Macromol. Symp. ***176****, 129–144 (2001)*

Creation of Novel Polymer Materials by Processing with Inclusion Compounds

L. Huang, M. Gerber, H. Taylor, J. Lu, E. Tapaszi, M. Wutkowski, M. Hill,
*C. Lewis, A. Harvey, A. Herndon, M. Wei, C. C. Rusa, and A. E. Tonelli**

Fiber & Polymer Science Program, North Carolina State University, Campus Box 8301, Raleigh, NC, USA 27695-8301
alan_tonelli@ncsu.edu

Summary: The processing of polymer materials from their inclusion compounds (ICs) formed with urea (U) and cyclodextrin (CD) hosts is described. Several examples are presented and serve to demonstrate the fabrication of unique polymer-polymer composites and blends, including intimate blends of normally incompatible polymers, and the delivery of additives to polymers by means of embedding polymer- or additive-U and CD- ICs into carrier polymer films and fibers, followed by coalescence of the IC guest, or by coalescence of two polymers or a polymer and an additive from their common CD-IC crystals.

Introduction

The compositions, structures, and properties of polymer films and fibers may be developed and controlled during their formation with inclusion compounds (ICs). ICs formed with urea (U) or cyclodextrin (CD) hosts and containing guest polymers or small-molecule additives are embedded into carrier polymer films and fibers by melt processing at temperatures below the melting point of the polymer- and/or additive-IC crystals. Once embedded, the IC crystals may be left undisturbed or may be disrupted by solvent treatment, which removes the host (U or CD), but neither the coalesced guests or the carrier polymer. Polymer-polymer, composite and additive-filled films and fibers have been prepared in this manner, and several examples from both classes of materials will be described and compared to samples prepared by the traditional solution-casting and melt-blending methods.

In a second approach to obtain polymer-polymer and polymer-additive composites, CD-ICs containing both constituents (polymer-1/polymer-2 or polymer/additive) have been formed simultaneously from their common solutions. Washing the CD-IC crystals, which include both composite components, with hot water results in the removal of the CD host and

CCC 1022-1360/00/$ 17.50+.50/0

coalescence of both guests to form a blend. Again the blends obtained by coalescence from their common CD-ICs are compared to blends of the same components prepared by the traditional solution- casting method.

Experimental

Materials and Methods

U and CDs were obtained from Aldrich and Cerestar, respectively. Poly (L-lactic acid)(PLLA), poly(ε-caprolactone)(PCL), poly(ethylene-oxide)(PEO), poly (ethylene terephthalate)(PET)polystyrene(PS), polycarbonate(PC, from bisphenol-A), and nylon-6 were obtained from Research Triangle Institute, Aldrich, Sigma, Aldrich, Aldrich, Aldrich, and Allied Signal, respectively. Preparation of polymer-U- and CD-ICs have been described (1-3). Films embedded with polymer-U- and CD-ICs were washed with methanol and water, respectively, to coalesce the guest polymer into the carrier polymer. The antibacterials neomycin sulfate and trichlosan were obtained from Calbiochem and Ciba Specialty Chemicals; the flame retardant was obtained from Albright and Wilson; hexanoic acid(HA) was obtained from Aldrich; and the surfactant/spermicide nonoxynol-9 was obtained from Jean International. Formation of additive-CD-ICs and CD-ICs containing two different polymers or a polymer and an additive have been previously described (4-8). All ICs were characterized by x-ray diffraction, DSC, TGA, FTIR, and NMR observations, while in addition to these techniques, the resulting films and fibers were also examined by optical microscopy and permeation measurements.

Results and Discussion

We have successfully obtained void-free, polymer-polymer composite films *via* the embedding and subsequent release of guests from polymer-IC crystals (3). Figure 1 presents the DSC scans of PCL and PLLA films embedded with PCL-U-IC crystals observed before and after soaking in methanol. Note that the higher temperature endotherm in scan (a), which is generated by the melting of the embedded PCL-U-IC crystals is absent in scan (b), where only the melting endotherm for PCL remains. In scans (c) and (d) we observe the elimination of the melting endotherm for PCL-U-IC produced by the methanol soak, with only the melting endotherm of PLLA remaining. Though we do not observe a melting endotherm in (d) for the PCL coalesced from PCL-U-IC after soaking the embedded PLLA film, solid state ^{13}C NMR observations not presented here confirm the presence of PCL. Apparently the PCL coalesced into the PLLA film has not crystallized.

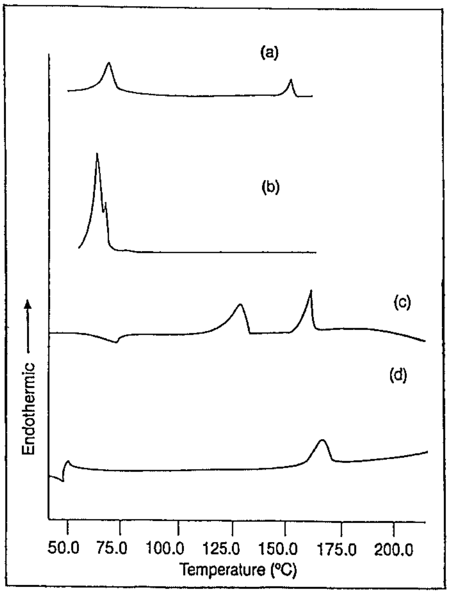


Figure 1. DSC scans of PCL embedded with PCL-U-IC before (a) and after (b) washing in methanol, and DSC scans of PLLA embedded with PCL-U-IC before and after (d) washing in methanol.

Table 1 compares the permeabilities of pure and U- or PCL-U-IC embedded PCL and PLLA films to water vapor both before and after soaking in methanol. Though it is apparent that removal of U from the PCL and PLLA films embedded only with pure U results in large increases in water vapor permeability, apparently through holes created by the removal of the U crystals, significant increases in the permeabilities of PCL and PLLA films embedded with PCL-U-IC do not occur after a methanol soak. It appears that the coalescence of PCL from the PCL-U-IC crystals, which are disrupted on exposure to methanol, fills in or heals any potential holes that might have been created by the removal of the U host.

Table I Comparison of Thicknesses and Permeabilities of PCL, PCL-Urea, PCL-IC, PLLA, PLLA-Urea, and PLLA-IC Solution-Cast Films Before and After Dipping in Methanol

Sample Name	Average Thickness (mm)	Moisture Vapor Permeability ($g/m^2/24$ h)
PCL Film	0.022	375
Dipped PCL Film	0.010	440
PCL-Urea Film	0.139	413
Dipped PCL-Urea Film	0.313	747
PCL-IC Film	0.054	418
Dipped PCL-IC Film	0.076	583
PLLA Film	0.024	173
Dipped PLLA Film	0.041	187
PLLA-Urea Film	0.180	207
Dipped PLLA-Urea Film	0.155	540
PLLA-IC Film	0.045	183
Dipped PLLA-IC Film	0.052	236

DSC scans of PLLA and nylon-6 films embedded with PEO-α-CD-IC observed before and after soaking in hot water are presented in Figure 2. After washing in hot water we observe a low temperature melting endotherm for the coalesced PEO chains which have crystallized.(PEO-α-CD-IC melts above 275 ° C and is not shown in the DSC scans of Figure 2. It is clear from the results presented in Figures 1 and 2 and Table 1 that composite polymer films can be fabricated by embedding polymer IC crystals in a carrier polymer and then removing the host and coalescing the guest polymer from the embedded IC crystals into the carrier polymer. In this manner the structures of polymer blends can be conrolled to obtain morphologies which are substantially different from those produced by the usual solution casting and melt blending approaches.

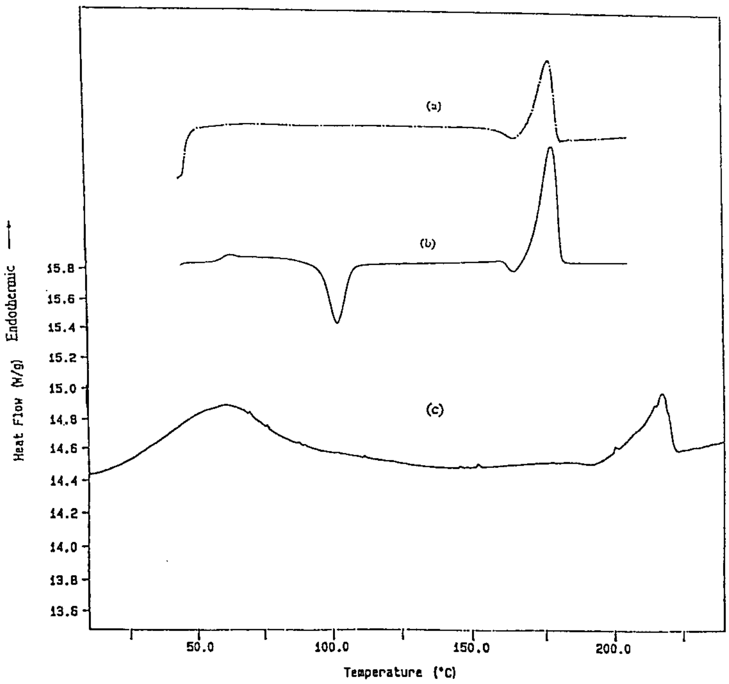


Figure 2. DSC scans of PLLA embedded with PEO-α-CD-IC before (a) and after (b) washing in hot water and the DSC scan of nylon-6 Embedded with PEO-α-CD-IC after (c) washing in hot water.

Polymer-ICs may be used in an alternative manner to achieve polymer blends. By forming a common solution of two polymers and adding this solution slowly with heating and/or sonication and stirring to a solution containing the IC host, a polymer-A/polymer-B-IC containing both polymers maybe obtained. A film of intimately blended PLLA and PCL has been achieved by their coalescence from α-CD-IC crystals containing both polymers. By contrast, when PLLA and PCL are cast from a common solution in dioxane, for example, the resulting film is phase separated with distinct small PLLA and large PCL crystalline spherulites.

The FTIR spectra and polarized micrographs of the PCL/PLLA films obtained by coalescence from their common α-CD-IC and cast from their common solution in dioxane are presented in Figures 3 and 4 (6). Both PCl and PLLA are evident in the FTIR spectra of both films, and by comparing the intensity ratio of the PCl and PLLA carbonyl bands at 1736 and 1759 cm^{-1}, respectively, we are able to determine that PCL/PLLA weight ratios of 55/45(IC-coalesced) and 50/50(solution-cast) are present in the film blends. From the summary of DSC data obtained for both film blends presented in Table 2, we observe that both PCL and PLLA are substantially crystalline in the solution-cast blend, and so must be significantly phase-separated. On the other hand, the coalesced PCL/PLLA film shows no PCL crystallinity and only a very small amount of crystallinity for the PLLA component.

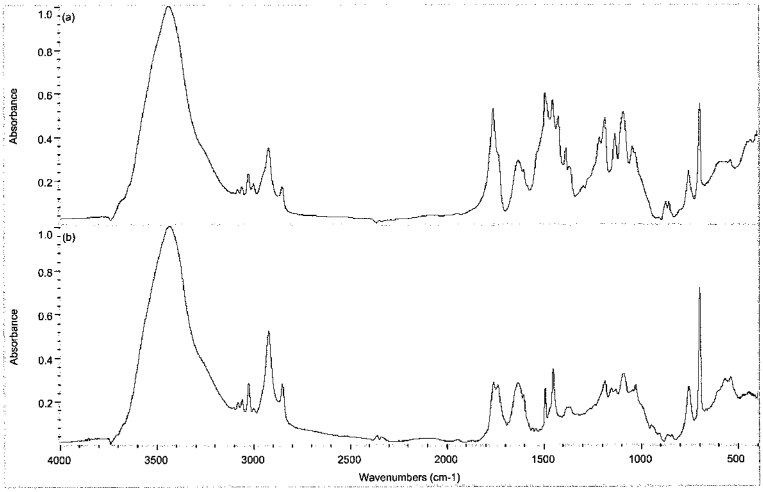
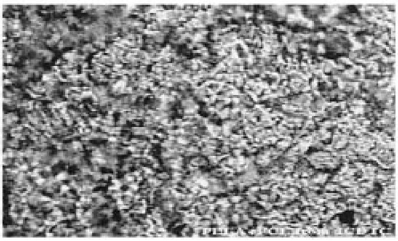


Figure 3. FTIR spectra of solution-cast (a) and coalesced (b) PLLA/PCL blends.



Coalesced PLLA/PCL from aCD-IC

PCL/PLLA blend cast from dioxane

Figure 4. Polarized photomicrographs of PLLA/PCL blends.

Table 2. Calorimetric data of PLLA/PCL blends.

Blend	Tm (°C)		ΔHm (J/g)		Crystallinity (%)	
	PCL	PLLA	PCL	PLLA	PCL	PLLA
PLLA/PCL blend cast from dioxane (50/50, wt/wt) annealed @ 200 C for 3 min	58.6	168.6	64	41	45.8	44
Coalesced PLLA/PCL from its α-CD IC (45/55, wt/wt) annealed @ 200 C for 3 min		166.1	-	5.11	-	5.5

In the polarized micrographs of the coalesced and solution-cast PCL/PLLA films seen in Figure 4, the phase-separated morphology is clearly evident in the solution-cast film, but the micrograph of the coalesced film strongly suggests a homogeneous blend structure. Because no PCL crystals were detected by DSC in the coalesced blend, the small spherulites observed there must belong to PLLA. Thus we appear to have achieved a homogeneous blend of amorphous PCL and PLLA chains which is embedded with a small quantity of PLLA spherulites. We have not as yet been able to dissolve the homogeneous PCL/PLLA blend, nor induce phase-separation by extended annealing (12-24 hrs) at temperatures (200° C) above the melting points of both components.

We are currently attempting to produce a compatible blend from the immiscible polymer pair PC/PS, which are generally substantially and totally amorphous, respectively. Preliminary DSC results on PC and PS and their blends coalesced from their common γ-CD-IC and cast from solution are presented in Figure 5. We observe single T_g's in the coalesced blends that are different from those observed in the neat polymers and their solution-cast blend. Thus we have preliminary evidence of miscibility in the PC/PS blends coalesced from their common γ-CD-IC.

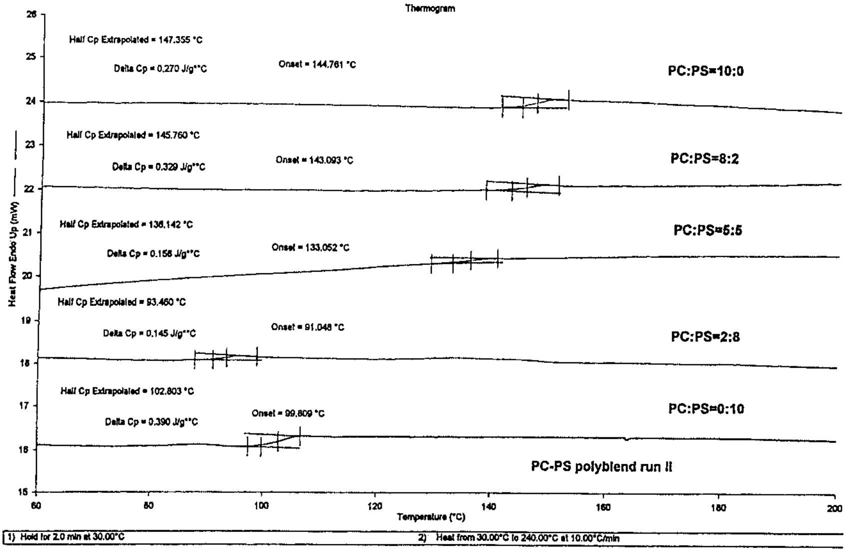


Figure 5. DSC scans of PC-PS blends with 1:0 (a), 4:1 (b), 1:1 (c), 1:4 (d), and 0:1 (c) molar ratios of PC:PS prepared by coalescence from their common γ-CD-ICs.

PC and PET have been induced to crystallize by formation of γ-CD-ICs followed by washing with hot water to remove the CD and coalesce the PC and PET. Evidence for this can be seen in Figure 6, where in the DSC scans of the coalesced PC a substantial melting endotherm is observed. In addition, the melting endotherm of PC coalesced from its γ-CD-IC occurs 15 °C higher than the melting endotherm observed for PC cast from the mixed DMS/THF solution (See Figure 7). This suggests that PC chains coalesced from their γ-CD-IC crystals may organize into a chain-extended crystalline morphology, which is more thermally stable than the chain-folded crystalline morphology obtained by casting PC film from solution, where the chains are completely disordered.

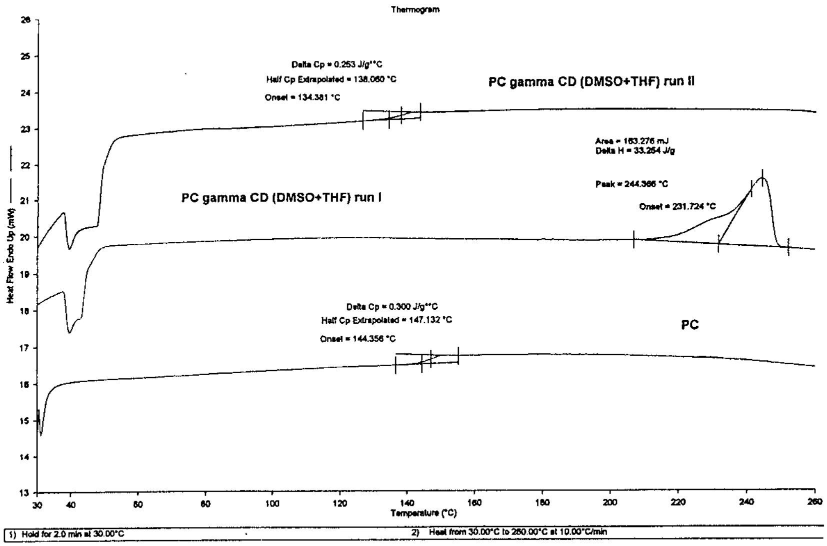


Figure 6. DSC scans of PC as received(a) and after coalescence from its γ-CD-IC [first,second heats(b),(c)].

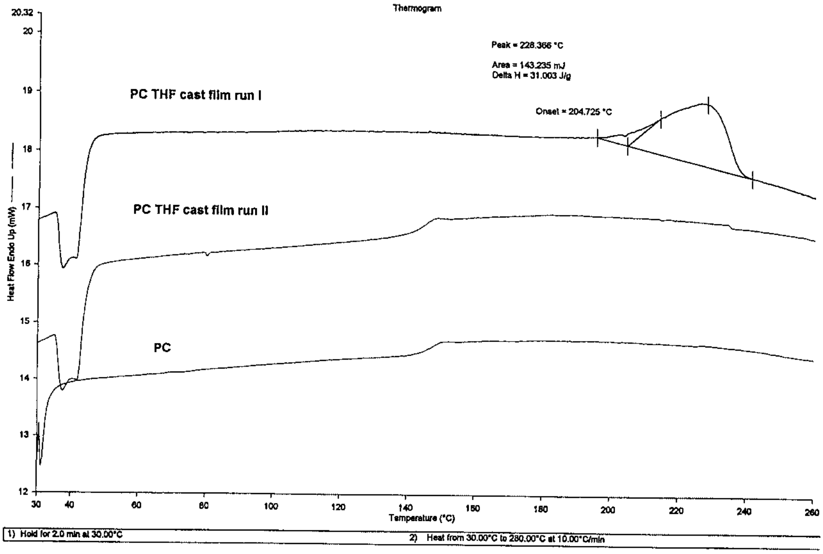


Figure 7. DSC scans of PC as received (a) and after casting from THF solution [first,second heats (b),(c)].

Antibacterial films and fibers of bioabsorbable/biodegradable PLLA and PCL have been produced by embedding small quantities(a few wt%) of antibacterial-CD- IC crystals. A normally liquid flame retardant has been delivered to PET films in the form of high melting(~270 °C) CD-IC crystals, which have been demonstrated to effectively extinguish the combustion produced by exposing PET films to open flames. Well-mixed blends of HA and PCL were achieved by coalescence from their common α-CD-IC. Also recently we have formed an α-CD-IC with the mostly widely used spermicide nonoxynol-9, which is a liquid surfactant, for possible future use in fabricating spermicidal latexes and fabrics.

β-CD-ICs have been formed with both antibacterials shown in Figure 8. When either antibacterial-β-CD-IC is embedded at low levels into PCL or PLLA films or fibers, they are observed (4,9) to inhibit the growth of E. coli bacteria. In fact, as demonstrated in Figure 9, fabrics laminated with adhesives embedded with antibacterial-β-CD-IC also prevent the growth of E. coli bacteria. Clearly a host of other textile additives/auxiliaries may be delivered to laminated fabrics by this means.

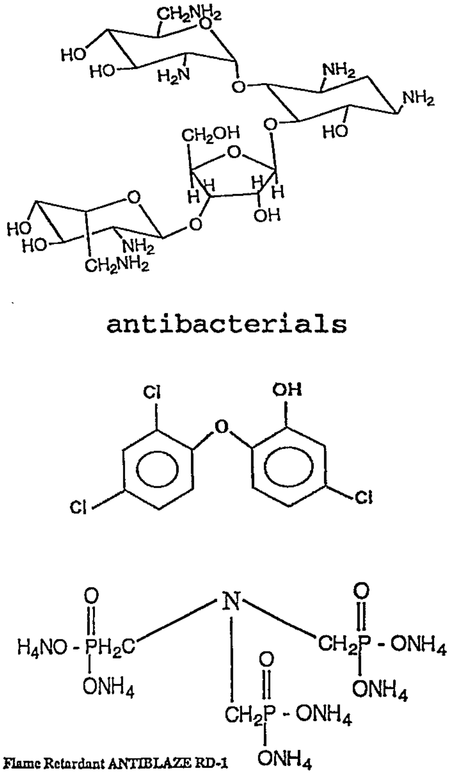


Figure 8. Chemical structures of the antibacterials and the flame retardant (FR) used in this study.

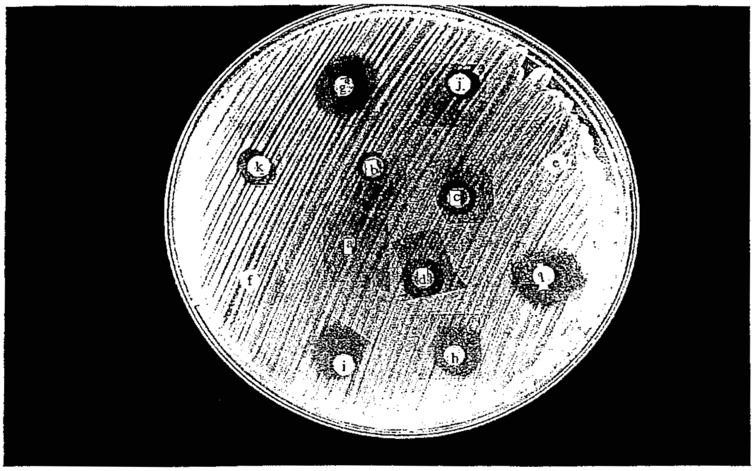


Figure 9. Photograph of an Agar plate loaded with discs cut from laminated fabrics glued together with PCl films which do and do not contain Trichlosan-β-CD-IC., and to which E. coli bacteria have been introduced. Filter paper discs with 0 (a), 7.5 (b), 15.0 (c), and 30.0 (d) mg of neomycin sulfate, PCL discs with with 2.5 wt% (e) and (f) and 5 wt% (g) and (h) of Irgasan-β-CD-IC, and discs of cotton fabric laminated with PCL containing 2.5 wt% (i) and (j) and 5.0 wt% (k) and (l) of Irgasan-β-CD-IC.

When the commercial flame retardant(FR) shown in Figure 8 is included as a guest in its β-CD-IC and this FR-β-CD-IC is embedded in PET films, the embedded PET films show a resistance to burning which is superior to PET films normally treated with the same FR (5). This FR is sold as a viscous solution which is normally padded onto PET fabric from a bath. It can be readily seen from Table 3 that PET films with FR-β-CD-IC directly embedded into them provides flame retardancy which is superior to that provided by padding comparable amounts of the liquid FR directly onto the PET film. In addition to the superior performance achieved in this instance by delivering a liquid additive in the form of its solid, high melting

CD-IC directly to the polymer film or fiber, it also illustrates the possibility of delivering additives that are liquids and even possibly gases to polymers, because in the form of a CD-IC even the inherently liquid or gaseous guest is delivered as a high-melting solid that can be easily processed into the polymer.

Table 3. Three kinds of PET film thicknesses and flame retardancy test results[a].

	Film Thickness (mm)			**Char Length[b] (cm)**			**Burning Time After Removing Flame (sec)**		
	1	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
Pure Untreated PET Film	0.14	0.15	0.14	BEL	BEL	BEL	26.0	28.0	25.0
FR finished PET Film	0.16	0.14	0.13	5.3	BEL	BEL	14.0	16.0	16.0
Control PET Film with CD	0.19	0.18	0.20	BEL	BEL	BEL	15.0	19.0	15.0
FR-IC Embedded PET Film	0.23	0.20	0.25	1.0	0.8	1.0	6.0	4.0	6.0

[a] Each test repeated three times.

[b] BEL=Burned entire length.

Another approach to the delivery of additives to polymers may begin with the simultaneous inclusion of both additive and polymer as guests in a common IC. FTIR spectra of PCL and hexanoic acid(HA)-ICs formed with α-CD-IC are presented in Figure 10 along with the FTIR spectra of common α-CD-ICs formed simultaneously with PCL/HA (7,8). Comparison of the intensities of PCL and HA carbonyl bands at ~1735 and ~1716 cm^{-1}, respectively, illustrates that the amounts of both components in the common α-CD-IC can be controlled by the stoichiometry of the starting guest and host solutions. In the α-CD-IC formed with a 1:1:1 molar ratio of PCL:HA:CD, the included guest is found to be predominantly PCL, while for a 1:1:2 ratio with sufficient CD to include both guests, we do in fact see comparable amounts of PCL and HA included. This observation points to the preference for α-CD to include PCL compared with its repeat unit model compound HA, an observation similar to that reported previously for PEO oligomer and polymer (10).

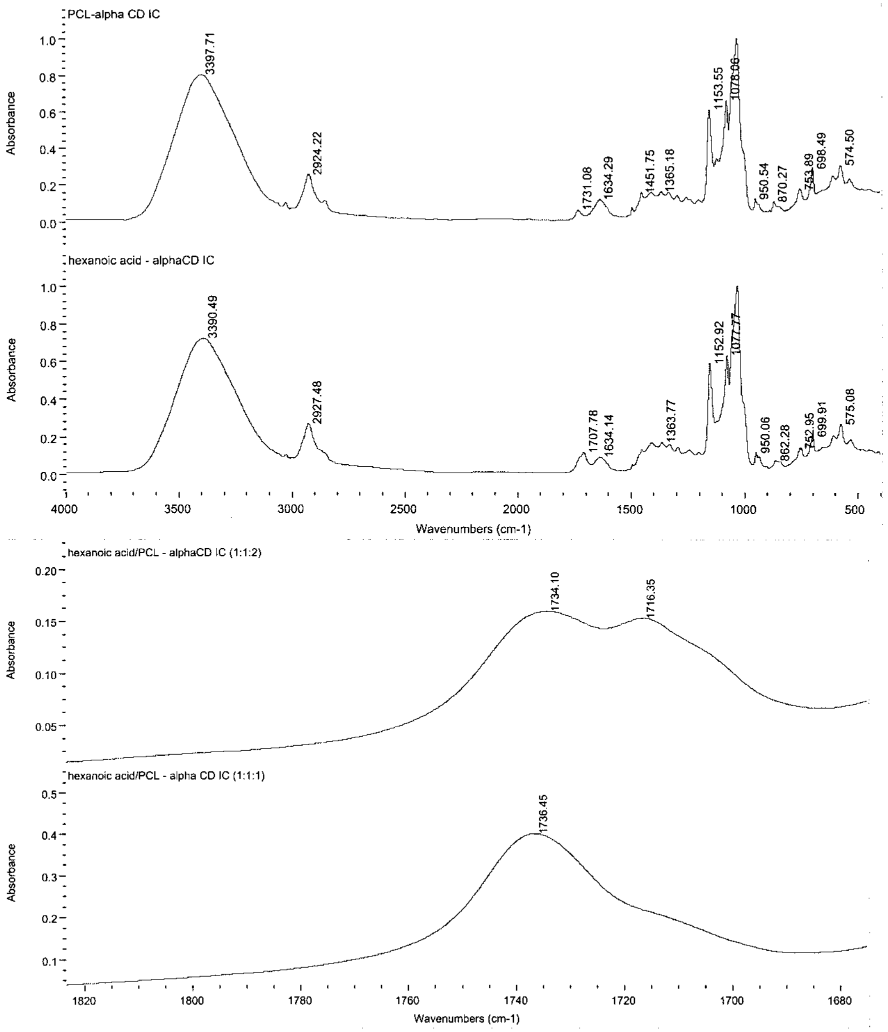


Figure10. FTIR spectra of the α-CD-ICs of PCL, HA, and PCL/HA.

Finally, the x-ray powder diffractograms of valeric acid and nonoxynol-9 ICs formed with α-CD are presented in Figure 11. X-ray diffraction analysis (11) of single crystals of valeric acid-α-CD-IC has revealed a channel crystal structure. The closely similar appearance of the powder diffraction for nonoxynol-9-α-CD-strongly indicates it is also likely of the channel crystalline variety. Nonoxynol-9 is an amphiphilic, non-ionic surfactant, which also happens to be the most widely used spermicide, as the active ingredient in spermicidal jellies. We will soon learn whether spermicidal activity can be conferred upon polymer plastics, latexes, and/or gels through the incorporation of nonoxynol-9-α-CD-IC, thereby delivering this inherently liquid additive as a guest in this high-melting,crystalline solid form.

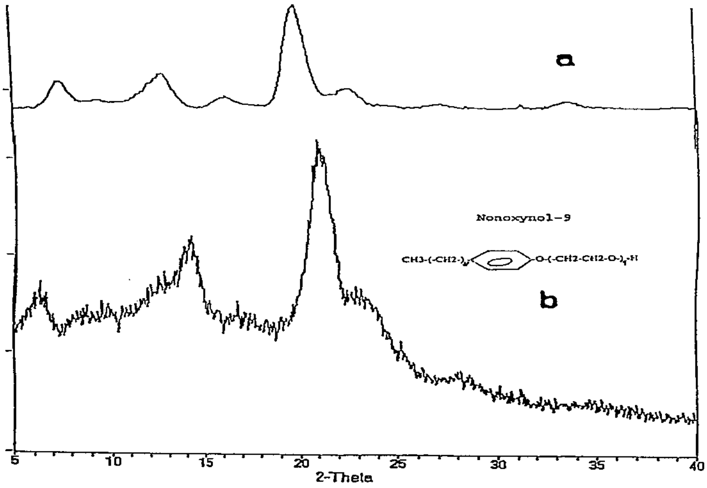


Figure 11. Wide-angle x-ray diffractograms of (a) valeric acid- (b) nonoxynol-9-α-CD-ICs.

Conclusions

By means of the several examples discussed above, we hope to have demonstrated the possibility of obtaining unique polymer materials *via* fabrication with CD-ICs.

Acknowledgements

We are grateful to the US Army Office of Research, the National Textile Center(US Dept. of Commerce), and NC State University for financial and other support.

References

1)C. Choi, D. D. Davis, A. E. Tonelli, Macromolecules, *26*, 1468 (1993).

2)L. Huang, E. Allen, and A. E. Tonelli, Polymer, *39*, 4857 (1998); *40*, 3211 (1999).

3)L. Huang , A. E. Tonelli, in "Intelligent materials for Controlled Release", S. M. Dinh, J. D. DeNuzzio, A. R. Comfort, Eds., Amer. Chem. Soc. Symp. Ser. # 728, Washington, DC, 1999, Chap. 10.

4)L. Huang, H. Taylor, M. Gerber, P. E. Orndorff, J. R. Horton, A. E. Tonelli, J. Appl. Polym. Sci., *74*, 937 (1999).

5)L. Huang, M. Gerber, J. Lu, A. E. Tonelli, Polym. Degrad. Stabil., *71(2)*, 279 (2001).

6)C. C. Rusa, A. E. Tonelli, Macromol., *33*, 5321 (2000).

7)J. Lu, P. A. Mirau, C. C. Rusa, A. E. Tonelli, Proceedings of the 10th International Cyclodextrin Symposium, U. of Michigan, Ann Arbor, May 21-24, 2000.

8)C. C. Rusa, C. Luca, and A. E. Tonelli, Macromolecules, *34,* 1318 (2001).

9)J.Lu, M. A. Hill, M. Hood, D. F. Greeson Jr., J. R. Horton, P. E. Orndorff, A. S. Herndon, and A. E. Tonelli, J. Appl. Polym. Sci., *82,*, 300, 2001.

10) C. C. Rusa and A. E. Tonelli, Macromolecules, *33*, 1813 (2000).

11) R. K. McMullan, W. Saenger, J. Fayos and D. Mootz, Carbohydr. Res., *31*, 37 (1973).