

National Textile Center

FY 2003 (Year 12) Continuing Project Proposal

Project No.

M02-NS01

Competency: **Materials**

Polymers Processed with Cyclodextrin Inclusion Compounds

Project Team:

Leader: **Alan E. Tonelli/NCState/Polymer Physical Chemistry**

Email: **alan_tonelli@ncsu.edu** Phone: **919-515-6588**

Members: **C. M. Balik/NCState/balik@ncsu.edu/Diffusion in and characterization of polymers**
M. Srinivasarao/Ga.-Tech/mohan@tfe.gatech.edu/Polymer Physics and Optics

Objective: To alter the properties of polymer fibers and films by first isolating and extending the constituent polymer chains in the narrow channels of the crystalline inclusion compounds (ICs) formed with host cyclodextrins (CDs) (See Figure 1) and then consolidating the guest polymer chains *via* coalescence from their CD-ICs. As indicated in the next section, coalescence of polymers from the ordered environment of their CD-IC crystals can result in a reorganization of the structures, morphologies, and even conformations observed in samples normally solidified from their solutions and melts where the polymer chains are disordered, randomly-coiling, and entangled. We hope the properties of polymer materials, including textile fibers, will be improved by processing with CD-ICs.

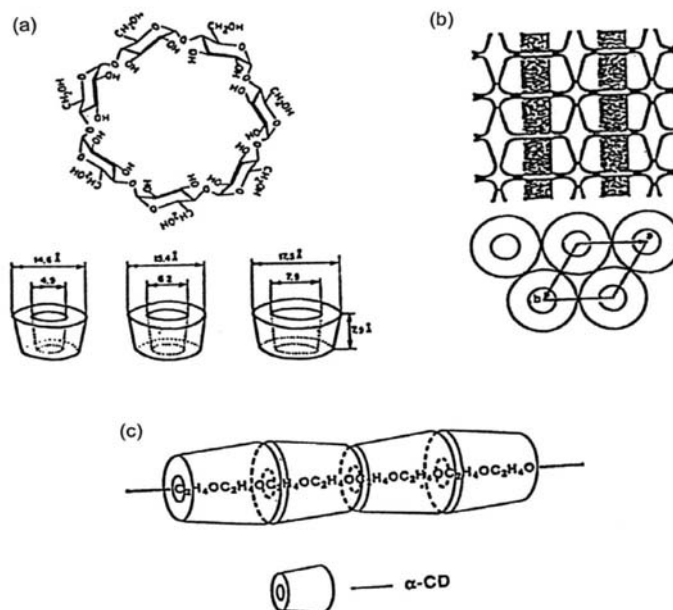


Figure 1 . β -CD structure and dimensions of α -, β -, and γ -CD bracelets (a); CD-IC channel crystal structure (b); and a single α -CD-IC channel with included poly(ethylene oxide) guest (c).

Progress Statement: We have demonstrated that (i) crystallizable homopolymers coalesced from their CD-ICs can evidence increased levels of crystallinity and higher melting and decomposition temperatures than samples consolidated from their disordered solutions and melts; (ii) molecularly mixed, intimate blends of two or more polymers that are normally believed to be immiscible can be achieved by coalescence from their common CD-IC crystals, (iii) the phase segregation of incompatible blocks can be greatly suppressed when block copolymers are coalesced from their CD-IC crystals, and (iv) the thermal and temporal stabilities of the well-mixed homopolymer

blends and block copolymers obtained by coalescence from their CD-ICs appear to be substantial, thereby suggesting retention of their as-coalesced structures and morphologies under normal thermal processing conditions.

In addition to a doubling of crystallinity, PET coalesced from its γ -CD-IC is repeatedly, rapidly crystallizable (See Figure 2), with a half-time of crystallization \sim 2-3 orders of magnitude faster than solution or melt consolidated PET. PET coalesced from its γ -CD-IC should be capable of being melt-blown into a nonwoven web, for example. As indicated by the x-ray diffractograms presented for the poly(ϵ -caprolactone)-poly(L-lactic acid) block copolymer (PCL-b-PLLA) in Figure 3 for as-synthesized and coalesced samples subjected to enzymatic degradation for various periods, PCL-b-PLLA coalesced from its α -CD-IC crystals is much less crystalline and therefore less phase-segregated than the as-received sample. PCL and PLLA blocks are apparently well-mixed in the largely amorphous coalesced sample, and consequently are more easily degraded by enzymes. Thus, the biodegradation of PCL-b-PLLA can be controlled by coalescence from its α -CD-IC crystals.

Though not detailed here, we have also been able to modify the crystallization behaviors of nylons-6 and -66, and to form intimately miscible blends between PCL/PLLA, PCL/poly(β -hydroxybutyrate), polycarbonate (PC)/poly-(methylmethacrylate) (PMMA), PC/polystyrene, and even form a well mixed PC/PMMA/poly(vinyl acetate) terpolymer blend by coalescence from their CD-ICs.

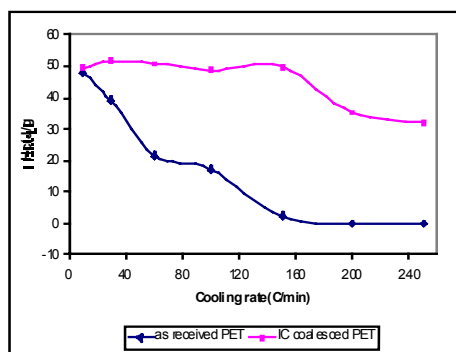


Figure 2. Crystallization enthalpies, H_c , observed at different cooling rates for as-received (lower) and γ -CD-IC-coalesced (upper) PET samples.

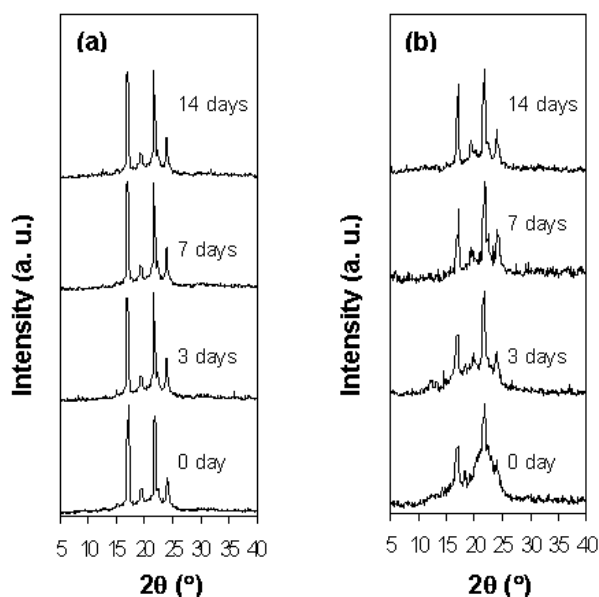


Figure 3. X-ray diffraction patterns of as-synthesized (a) and coalesced (b) PCL-b-PLLA films observed following various enzymatic degradation times.

Very recently, we have learned how to form crystalline columnar structure α -CD (α -CD_{CS}) [See Figure 1 (b)] that contains no included guests in its channels aside from water. α -CD_{CS} can include both polymeric and small-molecule guests by simple suspension in a solution or melt of the guest to be included. Thus, we have created a **nanofilter** that can be used to separate polymers by chemical type and polymers from various small-molecule guests, and we can now more easily form polymer-CD-ICs. In addition, when as-received α -CD, which assumes a cage crystalline structure, is mixed with low molecular weight poly(ethylene glycol) (PEG 200 or 400 g/mol) at room temperature, the cage crystalline structure is transformed to the columnar crystal structure, apparently *via* a solid-solid phase transition, as the PEG chains are included. This is illustrated by the series of x-ray diffractograms shown in Figure 4, where the peak at $2\theta = 12^\circ$ associated with the α -CD cage structure decreases, while the peak at $2\theta = 20^\circ$ associated with the columnar crystal structure of α -CD increases steadily with time.

Next Year's Goals: We plan to scale-up the production of CD-IC processed polymer samples in order to obtain quantities of these uniquely reorganized polymers sufficient to perform measurements of such macroscopic properties as permeability and modulus. Further investigations of the ability of columnar α -CD_{CS} to function as a **nanofilter** and to more easily form both polymer- and small-molecule-CD-ICs will be pursued. We will also begin to study the coloration of polymer fibers by dyes that are complexed with CDs, because Mohan Srinivasarao at

Georgia Tech. has shown that they have improved light and wash fastness, show greater depths of shade, and are non-toxic.

Approach: In addition to the usual battery of characterization techniques we normally use to characterize the polymer materials after coalescence from their CD-ICs, we plan to expand their investigation by FTIR microscopy and solid-state NMR techniques. With the heating/cooling stage recently purchased under this NTC project for our FTIR microscope, we hope to be able to observe the spatial organization and structures of our coalesced polymer materials and their temporal stability by the selective observation of FTIR spectra recorded from specific regions of the samples at various temperatures. This will provide valuable information concerning the thermal stabilities of the CD-IC organized polymer samples and enable us to study, for example, the kinetics of phase segregation in an initially coalesced and well-mixed blend of inherently incompatible polymers. Several solid-state NMR techniques, such as ^{13}C -observed $T_{1\rho}({}^1\text{H})$ relaxation, 2-D HETCOR, and WIM-WISE experiments, should give us a microscopic measure of the state of mixing in our coalesced polymer blends and provide a measure of the dynamics of the constituent polymer chains for comparison with those in normally processed samples.

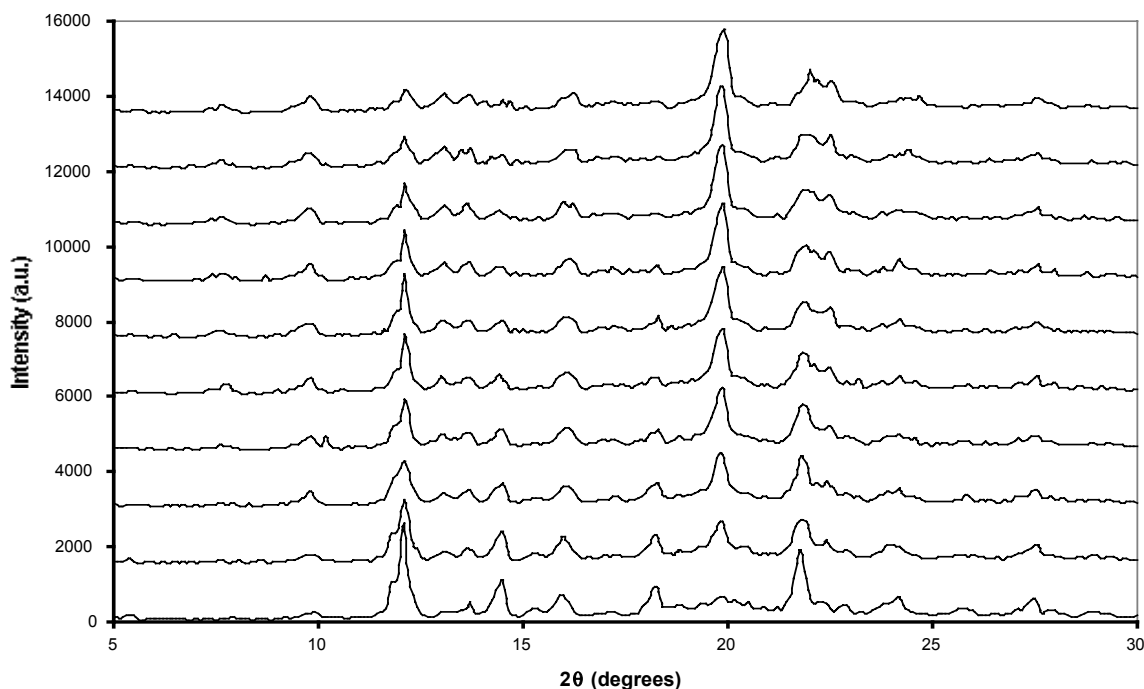


Figure 4. Time-dependent x-ray diffraction patterns for the complexation of PEG (mol. wt. = 200 g/mol) with α -CD at 20°C. Bottom to top: 0, 1, 2, 3, 4, 5, 6, 7, 8 and 24 hrs, respectively. The α -CD crystals undergo a solid-state transformation from the cage structure to the columnar structure.

Outreach to Industry: We have written two Invention Disclosures – “Repeatedly, Rapidly Crystallizing PET” and “Columnar Structures of Hydrated, Crystalline Cyclodextrins”, which are currently under Patent review by the NC State Technology Transfer office.

New Resources Required: Aside from funding the Post-Doctoral researcher requested in our initial budget, we do not anticipate any new resources will be required in the second year of this project.

References:

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