Macromol. Symp. ***130****, 151–160 (1998)*

BINARY AND TERNARY POLY(LACTIC ACID)/POLY(ε-CAPROLACTONE) BLENDS: THE EFFECTS OF OLIGO-ε-CAPROLACTONES UPON MECHANICAL PROPERTIES

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ABSTRACT

Oligo-ε-caprolactones(o-CL) have been utilized as principle secondary components within poly(lactic acid)[PLA]-based blends as well as additives within larger-sized PCL/PLA blends in an effort to fully complement the mechanical attributes of the respective polyesters. Dynamic mechanical thermal analysis(DMTA) shows that the presence of o-CL plasticizes the PLA non-crystalline phase with a more pronounced effect seen as the size of o-CL is reduced. Moreover, it appears that the size of o-CL could also affect the static mechanical properties of the ternary systems as material stiffness and strength reside between those properties measured for high molecular weight PCL/PLA binary blends and the PLA homopolyester. Future work will examine the ability of these blends to sustain these properties during hydrolytic exposure.

INTRODUCTION

Recently, the material deficiencies of poly(lactic acid)[PLA] in terms of hydrolytic stability and toughness have been addressed through copolymerization(1-11) and physical blending(12-14) with the more hydrophobic and energy dispersive poly(ε-caprolactone) [PCL]. From a financial perspective, physical blending of PCL and PLA is the preferred methodology. However, in order to optimize this method of choice, it must be understood that the degree to which PLA is improved will ultimately depend upon the energy of interaction between the homopolyesters. Unfortunately, with the exception of Hiljanen-Vainio et al.(13), this topic has received less than adequate attention.

As a result, this study intends to explore the range of miscibility that may be attained by incorporating oligo-ε-caprolactones(o-CL) as compatibilizing agents within PCL/PLA blends. In essence, by altering the concentration and size of the o-CL additive, it is anticipated that the propensity of the oligoester to associate with PLA could promote the reduction of interfacial tension between PCL and PLA as an o-CL/PLA phase is

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formed. Also, this phenomenon may be further realized with the induction of ester exchange reactions across the interfacial domains(14).

EXPERIMENTAL

Materials: Highly amorphous PLA[91%(L), T_g~64°C, T_m~155°C, M_n~63,000 Daltons] was supplied by Cargill, Inc. High molecular weight PCL[T_g~-60°C, T_m~60°C, M_n~43,000 Daltons] was obtained from Union Carbide Co. as dihydroxy-terminated materials. This functionality was also present within the selected o-CL[530 and 2000 Daltons] which were purchased from Aldrich Chemical Co.

Melt Blend Preparation: Binary and ternary melt blends of PCL and PLA were prepared as 530, 2000 o-CL/diols and 43,000 PCL-diol were charged to the reaction vessel in progressive weight percent increments relative to the total blend composition. In each instance, PLA constituted 75 percent by weight of the various mixtures. A C.W. Brabender® was employed at 180°C and 40rpm for 20 minutes to ensure thorough mixing of the blend components.

Compression-Molded Film Preparation: In order to gain a preliminary understanding of the comparative ability of 530 and 2000 o-CL/diols to migrate and interact with the PLA non-crystalline phase, small-scale films(~0.5g, 2.5cm x 2.5cm x 0.05cm) of the melt blends were made by compression-molding at 180°C and 500psi for 2 minutes and 1500psi for an additional 2 minutes at the identical temperature.

Solution-Cast Film Preparation: Binary and ternary PCL/PLA blend films were prepared according to the following methodology: i.) After reactive melt blending and cooling to room temperature, the materials were dissolved in chloroform(Acros, 99+% with 0.75% ethanol) at 10% w/w solid content, ii.) The solutions were poured into glass Petri dishes(170mm x 90mm) and placed under nitrogen flux at room temperature for 24 hours, iii.) The films were removed from the Petri dishes and transferred to a vacuum atmosphere at room temperature for 36 hours to completely remove any residual solvent. Film thickness was approximately 200 μm.

Note: The preceding method was chosen as a large-scale(~6.5g) alternative to thermal-pressing due to the potential problems of molar mass loss that could accompany repeated thermal treatments at elevated temperatures(15-17).

Characterization

Ternary Melt Blends: Molecular weight analysis was carried out with gel-permeation chromatography(GPC)[Waters Model 150-C ALC] using PCL standards in a tetrahydrofuran mobile phase(1.0ml/min) at 30°C to determine if a discrepancy exists between theoretical and experimental molecular sizes within the binary and ternary blends.

Compression-Molded Films: Dynamic mechanical thermal analysis(DMTA)[Model MkII] was applied to these samples under tensile loading at a heating rate of 2°C per minute from -80°C to follow the plasticizing effect of PCL and o-CL upon the PLA non-crystalline phase.

Solution-Cast Films: Differential scanning calorimetry(DSC) was administered using a TA 2920 differential scanning calorimeter with the melt endotherms of indium and distilled water serving as reference materials to calibrate the apparatus. The reported percent PLA crystallinity values were calculated from the normalized heats of fusion(15) that were obtained from initial heatings of the films from -20°C to 200°C at 20°C per minute. Phase morphology changes were detected with scanning electron microscopy (SEM)[Amray Model 1000A] of freeze-fracture surfaces. Tensile tests on the cast films were done on dog-bone shaped specimans(ASTM D638-89) with the aid of an Instron 1011 tensile testing machine. A crosshead speed of 5mm/min was used with six samples tested for each different film.

RESULTS AND DISCUSSION

The Effects of Thermal Processing upon PCL/PLA Blends:

Table 1 in conjunction with Figures 1 and 2 describe the molecular weight characteristics of each reactive melt blend. If one compares the experimental and theoretical number-average molecular weights following thermal processing, the blends exhibit a trend towards decreased M_n values, substantiating the notion that degradative processes(16-18) are most probably occurring at the elevated mixing temperature.

Table 1. Molecular Weights and Heterogeneity Indicies of Binary and Ternary Systems.

System	%o-CL	%43K PCL	% PLA	Mw	Mn	Mw/Mn
PLA	0	0	100	115800	63200	1.8
25-43K	0	25	75	82400	20600	4.0
6-530	6	19	75	51900	6100	8.5
12-530	12	13	75	43600	3000	14.4
19-530	19	6	75	44000	3200	13.8
25-530	25	0	75	31200	2100	14.9
6-2000	6	19	75	49300	8500	5.8
12-2000	12	13	75	44400	5000	8.9
19-2000	19	6	75	32900	3500	9.4
25-2000	25	0	75	73000	7800	9.4

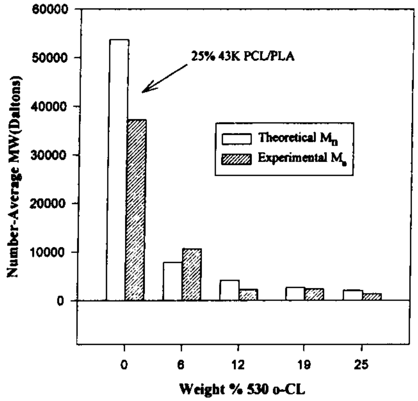

Figure 1-Experimental versus theoretical M_n values within 530 o-CL additive systems.

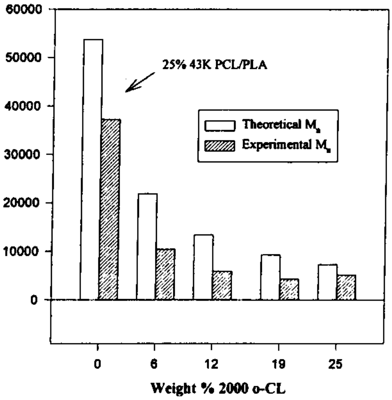

Figure 2-Experimental versus theoretical M_n values within 2000 o-CL additive systems.

Regardless of this reduction in molar mass, a detailed investigation of PLA non-crystalline behavior was continued with DMTA. Figures 3 and 4 show that the introduction of 530 o-CL versus 2000 o-CL provides markedly different dynamic mechanical property profiles as the composition of oligomer is increased. For instance, at 19 weight percent of the respective additives, the glass transition regime of PLA is lowered by approximately 20°C with a precipitous drop in log E' seen just beyond 40°C for the 530 o-CL system. In addition, at the defined level of molecular weight, it would appear that this effect may be attributed to a more intimate degree of compatibility between 530 o-CL and PLA as well as an issue of molecular size and polydispersity.

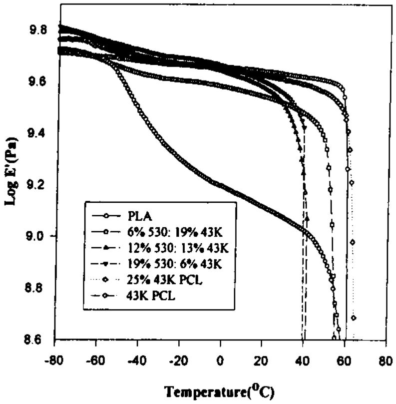

Figure 3-The effect of 530 o-CL upon the PLA non-crystalline transition regime.

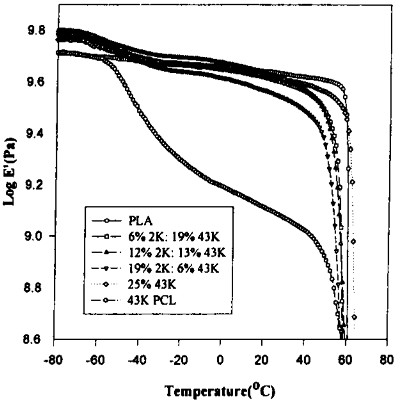

Figure 4-The effect of 2000 o-CL upon the PLA non-crystalline transition regime.

Tensile Properties of Solution-Cast Films:

Prior to tensile testing, a superficial study of blend morphology was undertaken through DSC analysis. A typical thermogram shows melt endotherms indicative of a PLA crystalline phase with complex changes in heat flow seen at 45-65°C. This undefined series of transitions are most likely due to the PLA glass transition and a PCL crystalline phase that are not precisely separated through calorimetry. In any event, while an in-depth study of these overlapping thermal transitions goes beyond the immediate scope of this work, with similar induced PLA crystallinity values[Figure 5], the likelihood of a strengthening effect due to PLA crystal structure is diminished.

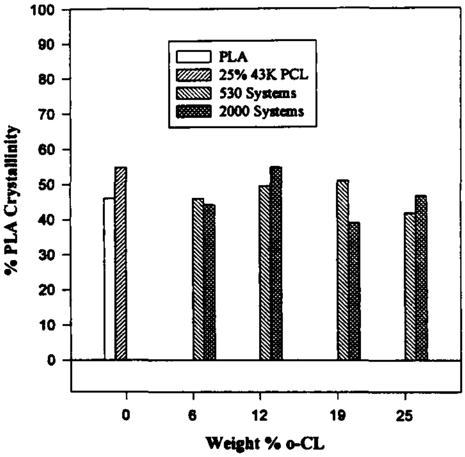

Figure 5-Induced PLA crystallinity within reactive melt blends following solution-casting.

Figure 6 illustrates that PCL and o-CL reduce the elastic moduli of the binary and ternary blends. However, the presence of 530 o-CL shows more statistically significant increases in material rigidity throughout the compositional range of oligoester if utilizing the 43K PCL/PLA blend as a point of reference. The fact that similar results are not as clearly manifested within the 2000 o-CL systems may stem from the variable degree of phase separation initiated by changing the average sequence length of o-CL. Since 530 o-CL plasticizes the PLA non-crystalline phase in a more obvious fashion than 2000 o-CL, the smaller o-CL may act to minimize the effect of the PCL glass transition as the adhesion between longer segments of PCL and PLA is improved(19-20). In contrast, the 2000 o-CL preferentially interacts with 43K PCL and thus, reinforces the α-transition of PCL, causing the blends to be less rigid. Nevertheless, it should be simply stated that molecular weight may play a role in the magnitude of blend embrittlement as the M_n values of the 2000 o-CL blends significantly exceed those of 530 o-CL.

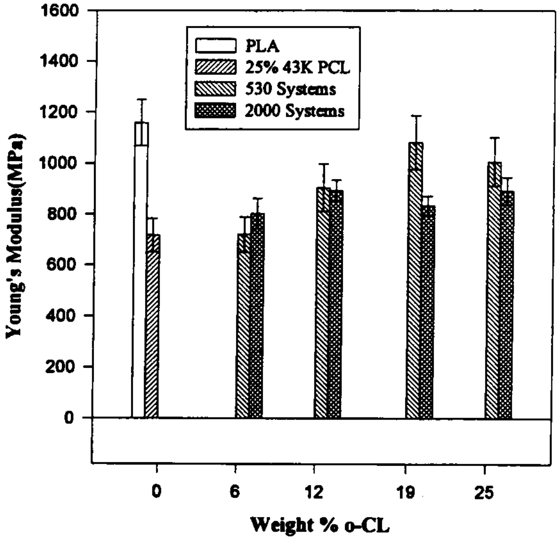

Figure 6-Elastic moduli of binary and ternary blends relative to PLA.

Table 2 depicts the consistent reduction of stress-at-yield(σ_y) and elongation-at-yield(ε_y) values of the binary and ternary blends relative to the PLA homopolyester. Once again, such behavior may be explained with regards to the flexible nature of PCL that facilitates less impeded molecular motion(chain slippage) which is integral in relieving stress concentrations. As plastic deformation ensues, the size and abundance of spherical

Table 2. Yield Properties of Binary and Ternary Systems relative to PLA.

System	% o-CL	% PCL	% PLA	σ_y(MPa)	% Loss(σ_y)	ε_y($x10^{-3}$)	% Loss(ε_y)
PLA	0	0	100	22.5+/-1.4	-----	46+/-4.3	-----
25-43K	0	25	75	12.0+/-0.7	47	37+/-2.5	20
6-530	6	19	75	10.5+/-1.3	53	36+/-2.6	22
12-530	12	13	75	17.0+/-0.5	24	28+/-1.4	39
19-530	19	6	75	20.7+/-1.1	8	24+/-1.5	48
25-530	25	0	75	16.9+/-1.7	25	23+/-1.8	50
6-2K	6	19	75	13.8+/-0.8	39	23+/-1.3	50
12-2K	12	13	75	15.0+/-1.4	33	27+/-2.5	41
19-2K	19	6	75	15.5+/-0.9	31	30+/-2.7	35
25-2K	25	0	75	18.0+/-1.5	20	35+/-2.5	24

inclusions[Figure 7] coupled with the notion that the shorter o-CL chains cannot sustain substantial deformation leads to a higher probability of catastrophic failure at low elongations[Figure 8] as the material imperfections agglomerate and propagate under a tensile load.

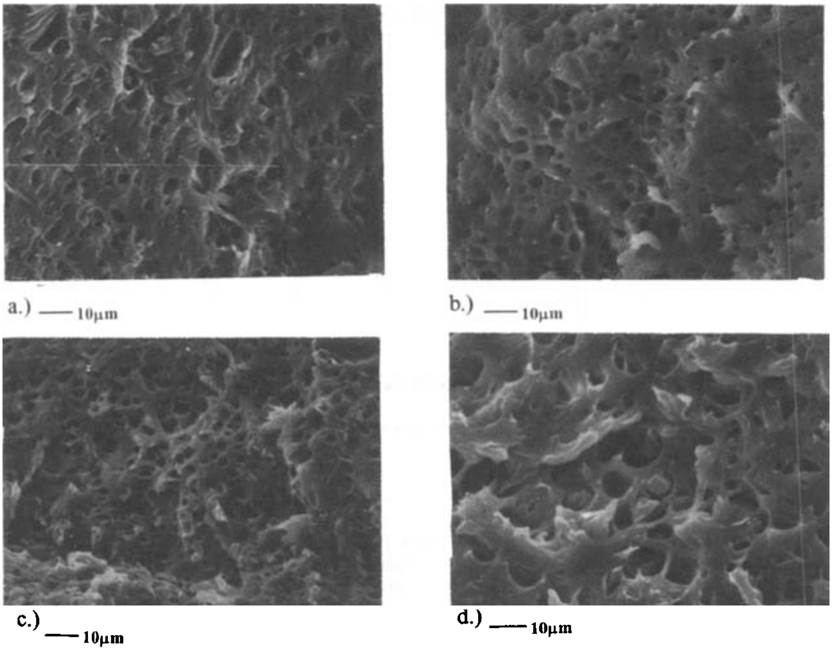

Figure 7-Freeze-fracture surfaces of binary and ternary blends: a.) 25% 43K PCL, b.) 25% 530 o-CL, c.) 25% 2000 o-CL, d.) Representative ternary system.

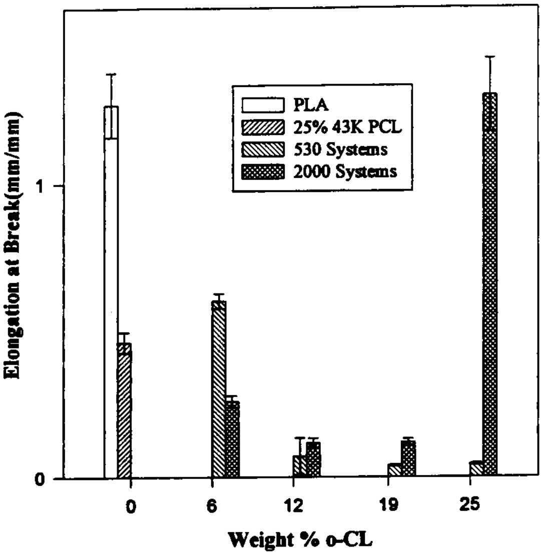

Figure 8-Ultimate elongation of binary and ternary blends relative to PLA.

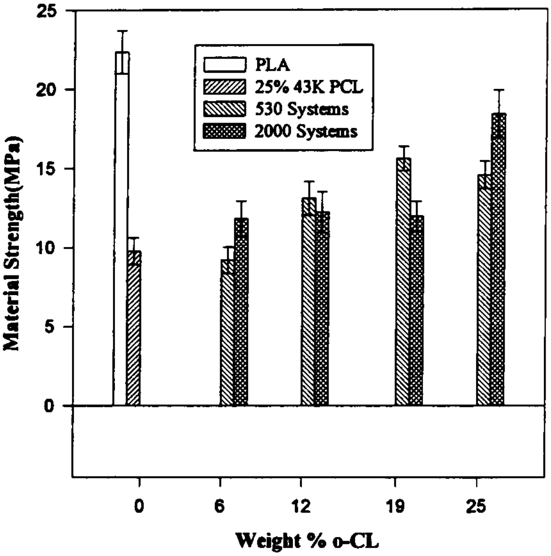

Figure 9-Strength of binary and ternary blends relative to PLA.

In accord with the principles established in response to the elastic moduli of the blends, Figure 9 solidifies the prevailing question of o-CL diffusion/interaction versus a molecular weight effect as the predominant mode of modification since material strength values reside between the 43K PCL/PLA blend and PLA itself. Even with this uncertainty, these results could prove to be beneficial if considering applications that require comparable and somewhat predictable properties with respect to PLA with the added feature of hydrolytic resistance.

CONCLUSIONS

During the melt processing of the binary and ternary PCL/PLA blends, the tendency of these materials to undergo thermal and hydrolytic degradation warranted the decision to solution-cast the blends following the initial reactive condition. While this choice of film preparation raises the question of morphological differences that may result from solvent-polymer interaction, the mechanical properties of the blends seem to retain their dependence upon the average size of PCL. The mere presence of PCL, irrespective of size, provides considerable ductility to the blends if contemplating the characteristic yield behavior of PLA. The effects of size become more evident as a narrow range of Young's moduli and strength may be defined according to the composition of o-CL. Despite these intermediate properties seen between 43K PCL/PLA and PLA, speculation regarding the exact reason for this occurrence must not overlook the possibility of o-CL diffusion within the PLA phase along with the contributing factor of stress concentrations that accompany changes in molecular weight.

ACKNOWLEDGEMENT

Financial support from the National Corn Growers Association and the State of Connecticut Critical Technology Funds as well as samples of PLA from Cargill and PCL from Union Carbide are gratefully acknowledged.

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