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# Aliphatic Polyester Blends Based upon Poly(Lactic Acid) and Oligomeric Poly(Hexamethylene Succinate)

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# ALIPHATIC POLYESTER BLENDS BASED UPON POLY(LACTIC ACID) AND OLIGOMERIC POLY(HEXAMETHYLENE SUCCINATE)

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## ABSTRACT

In an attempt to gain a degree of control over the mechanical and degradation properties of poly(lactic acid) [PLA], large-scale efforts are underway to alter the phase morphology of PLA through chemical and physical modification. Consistent with this theme, our work aims to adjust the molecular architecture of highly amorphous PLA with an increasing concentration of hydroxy-terminated oligomeric poly(hexamethylene succinate) [PHS]. Gel-permeation chromatography (GPC) verifies the enhanced presence of PHS in the blends with a concomitant reduction in number-average molecular weight as the weight fraction of PHS is raised from 0.10 to 0.40. Differential scanning calorimetry (DSC) indicates amorphous phase compatibility between PHS and PLA at weight compositions of 10/90 and 20/80. However, as the amount of PHS approaches 30 and 40 wt%, the PHS exhibits the ability to crystallize independently from the induced PLA crystalline phase. Dynamic mechanical thermal analysis (DMTA) illustrates variable behavior of the materials under tension as a consequence of structural alterations generated by the oligoester. Finally, preliminary results suggest that these alterations may suppress the hydrolytic degradation of PLA.

## INTRODUCTION

PLA has been considered for high-volume commodity use [1, 2] as a result of its biocompatible degradation products and attractive physical properties. Such properties have been manipulated extensively within the field of biomaterials [3-10]. Unfortunately, PLA does not possess the thermal and hydrolytic stability [11-13] that are crucial when applying the typical high processing temperatures. If these deficiencies of PLA are coupled with a mechanical performance profile that is highly dependent upon stereoregularity [1], it is evident that the recent attention given to PLA within the scientific community is warranted.

In order to address these shortcomings, a generalized approach has been established:

(i) Introduce systemic flexibility
(ii) Alter the specific hydrophilic/ hydrophobic balance
(iii) Impart additional multiphasic character

A credible method to implement these proposed solutions is physical blending of PLA [14-20] with appropriate secondary components. This work serves to contribute to the vast amount of research and development currently directed towards PLA modification by incorporating a succinate-based [21-25] oligoester with the expectation of providing an avenue to control the multiphasic character of highly amorphous PLA. Furthermore, future utility of these blends may be realized from a financial standpoint as the lactate and succinate residues of the respective polyesters may be derived from fermentation of naturally abundant carbohydrates [26].

## EXPERIMENTAL

### Characterization Methodology

Infra-red (IR) spectroscopy was applied to chloroform solutions of the samples of interest with the aid of a Mattson Cygnus® IR spectrometer. $^1$H-NMR spectroscopy was carried out using Bruker DMX-500MHz solution NMR instrumentation with $CDCl_3$ as the solvent of choice. Molecular weight analysis was performed with gel-permeation chromatography (GPC) [Waters Model 150-C ALC] using poly(ε-caprolactone) [PCL] standards in tetrahydrofuran at 30°C. Differential scanning calorimetry (DSC) was administered using a TA 2920 differential scanning calorimeter. The reported thermal transitions and heats of fusion were obtained from second heatings of the materials at 20°C/min from -80°C to 180°C. Dynamic mechanical thermal analysis (DMTA) [Model Mk II] was utilized at a heating rate of 2°C/min from -80°C to observe additional multiphasic character that may go undetected due to the sensitivity limitation of DSC. Hydrolytic stability of the materials was tested in NaOH buffer, pH 7.4, at 37°C by monitoring the weight loss of compression-molded films over 35 days.

### Materials

1,6-hexanediol (Aldrich, 99%) [HDL], diethyl succinate (Aldrich, 99%) [DES] and stannous 2-ethyl hexanoate (Sigma, 95%) [SnOct] catalyst were used according to the reported commercial purity. A highly amorphous PLA[91%(L), $T_g$~64°C (DSC)] was generously supplied by Cargill, Inc. The number-average molecular weight (Mn) of the polyester was approximately 65,000 Daltons as determined through PCL standard calibration.

### Synthesis of Oligoester

234 mmol HDL, 213 mmol DES and 0.110 mmol SnOct were charged to a reaction vessel previously flame-dried and thoroughly flushed with nitrogen. The vessel was fully equipped with adequate stirring, a nitrogen inlet and a distillation flask to collect ethanol as the reaction by-product. To generate oligomeric poly(hexamethylene succinate) [PHS], the contents of the vessel were heated to 150°C for 1 hour followed by incremental heating at approximately 20°C per hour up to 190°C. The temperature was held at 190°C for 2 hours followed by heating to 230°C over 1 hour. The mixture was maintained at 230°C for 3 hours. Following a slow cool to room temperature, the crude solid was dissolved in chloroform, filtered gravimetrically and precipitated in cold methanol. After filtration, the product was washed with methanol and vacuum dried at 30°C for 24 hours. The preceding synthetic procedure produced an oligoester with a Mn of ~1300 Daltons (GPC). End-group analysis ($^1$H-NMR) of the oligoester yielded a Mn of 1865 Daltons. The hydroxy-terminated PHS melted at 42.8°C with a glass transition temperature detected at -54.8°C.

IR($CHCl_3$): 3365 cm$^{-1}$(O-H stretching), ~2947 cm$^{-1}$ and 2867cm$^{-1}$(C-H stretching), 1728 cm$^{-1}$(C=O stretching), 1413 cm$^{-1}$(C-H bending), 1219 and 1161 cm$^{-1}$(C(=)-O and O-C-C assymetric coupled stretching).

$^1$H-NMR($CDCl_3$, 1% TMS v/v): 1.24-1.27ppm(2H, Terminal $CH_2$, HDL), 1.38 ppm (4H, $CH_2$, HDL), 1.58-1.64 ppm (4H, $CH_2$, HDL), 2.62 ppm (4H, $CH_2$, Succinate), 3.38-3.40 ppm (2H, Terminal OH, HDL), 3.64 ppm (2H, $CH_2$, HDL), 4.07- 4.17 ppm (4H, $CH_2$, HDL).

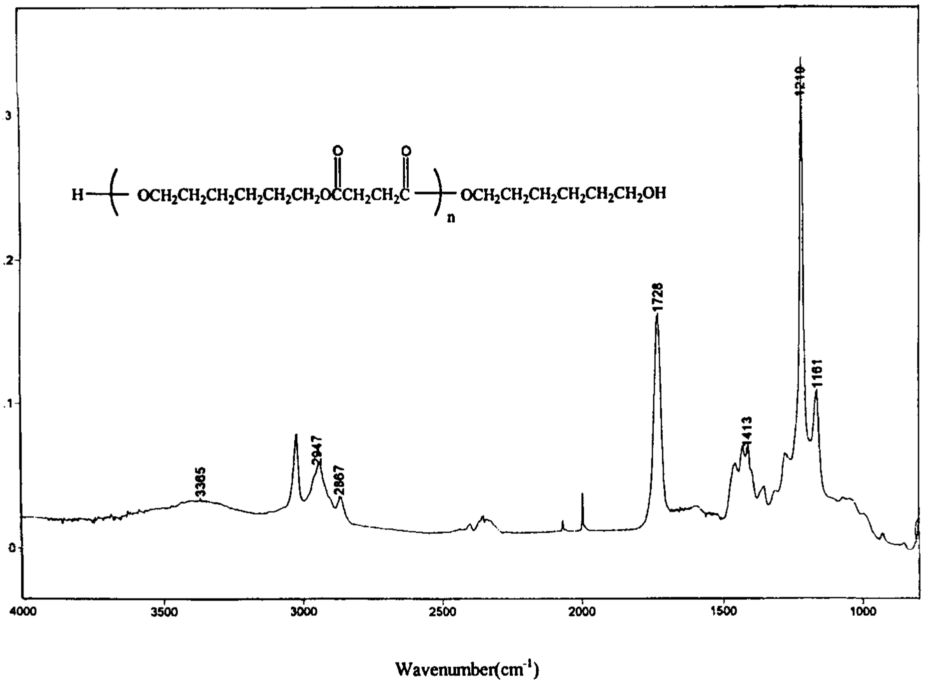

**Figure 1.** R Spectrum of Poly(hexamethylene succinate) [PHS] in $CHCl_3$.

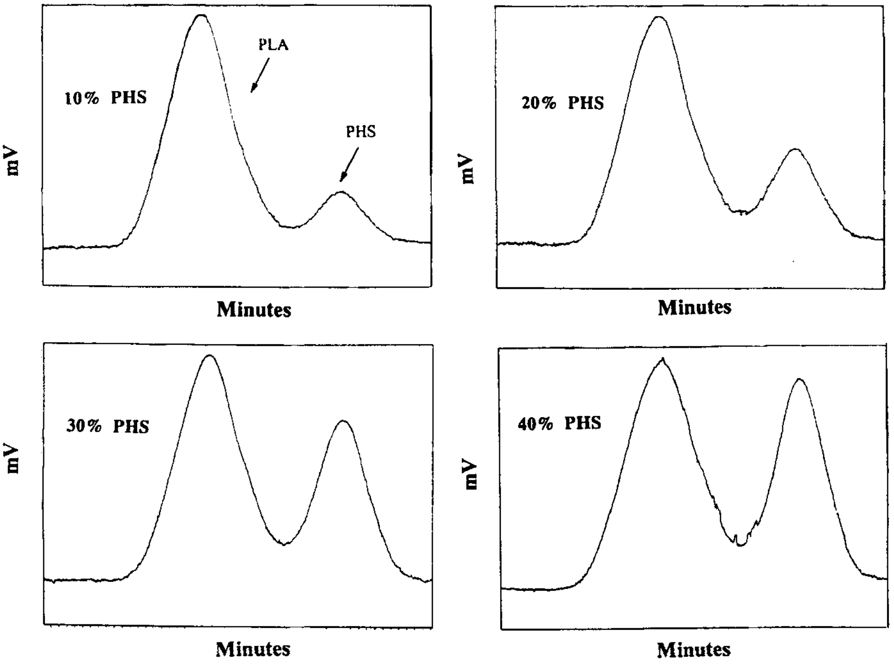

**Figure 2.** $^1$H-NMR Spectrum of Poly(hexamethylene succinate) [PHS] in $CDCl_3$.

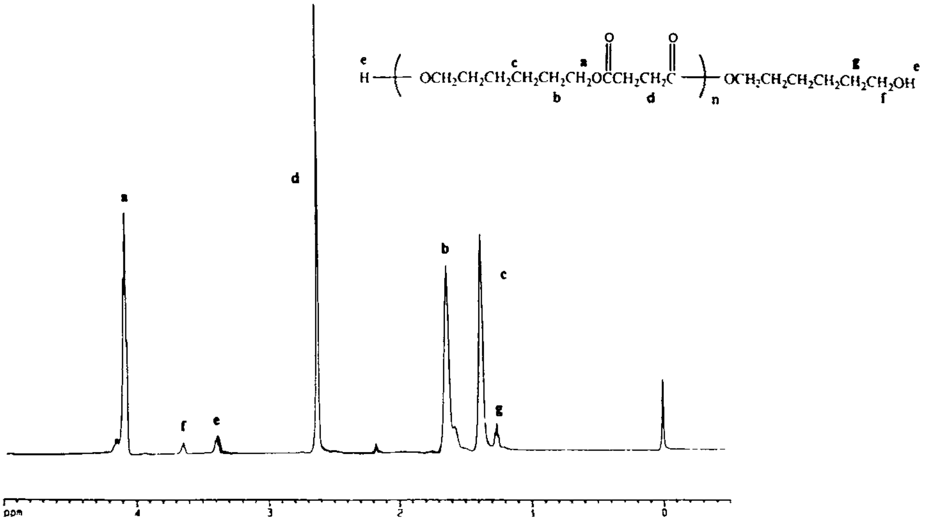

**Figure 3.** Gel-permeation chromatographs of PHS/PLA reactive melt blends.

### Blend Preparation

Melt blends of 10, 20, 30 and 40 wt% PHS relative to PLA were prepared in a C.W. Brabender®at 180°C and 40 rpm for 20 minutes. The blends were subsequently analyzed without further purification (Figures 1 and 2).

## RESULTS AND DISCUSSION

### Blend Characteristics

Figure 3 illustrates the enhanced presence of PHS oligoester within the reactive melt blends as the relative chromatographic intensity of the variably-sized polyester components approaches unity. Also, each elution time does not appear to vary significantly as concentration adjustments are made. With regards to changes in molar mass within the blends, Figure 4 outlines a comparative analysis between the theoretical and experimentally calculated number-average molecular weights. Any discrepancy between theoretical and experimental values may be attributed to inter- and intramolecular transesterification [11-13] as well as the presence of residual tin catalyst which may serve to contribute and/or accelerate the degradative exchange reactions [13].

Figure 5 displays an overlay of the DSC thermograms for the PHS/PLA blends. The blends exhibit different degrees of amorphous compatibility at 10 and

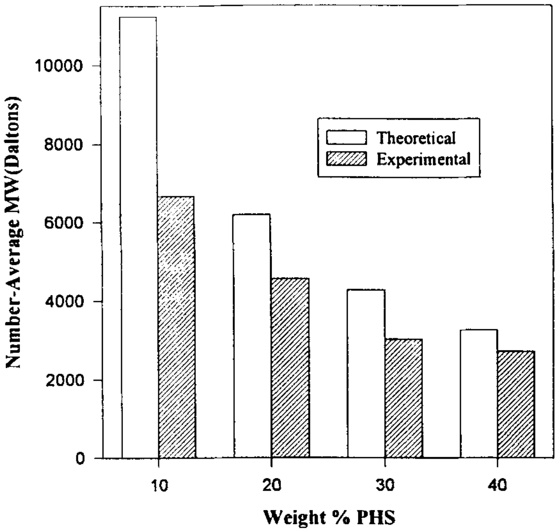

**Figure 4.** Comparative molecular weight analysis: The effect of reactive blending at 180°C.

20% PHS if the Fox equation (27) is employed:

$$(1/T_{gblend}) = (w_1/T_{g1}) + (w_2/T_{g2})$$

-where $w_1$,$w_2$ are the weight fractions of the blend constituents and the absolute temperature scale is utilized. According to this relation, if thermodynamically miscible blends exist at 10 and 20% PHS, the glass transition temperatures would be at 46.8°C and 31.2°C, respectively. The observed $T_g$ at 10% PHS (47.5°C) agrees favorably with the value predicted by the Fox equation. At 20% PHS, a $T_g$ of 42.0°C suggests a level of phase separation that is not manifested through DSC analysis. Contrary to these thermal characteristics, blends containing 30 and 40% PHS show transitions that resemble first order, melt endotherms for each blend constituent [i.e.-~40°C for PHS and ~155°C for the PLA phase]. The induced PLA crystalline phase is evident within each blend. However, the normalized heats of fusion (Figure 6) of this phase do not show a simple progressive relationship as the PHS content is increased. Instead, it appears that the extent of PLA crystallization may be a function of PHS concentration as the frequency of PHS-PHS and PHS-PLA interactions becomes an issue.

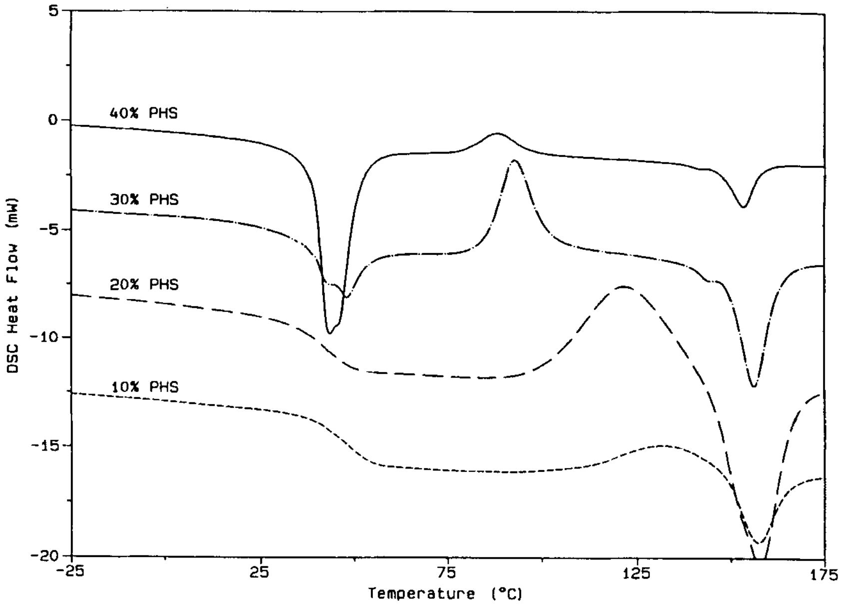

**Figure 5.** DSC thermograms overlay of PHS/PLA reactive melt blends.

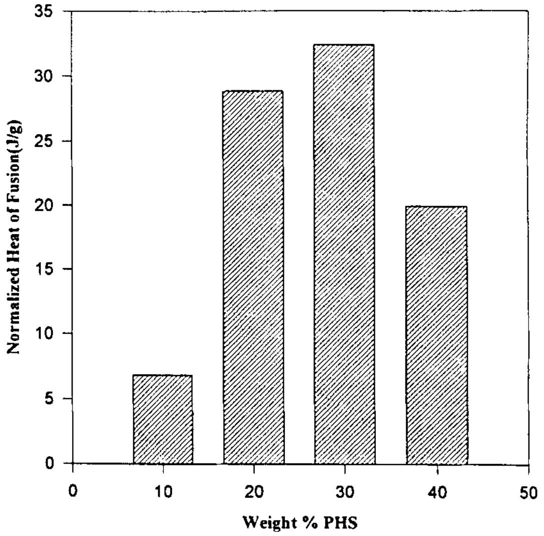

**Figure 6.** Comparative normalized heats of fusion: Induced PLA crystalline phase.

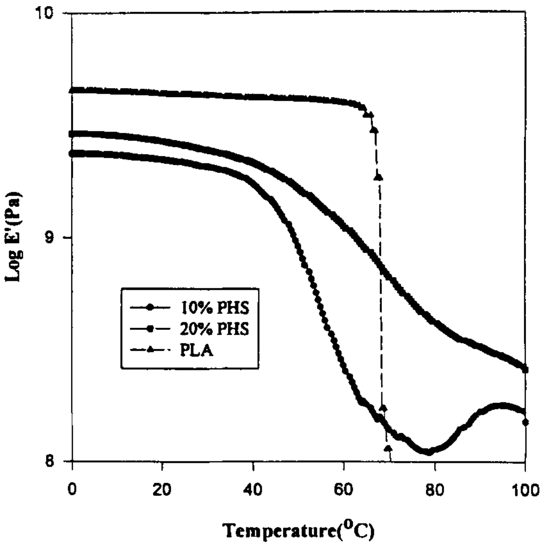

**Figure 7.** DMTA overlay of 10 and 20% PHS/PLA reactive blends: Comparative effect upon PLA.

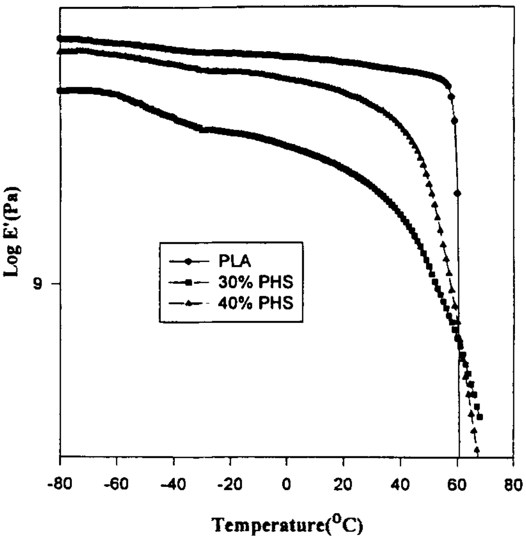

**Figure 8.** DMTA overlay of 30 and 40% PHS/PLA reactive blends: Comparative effect upon PLA.

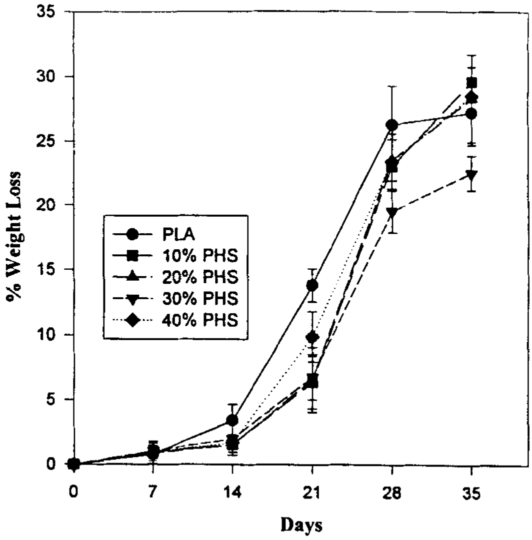

**Figure 9.** Preliminary comparative analysis: Weight loss profile of PLA versus PHS/PLA blends.

A more detailed investigation of the thermal behavior of the blends through DMTA yields results that coincide with the reported thermal transitions from DSC. Figures 7 and 8 describe the plasticizing effect of PHS upon the PLA amorphous phase with the added feature of extending the rubbery plateau due to the reinforcing effect of the systemic crystallinity. These effects are more pronounced for the 10 and 20% PHS blends. Furthermore, as the oligoester and PLA begin to show the ability to crystallize independently within the 30 and 40% PHS blends, an additional inflection is seen at ~-50°C, indicative of the PHS amorphous phase. This inflection is more distinct for the 30% PHS blend as the elevated magnitude of PHS crystallinity within the 40% blend tends to flatten the corresponding glass transition.

With this variable phase behavior in mind, Figure 9 depicts the hydrolytic stability of the blends relative to the PLA homopolyester. The weight loss profiles imply the hydrophobicity of PHS coupled with its effect upon morphology at the defined concentrations could promote the suppression of hydrolytic degradation of PLA between 14 and 28 days as the accessibility of the PLA amorphous phase is altered [28]. Nevertheless, this statement must be further substantiated before any broad generalization is established as an intimate understanding of degradation kinetics is far from trivial.

## CONCLUSIONS

Throughout the compositional range of the reactive melt blends, varying levels of phase separation are observed. While separation is most evident at 30 and 40% oligoester with the appearance of PHS and PLA phase crystallinity, a comparison between theoretical and experimental glass transition temperatures at 20% PHS implies microphase separation. In any event, aside from the potential financial benefits that may originate from the availability of succinate and lactate residues, the structural alterations generated by the oligoester could provide broad utility in terms of mechanical properties and hydrolytic stability. However, the likelihood of degradation during high temperature processing and the accompanying changes in average sequence length/distribution must not be overlooked if considering these materials for specific applications.

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