mixture crystallize first and provides nucleation sites. These active sites shorten the induction time and enhance the rate of crystallization from the molten phase. They also lower the free energy barrier for stable nucleus formation and initiate simultaneous growth of spherulites. Formation of these nucleation sites can be referred to as primary crystallization, which is followed by secondary crystallization, wherein crystal growth is propagated from these nucleation sites, resulting in a finer-scale more uniform semi-crystalline morphology.

P-PET is clearly an effective nucleating agent for the melt-crystallization of asr-PET, and it is important to compare its nucleating ability with some of the common nucleating agents. For this purpose asr-PET was nucleated with γ-CD, talc, and glass particles, and their resultant DSC behaviors were observed. These nucleating agents are incompatible with a PET melt and so are insoluble and phase separated in the melt. Because they remain solid above the T_m of PET, they necessarily follow a heterogeneous mode of nucleation, unlike p-
PET, which melts and induces homogeneous nucleation. Though their DSC scans are not presented here, it can be said that only talc appeared to effectively nucleate asr-PET, and it is likely that the very fine nature of its powder contributed to its effectiveness [16], even though it is a heterogeneous nucleating agent.

**Polarized Optical Microscopy**

Polarized optical microscopy images were obtained for asr- and nuc-PET films in order to observe the crystal size and distribution. The polarized optical microscope enables us to view magnified images of the PET films under polarized light and the images can be seen in the Supplementary Material. Because each film sample has little overall crystallinity (~10%), overall few crystallites/spherullites were observed. However, the nuc-PET film evidenced more and smaller crystallites.

**Densities and CO₂ permeability in PET films**

The quenched asr- and nuc-PET films are clear in appearance. DSC scans of the two films are not shown here, but indicate that both PET films have the same level of crystallinity (~10%). The higher density of the nuc-PET film (~ 1.3% higher, Table 1) with the same low level of crystallinity as in the asr-PET film can likely be attributed to the higher orientation and increased order and packing of chains in its predominant amorphous domains, which is seen even after the polymer film was quenched from the melt into ice water. This shows that nuc-PET has a tendency to organize differently than asr-PET, even when melt quenched at very high cooling rates. These density results are consistent with those obtained in reference
4, where the densities of asr-PET annealed at 100 °C to achieve ~40% crystallinity and p-PET with a similar crystallinity were similarly measured. The density of p-PET was found to be higher than that of the annealed asr-PET, consistent with a higher density for the non-crystalline regions in the p-PET sample.

Table 4.1: Density measurements and CO₂ (0.2MPa) permeability in PET films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density at 25°C (g/cm³)</th>
<th>Permeability (P x 10¹⁴) (cm².s⁻¹.Pa⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>asr-PET</td>
<td>1.368</td>
<td>1.64</td>
</tr>
<tr>
<td>nuc-PET</td>
<td>1.386</td>
<td>0.57</td>
</tr>
</tbody>
</table>

This improvement in the chain packing also has an effect on the gas barrier properties of PET. Impermeability to gases is generally a critical requirement for polymers used as packaging materials. The coefficient of permeability (P) is related to the diffusivity (D) and the solubility (S) of gases in the polymer under study (P = S×D). Diffusivity is associated with the movement of the gas molecules through the cross section of the polymeric film, while solubility corresponds to the amount of gas that gets dissolved in the polymer. During the packaging process, the pressure of the gas is usually different than under ambient conditions, so it is important to study the effect of the working pressure on the permeability
of the packaging material. Table 1 summarizes the density and gas permeability results, while Figure 7 provides the curves of CO₂ absorption in PET films.

Figure 4.7: CO₂ absorption curves for asr-PET (upper) and nuc-PET (lower)
Under ambient conditions, CO₂ permeability is low in most polymers. However, when they are processed at higher pressures their permeability becomes critical, particularly for polymers used in packaging of carbonated beverages, where they are subjected to pressurized CO₂. Gas barrier properties of polymers are related to their morphologies. They are influenced by the level of crystallinity, available free volume, and sizes and alignment of the amorphous domains in the polymeric material.

Since the asr- and p-PET samples have the same low level of crystallinity (~10%), their resultant gas permeabilities are largely dependent on the polymer chain alignment and packing in their non-crystalline regions. Absorption of gases in polymers is usually related to the free volume available for the gas to be absorbed in, while diffusivity is dependent on the crystallinity and chain orientation in the amorphous domains. For our PET films it is clear that CO₂ permeability values are much higher for asr-PET than for nuc-PET. Nuc-PET has a much lower CO₂ solubility and only marginally lower diffusivity, possibly due to aligned and more densely packed chains in the amorphous regions that provides a much greater barrier (~3 times that of asr-PET) to permeation of CO₂ molecules through the film.

This is in agreement with the expectation that processing PET via self-nucleation has brought about changes from the usual random coiling entangled structure to a largely unentangled extended-chain morphology (See Figure 2). The gas barrier results are consistent with the density observations, which show that the PET chains in the self-nucleated sample are more densely packed than those in asr-PET.

Though we have little direct structural evidence for the unentangled and extended arrangement of polymer chains in coalesced or p-PETs drawn in Figure 2 (See the next
Section below), we have recently discussed this issue [8,9,12,13] and the observations which support it. These include their abilities to melt-crystallize more readily, with higher $T_c$s, over a narrower temperature range, sometimes in unusual polymorphs, and apparently without chain-folding; their elevated $T_g$s; amorphous regions that are more dense; the much lower zero shear viscosities of their melts; production of stronger, less extensible films and fibers; and they are less permeable to gases (CO$_2$). In addition, these unique behaviors remain, even after extensive periods (weeks) spent in their melts, and are independent of their molecular weights and their IC hosts (CD or urea).

**X-ray Diffraction from Amorphous PET Films**

Figure 8 shows the WAXS observed from asr- and p-PET films that were melt-pressed and rapidly quenched into liquid N$_2$. Their first heating DSC scans indicated less than ~10% crystallinity for both PET films. Though both appear to be predominantly amorphous, the scattering envelope from the p-PET film is shifted slightly to larger angles/shorter spacings from the asr-PET scattering envelope. This is reminiscent [17] of the 0.45Å displacement observed for undrawn PET fibers when compared to an isotropic amorphous PET sample in the equatorial WAXS scans reported by Lindner [17]. A closer spacing more dense packing of chains in the p-PET sample is suggested, which is consistent with our density and permeability measurements.

It should be noted that the un-smoothed X-ray diffractograms show a similar small displacement to larger angles/shorter spacings for the p-PET film in comparison to the asr-PET film.
Nano-Indentation of PET Films

Nano-Indentation provides a quantitative technique to evaluate near surface mechanical properties of thin films aided by its depth sensing capability. This is accomplished with the help of a diamond indenter with a well defined tip [18]. The instrument when operated in a quasi-static mode helps us in evaluating the hardness and Young’s modulus of films. Plots of Young’s modulus and Hardness as a function of the applied load may be seen in the Supplementary Material. The software calculates the reduced young’s modulus and the hardness values. The following equation is used to calculate the actual Young’s modulus from the reduced Young’s modulus data obtained from the software,
Where,

\[ \frac{1}{E_r} = \frac{(1-\nu_i^2)}{E_i} + \frac{(1-\nu_s^2)}{E_s} \]

\( E_r \) – Reduced Young’s Modulus (GPa)

\( E_i \) – Elastic Modulus of the Diamond Indenter (GPa)

\( E_s \) – Young’s Modulus of PET Sample (GPa)

\( \nu_i \) – Poissons Ratio for Diamond Indenter

\( \nu_s \) – Poissons Ratio for PET Sample

The elastic modulus and poisons ratio for the diamond indenter are 1140 GPa and 0.07 respectively, [19] while the poisons ratio for the largely amorphous asr-PET film is 0.37 [20]. The hardness and Young’s modulus obtained for the asr-PET film are comparable to those mentioned in the literature [21]. On the other hand, nuc-PET film showed both a significantly higher hardness and stiffness. The load bearing capacity of nuc-PET is likely higher on account of better alignment of its polymer chains in the predominant amorphous regions, resulting in their closer packing to a higher density.

**Formation and Tensile Testing of PET Fibers**

One of the major applications of PET is in its fiber form. The optical microscope image of undrawn melt-spun asr-PET fiber presented in the Supplementary material does not evidence any defects, like the presence of air bubbles that could affect the tensile results. Typical specific stress - % elongation curves for asr- and nuc-PET fibers are displayed in Figure 9.
They show an initial linear region, where the load on the fiber is proportional to its elongation. This is followed by limited yielding and finally breaking of the fibers.

![Force/Elongation Diagram](image)

**Figure 4.9: Load-Elongation curves for asr- and nuc-PET Fibers.**

The modulus and tenacity of fibers are the two aspects most critical to their performance. Modulus is nothing but the stiffness of the fiber, while tenacity can be defined as the specific stress experienced by the fiber at break. The tenacity of asr-PET fibers (~0.4 gf/denier) is comparable to that of undrawn PET fibers found in the literature. Also it has been previously reported that the tenacity of undrawn PET fibers is usually less than 10% of that of drawn PET fibers [22]. Figure 10 presents the modulus and tenacity results for asr- and nuc-PET fibers.
The tensile results for asr- and nuc-PET fibers are statistically significant and indicate substantial improvement in the tensile properties of nuc-PET. In their undrawn state, the
average modulus for nuc-PET fibers is ~31% more than that of asr-PET fibers, while the
tenacity of nuc-PET is ~29% higher than that of asr-PET. It should be noted that the
improved strengths of nuc-PET fibers is not due to a higher level of crystallinity. DSC scans
of asr- and nuc-PET fibers reveal similar crystallinities (~12%) for both. This suggests that
the self-nucleation process has resulted in the formation of stronger fibers, which could very
well replace asr-PET fibers in many applications.

Repeated Self-Nucleation

Small quantities of p-PET have been demonstrated to act as self-nucleating agents
(see Figures 4-6). When we added 5% of nuc-PET to 95% of asr-PET and observed its
thermal behavior by DSC, it was also observed to behave like a fast crystallizing polymer,
wherein its crystallinity was completely developed during the rapid cooling cycle. Figure 11
illustrates such repeated self-nucleations.

This behavior can be attributed to the fact that nuc-PET crystallizes rapidly at a higher
temperature than asr-PET. Like p-PET, when added to asr-PET it can control the resulting
semi-crystalline morphology. The amount of p-PET actually present in the repeatedly
nucleated PET is only ~0.25 wt%. This demonstrates the small amount of p-PET needed for
self-nucleation, making its use more efficient and economically and industrially viable.

4.5 Summary and Conclusions

The structure and morphology of asr-PET samples have been successfully modified via
the precipitation of PET and its use as a self-nucleant for the melt-crystallization of asr-PET.
The resultant materials have been demonstrated to be distinct from the usual melt-processed asr-PET samples. DSC observations clearly demonstrate that p-PET has a distinct thermal behavior in comparison to asr-PET. Furthermore, it does not revert back to random-coiled entangled chain configurations even after repeated melt processing, where it spends substantial time in the melt, and, so, can be successfully used in small quantities as an effective self-nucleating agent.

Figure 4.11: Repeated Self-Nucleation.

In addition to different levels of crystallinity, our results indicate that there exists a difference in the structural organizations of the non-crystalline portions of asr- and nuc-PET.
Spectroscopic and viscometric observations indicate that these organizational differences are physical in nature and not the result of degradation or cross-linking occurring during the precipitation and nucleation processes. Density measurements confirm the non-crystalline portions of nuc-PET are denser than the amorphous regions of asr-PET. This is likely because the polymer chains in the amorphous regions of the asr-PET are completely disordered (randomly-coiled and entangled), while in nuc-PET they appear to be at least somewhat extended and less randomly-coiled and entangled.

As a result, nuc-PET has been shown to possess better mechanical, thermal, and gas barrier properties, with smaller crystals more homogeneously distributed, i.e., with a semi-crystalline morphology that was controlled by processing (precipitation/nucleation). The general conclusion that can be drawn from all our observations is that nuc-PET has a unique structural organization, with distinct non-crystalline regions, that differs both microscopically and macroscopically from normally processed asr-PET and leads to superior properties. In addition, these property enhancements are achieved without the addition of any foreign or incompatible materials, which would complicate its recycling.

4.6 Acknowledgements

We are grateful to the National Textile Center (US Commerce Dept. – M10-NS01) and the College of Textiles at North Carolina State University for their financial support. We would also like to thank Dr. Richard Spontak and Dr. Wendy Krause for their valuable help with gas permeability and nano-indentation measurements, respectively.
4.7 References


4.8 Supplementary Information

![Schematic representation of the preparation of precipitated-PET (p-PET)](image)

**Figure 4.12:** Schematic representation of the preparation of precipitated-PET (p-PET)
Figure 4.13: Schematic of the Magnetic Suspension Balance

Figure 4.14: FTIR spectra of asr- and p-PETs
Figure 4.15: Polarized Optical Micrographs of asr- and nuc-PETs (asr-PET - top & nuc-PET - bottom)
Figure 4.16: Young’s Moduli (upper) and Hardness (lower) for asr- and nuc-PET films
Figure 4.17: Optical Microscope Image of asr-PET fiber
CHAPTER 5

5. Research Outcomes and Future Directions

Structuring polymers at a molecular level offers a way to improve their behaviors and properties compared with those traditionally melt or solution processed into materials. In this research we have nano-structured various amorphous and semi-crystalline polymers and successfully established some of their structure-property relations.

Micro-phase separated blends of PMMA/PVAc were successfully prepared using urea and γ-CD-ICs as their common compatibilizers. The PMMA/PVAc (n-s)-IC blends show partial miscibility when relatively more PVAc is used in their initial formation mixture. The analyses of PMMA/PVAc blends (from U-ICs) revealed that they retain the coalesced polymer structures in the blend and contain domains of miscible phases whose composition can be altered by changing the PMMA/PVAc feed ratios. Microscopy images of these blends can reveal the types of structures that are being formed and a correlation can be established between their structures and $T_g$s. Similar work should also be done with other polymer systems of interest and can be compared with our findings.

We have carefully analyzed PVAc, an amorphous polymer with a low $T_g$, to understand and comprehend the effects on its properties of nano-encapsulating/releasing it. It was found that PVAc processed with both urea and γ-CD show similar properties but it was easier to remove urea during coalescence on account of its higher water solubility. Long term annealing does not cause the c-PVAc chains to revert back to random coiled entangled configurations, which suggests that it has very good thermal stability. Another study that would help probe the properties of c-PVAc in a deeper fashion would be to conduct DMTA
at elevated temperatures for a long time (long time DMTA analogous to long time annealing). This would evaluate the effect of mechanical distortion on the polymer chains at higher temperatures where there would possess higher chain mobility which could cause them to revert back to asr-behavior.

We have demonstrated p-PET can be used as an effective self-nucleating agent to control the semi-crystalline morphology of PET and to improve its thermal and mechanical properties. We have also shown that repeated self-nucleation is possible using nuc-PET. It would be interesting to evaluate how many cycles of repeated nucleation are possible with retention of superior thermal and mechanical properties.