Characterization of Multiphase Biogenic Polymer Blends from Poly(L-lactide) and Poly(methyl methacrylate)

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ABSTRACT

Melt processing of binary immiscible polymer systems has been a focus of our group as an economical and scalable route to achieve synergistic or superior mechanical properties at and around the co-continuous region without the need of compatibilization. System of poly(L-lactide) (PLLA) and poly(methyl methacrylate) (PMMA) was selected to target bio-related applications, including bone fillers and scaffolds, where the biodegradability of PLLA will enable the integration of native tissue into the material over time. Tunable properties such as morphology, interconnectivity, resorbability and interfacial bonding control the long-term integrity of the new material and influence the interaction and integration of new tissue. Binary blends of PLLA and PMMA has been prepared and characterized over a large range of compositions in which regions of co-continuity are of special interest. Such regions exhibit a well interconnected structure that ensures controlled release of resorbable PLLA. Modulated differential scanning calorimetry (MDSC) detected a broad and unexpected transition between 70 $^{\circ}$C and 100 $^{\circ}$C. The magnitude of this transition is greatest within co-continuous regions, suggesting the presence of a complex or other derivative of the two primary phases. This complex appears to provide a degree of compatibilization between the phases, thus inducing mechanical property synergism which has been confirmed by flexural and nano-indentation analyses.

INTRODUCTION

Thermo-mechanical mixing of two or more polymers is a preferred method for new material development since it does not involve costly synthesis while process scale-up can be achieved quickly and inexpensively. Under optimal processing conditions, thermal polymer blends may exhibit synergistic and advantageous properties [1]. Miscible blends and/or compatibilized immiscible blends are the main objectives for thermal blending, but uncompatibilized immiscible blends have recently gained significant attention [2] due to their ability to provide unexpected properties. Studies have shown that for certain applications such as bone fillers and tissue scaffolds, immiscible blends have specific advantages in morphological and mechanical properties. Presently, it is believed that co-continuous nature of certain immiscible compositions gives rise to the synergistic properties due to the intimate interaction between the components.

Multiphase polymer blends in which one phase is transient and another phase is persistent can provide the ideal balance of phases with the ratio modified to meet the specific application and to produce the desired results [3]. The initial processing of the blend is important and numerous physical properties of the polymers, particularly the rheology, are critical and determine the properties and morphology of the resultant blend. An additional issue that requires

consideration is the nature of the phase interface in immiscible blends. A weak interface can have an adverse effect on the mechanical properties of the blend [4], whereas a non-bonded interface or even the development of reaction products at the interface can impart important functionality to the blend.

Our research group is interested in the processing and properties of immiscible polymer blends. Previous works have shown that thermal processing of immiscible polymers is morphologically bio-mimetic and possess biocompatibility. For previous work as well as work described in this paper, we have selected PLLA and PMMA to render the blends degradability and mechanical support, respectively, over time. The selected materials are biocompatible (PLLA), bio-inert (PMMA), are thermally co-processable. Unlike other immiscible systems such as PLLA/PCL blends [4], this system does not suffer from poor adhesion between phase, as evident in the synergism of the blends' mechanical properties shown later in this paper.

EXPERIMENTAL DETAILS

Materials and Blend Formulation

Extrusion-grade PMMA was obtained in the form of clear pellets [Atofina Chemicals Inc., Philadelphia, PA, USA]. Medical-grade of poly(L-lactide) (PLLA), Purasorb® PL, was obtained in the form of white granular powders [Purac America, Lincolnshire, IL, USA]. Rheology measurements were performed on both polymers using a TA AR 2000 rheometer [TA Instruments, New Castle, DE, U.S.A] over a range of shear rates for relevant temperatures. The data are to be used in predicting the composition range over which co-continuous blends are expected. The elected method is by Jordhamo [5], which states co-continuity exists when the following relationship between the volume fraction (Φ) ratio and the viscosity (η) ratio of the components at the processing temperature is satisfied:

$$\frac{\eta_A}{\eta_B} \cong \frac{\Phi_A}{\Phi_B} \tag{1}$$

The PLLA/PMMA composition that conforms to this relationship is 45% for Purasorb® PL by volume as shown in Table I.

Table I. Viscosity data measured from Rheometer AR-2000
to be used to predict co-continuous compositions (200 °C)

Raw Materials:	PLLA	PMMA
Density (g/cm^3)	1.275	1.18
Viscosity (Pa.s)	4828	5844
η(PLLA) / η(PMMA)	0.826	
Co-continuous composition, volume percent PLLA	45.2	
Note: Viscosity values in this table were obtained at T = 200 °C and γ = 39.25 s^{-1}		

In previous work, only compositions in the immediate neighborhood of the predicted co-continuity were investigated. In this work, however, a full range of compositions were formulated, as shown in the complete list of blends in Table II, to further investigate the blends.

Table II. Composition of PLLA/PMMA Blends (all values in percent)

Blend Number	PLLA		PMMA	
	Volume	Weight	Volume	Weight
1	0	0	100	100
2	10	11	90	89
3	25	27	75	73
4	30	32	70	68
5	35	37	65	63
6	40	42	60	58
7	45	47	55	53
8	50	52	50	48
9	55	57	45	43
10	60	62	40	38
11	80	81	20	19
12	100	100	0	0

Processing and Sample Preparation:

The PLLA and PMMA polymers were dried for 47 hours in a vacuum oven (30 mmHg) at 45 °C and 70 °C, respectively, prior to processing. Batches of 140-g size were weighed out and melt processed in a 19-mm single screw laboratory extruder [C. W. Brabender, Inc., Hackensack, NJ] fitted with a mixing screw of 0.655" average root diameter. An average shear rate of 39.25 s^{-1} was achieved at 200 ^{o}C by operating the extruder at 50 revolutions per minute. A 20/100/20 screen pack was installed after the barrel and before the 1/8" screw-in nozzle. Selected processed rods were cut into 80-mm segments for flexural 3-point bending test utilizing a Dynamic mechanical analyzer (DMA) [Perkin-Elmer 7E, Wellesley, MA, USA]. Thin discs were sliced from extruded rods using sharp blade to be used for thermal analysis using Differential Scanning Calorimetry (DSC) [TA Instruments Q1000, New Castle, DE, USA]. Cross-sectional discs were also taken from 1/3 and 2/3 of the total extrudate using a saw blade, embedded in epoxy, allowed curing overnight at 40 ^{o}C inside a temperature-controlled chamber [Isotemp® Oven, Fisher Scientific, Pittsburgh, PA, USA], and polished for subsequent characterizations using nano-indentation [TriboIndenter, Hysitron, Minneapolis, MN, U.S.A]

Films (40 µm) of PLLA and PMMA were obtained by compression molding fine particle at 200 °C using a Carver Hydraulic Press [Carver, Inc., Wabash, IN, USA]. Fine particles with maximum dimension of 600 µm were obtained via cryogenic milling of granules (PLLA) and pellets (PMMA) using an IKA A10 analytical mill [Janke & Kunkel, Staufen, Germany]. The films were cut into 1x1 square inch and laminated in desired compositions. Subsequent cutting (into quartets), stacking and re-pressing were done to simulate increase in shear force. Total pressing time for each sample was 3 minutes; average final thickness was 70 µm. All films were quenched by cold water (10 ^{o}C) prior to de-molding.   Circular specimen of 1/8" in diameter

were punched out, stacked and crimped in aluminum pans for subsequent thermal analysis. Data reported in this paper were collected on one composition (50% PLLA by volume).

Characterizations

Differential Scanning Calorimetry experiments were conducted in modulated mode (MDSC) to separate thermal (reversing, e.g. glass transition) from kinetics (non-reversing, e.g. crystallization) events. All runs included an initial heating, followed by a cooling and a reheating cycle. MDSC modulation parameters consisted of: amplitude = 2 °C, period = 40 sec, ramp rate = 2 °C/minute and temperature range = 20 – 210 °C. The data shown here were taken from the reversing signal of the reheating cycle and shown as the derivative. Maxima of data represent inflection points on the original DSC thermograph, which indicated mid-point glass transition temperatures.

Dynamic mechanical analysis (DMA) using a Perkin-Elmer 7E with a modified sample holder helps determine the elastic modulus. Three-point bending flexural test was run on cylindrical samples, 4-5 mm in diameter with an 80-mm span to maintain a minimal L:D ratio of 16:1. Loading rate used on these samples was 250 mN/min. Nano indentation tests were performed with constant load rate of 300 μN/sec with peak load of 300 μN. 18 indentations were done on two sets of specimens for each composition.

DISCUSSION

When blending polymer thermally, the resulting material can be a miscible blend, in which case a single-phase alloy forms, or it can be immiscible, in which case the glass transition (T_g) of each component is distinct in the blend. As being reported elsewhere, PLLA/PMMA polymer blend system exhibits not only the two glass transitions of the two blended components (PLLA and PMMA), but also a third, immediate glass transition whose phase has been termed PG80 [6].
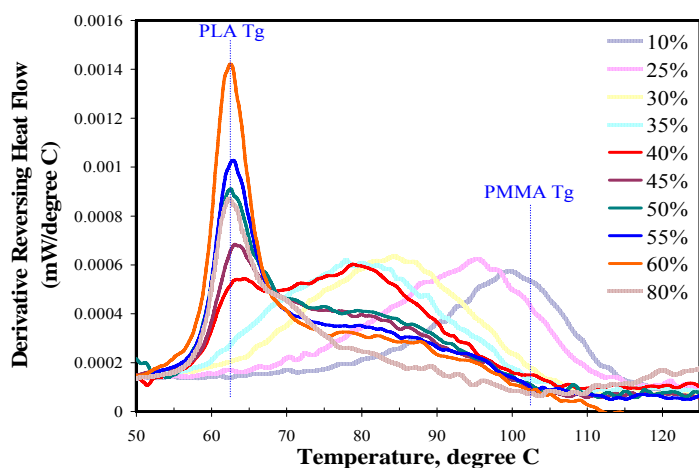
PG80 is confirmed in both extruded (figure 1) and compression molded (figure 2) samples. Derivative representation of thermographs in figure 1 encompasses 10 blends ranging from 10% to 80% PLLA by volume, including the predicted co-continuity composition (45%). The maxima here correspond to inflection points on the raw curves and depict glass transition temperatures. The area under the curve represents the enthalpy that goes into the transition, and could also be used as quantitative measurement to the amount of the material in the blend.

Figure 1: Derivative of reversing heat flow from MDSC analysis of PLLA/PMMA extruded blends.

When the same thermal analysis is performed on compression molded films, the system exhibits the same trend (not shown) but the absolute intensities of the peaks are roughly an order of magnitude smaller. The differences on the absolute enthalpy, together with the trend seen in figure 2, prove that shear has a profound effect on the forming of PG80. Relative power of mixing and shearing being imposed on final film products is increased proportionally with number of laminated layers, and corresponds to an increase in PG80 peak signals.
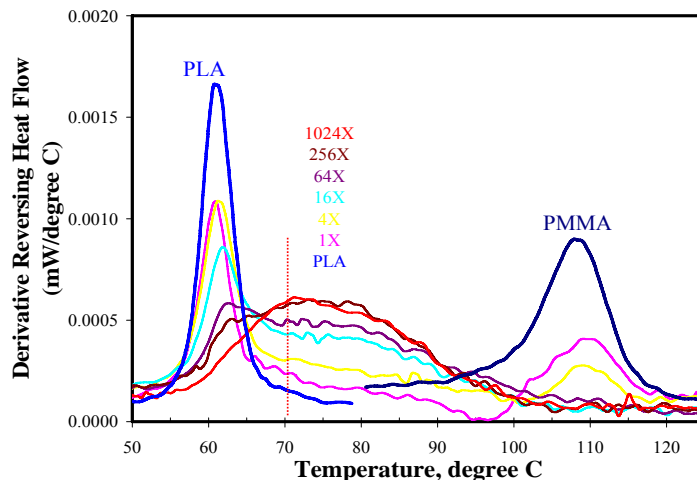
Figure 2: Derivative of reversing heat flow from MDSC analysis of PLLA/PMMA compression molded films. Data depict the effect of shearing on the formation of PG80 in 50/50 blend (by volume)
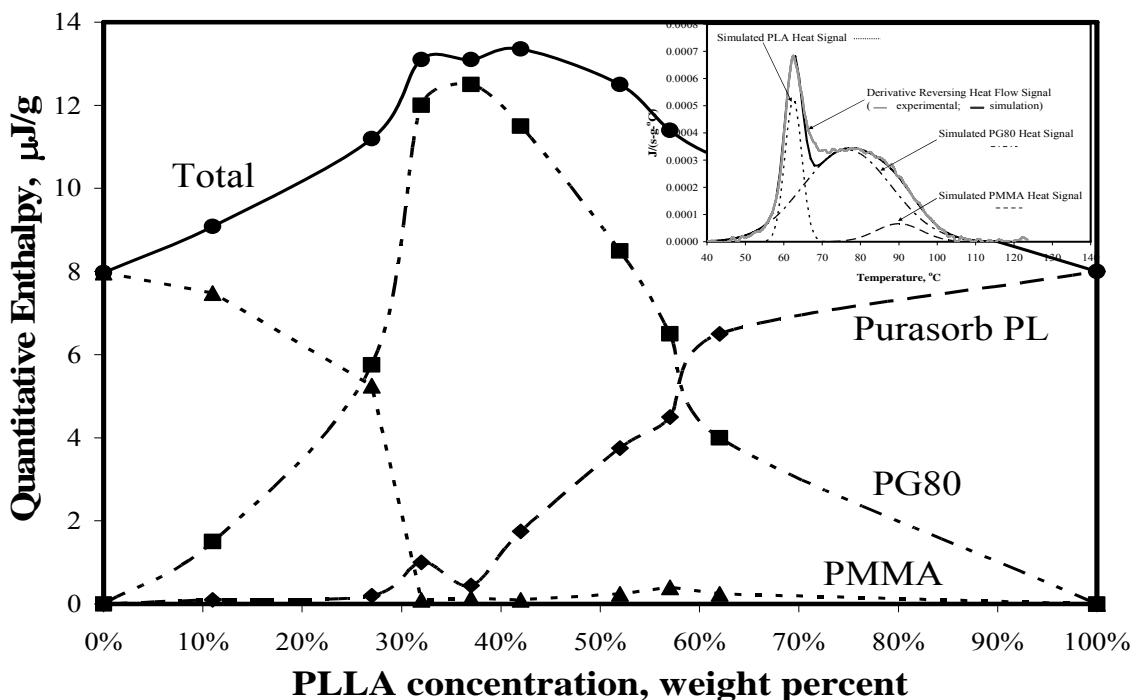
Figure 3: Quantitative DSC data for PLLA/PMMA blends show PG80 maximum near the co-continuous composition and illustrate reactant-product relationship among PLLA, PMMA and PG80, with PLLA becomes the excess reactant on or around 35% in concentration. Inset: Example of DSC curve deconvolution using normal distribution function simulations of constituent T_g derivative heat signals [6]

The degree to which PG80 is produced in earlier blends has been hypothesized to depend strongly on the co-continuity of the structure and the intimacy of the phases under this condition. Quantification of the DSC data is accomplished by deconvoluting the derivative reversing heat flow curves using a normal distribution model for the constituent derivative heat flows as being described elsewhere (figure 3 inlet) [6]. Again the 30 – 40 % PLLA is the region of greatest conversion of PLLA into PG80, illustrated by a maximum in figure 3 which is very close to the predicted co-continuity composition of 45%. At 35% when the amount of PG80 reaches the maximum, PLLA begins to behave as the excess reactant, as the formation of PG80 reduces with reduced concentration of PMMA (figure 3).

Flexural storage modulus across compositions illustrates the synergism of mechanical property in PLLA/PMMA blends. At every point over the composition range, measured values are above the rule of mixture line. Maximum increase of modulus (6%) is at 40% of PLLA, slightly below the co-continuity region (figure 4), and coincides with the region of maximum PG80 formation.
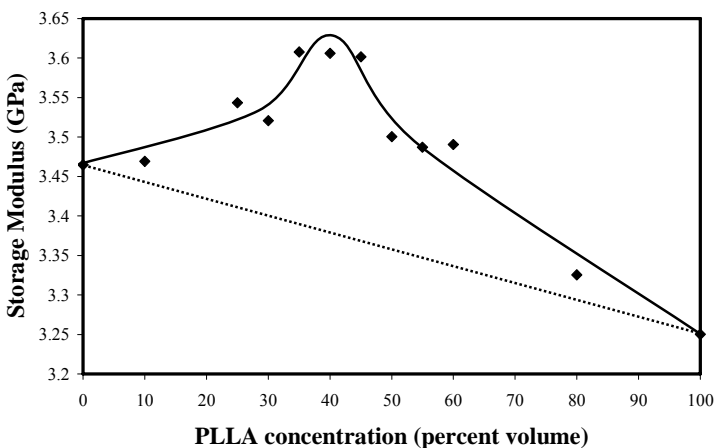

Figure 4. Flexural Young Moduli across blend compositions illustrate the synergism of mechanical properties in PLLA/PMMA blends. Maximum increase of modulus over the rule of mixing line (6%) found around the predicted co-continuity region.

Average reduced modulus obtaining from nano indentation suggested segmentations of three different regions on the tested cross sectional area (of extruded sample) and confirmed the existence of PG80. This intermediate phase seems to possess intermediate mechanical property, enable more effective stress transfer across phase boundaries. Detail modulus mapping might reveal a spatial presentation of domain size and shape, hence pending.

CONCLUSIONS

Melt processing is able to produce structures that have potential as implantable and scaffolding materials. Blending of PLLA and PMMA yields an immiscible multiphase polymer composite which at co-continuity generates a 3-D interconnecting network of the components. The formation of a reaction product, PG80, provides system stability and enhances the effect of co-continuity toward synergistic mechanical properties.

ACKNOWLEDGEMENTS

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