

Ternary polymer blends based on poly(lactic acid): Effect of stereo-regularity and molecular weight

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ABSTRACT: The effects of stereo-regularity and molecular weight of poly(lactic acid) (PLA) on ternary polymer blends was analyzed using optical clarity as the primary screening method. This enabled the ready identification of phase boundaries of optically clear and apparently miscible regions. Solvent-mediated blends of amorphous poly(DL-lactide) (PDLLA) and semi-crystalline poly(L-lactide) (PLLA) with various molecular weights from high to low, along with polycaprolactone (PCL) and cellulose acetate butyrate (CAB) were used in this study. The nature and extent of crystallinity of the blends was examined by X-ray diffraction, which, in conjunction with differential scanning calorimetry, scanning electron microscopy, and Fourier transform infrared spectroscopy, provided information about the competition between polymer crystallization (self-aggregating behavior) and intermixing of the macromolecules. Thus, allowing the primary physical cause of transparency loss to be identified. The results of the ternary blends optical clarity showed the position of the phase boundaries in PLLA/PCL/CAB and PDLLA/PCL/CAB blends are significantly affected by the stereo-regularity and molecular weight of PLA. The PDLLA (amorphous) blend shows comparable regions of phase separation with high molecular weight and semi-crystalline PLLA blends even though the molecular weight is much lower. The blends of the shorter chain PLLA1 tend to show more crystalline regions. The optical transparency, miscibility, and crystallinity of the blends are not only affected by the stereo-regularity and molecular weight of PLA but also the crystallizable PCL, especially at high loading. These findings give useful information to the film-packaging sector where good optical clarity is a critical performance requirement. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41780.

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INTRODUCTION

Poly(lactic acid) or polylactide (PLA), a biodegradable and bio-compatible polymer, shows good potential for use in many applications, such as drug delivery devices, tissue-supporting scaffolds, and film packaging. PLA has already been used for some of these applications; however, it has not been fully adopted as the usefulness of PLA is limited by its brittleness and other properties for example limited thermal processing.^{1–7} As a chiral polymer, the structural formation of PLA depends on the stereo-regularity on its backbone. Therefore, PLA can be classified into three different types; poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA)-crystallizable polymers, and poly(DL-lactide) (PDLLA)—an amorphous polymer.^{8,9}

In the literature, many researchers have shown that the properties of PLA binary blends (such as, mechanical and optical

properties, degradation rate, miscibility, and morphology) are influenced by the stereo-regularity of the PLA used. For example, Lv *et al.*¹⁰ studied the effect of amorphous PDLLA on the molecular orientation and crystallization on crystalline PLLA stretching. The results show that PDLLA prevents close intermolecular packing from the oriented segments, which leads to less cohesive mesophase formation in the blends. Several researchers have studied miscibility and crystallization behavior of PLLA and PDLLA blends in an effort to reduce the brittleness of crystalline PLLA.^{11–15} Another paper compared blends of PLLA and PDLLA with polyvinylphenol and polystyrene by means of molecular dynamics modeling to predict the miscibility of the blends.¹⁶ Both PLLA and PDLLA were predicted to be miscible with polyvinylphenol, while immiscible with polystyrene and the experimental behavior agreed with the predicted results. Also, Fukushima *et al.*¹⁷ found that the degradation of

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PDLLA proceeded much faster due to its amorphous structure. These related PDLLA papers show that the amorphous structure of PDLLA affects the compatibility of the blend as well as degradation ability, as the hydrolysis rate of PDLLA is faster than PLLA.

An important point to note is that the effect of stereo-regularity of PLA studied in binary blends are considerably represented in the literature; however, three component blends appear significantly less frequent and are not yet fully understood. In previous work, we investigated optical clarity of novel ternary blends of PLLA/polycaprolactone (PCL)/cellulose acetate butyrate (CAB) these blends improved the properties of PLLA by interactions between polymer pairs (i.e., PLLA/CAB, PCL/CAB).¹⁸ Although, optical clarity is not an absolute predictor of the miscibility of polymer blends as noted under the IUPAC definition,¹⁹ it is very useful as an indicator of transitions in phase behavior and of the existence of compositions that are able to produce suitable blends for those specific applications, especially in film packaging.

This work is concerned with expanding on what we learnt in our previous paper¹⁸ by not only focusing on molecular weight but the effect of stereo-regularity and molecular weight of PLA and how this effects both binary and ternary blends of PLA with other polymers (PCL and CAB). Optical clarity (as measured via the rapid screening method) was the primary analysis tool but to provide a more detailed study of the blends, crystallinity and morphology were studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. Fourier transform infrared spectroscopy (FTIR) was also used to identify the shifting of spectra of certain functional groups presented in the blends. These taken along with the optical clarity data give a good guide to understanding blend performance.

EXPERIMENTAL

Materials

Two isomers of PLA: L-isomer (PLLA, a semi-crystalline polymer) and DL-isomer (PDLLA, an amorphous polymer) were used for blending. Four different molecular weights of PLA were used, three of the L-isomer and one DL-isomer: PLLA1 ($M_n = 18,700$ g/mol, Cargill Dow, Minnetonka, MN), PLLA2 ($M_n = 67,000$ g/mol, Sigma-Aldrich Co., USA), and PLLA3 ($M_n = 100,000$ g/mol, Nature Work Co., Thailand). PDLLA ($M_n = 40,000$ g/mol) and PCL ($M_n = 7500$ g/mol) are from Sigma-Aldrich Co., Gillingham, Dorset, UK and CAB ($M_n = 40,000$ g/mol, butyryl 50 wt %, acetyl 2.8 wt %, hydroxyl 1.7 wt %) is from Eastman Chemical Co. Capelle aan den IJssel, The Netherlands. Their molecular structures are shown in Figure 1. A 96-well non-sterile polypropylene microplate (CL S3365, Sigma-Aldrich) was used owing to its resistance to the solvents used.

The Rapid Screening Method

It is normally extremely time- and resource-consuming process to do solution blends with full sized solvent or thermally casted films, thus in order to enable a large number of samples to be measured quickly and effectively, the rapid screening method that we developed in our previous work was used. It allows the optical clarity for a full range of solvent blend cast films to be

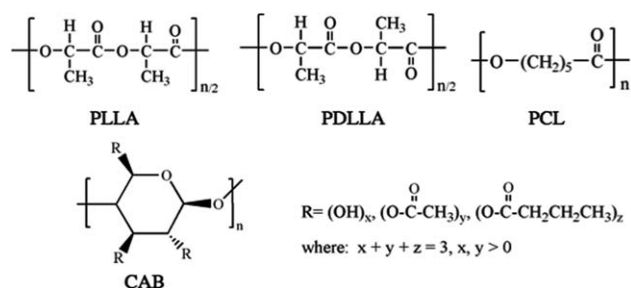


Figure 1. Molecular structures of PLLA, PDLLA, PCL, and CAB.

measured. This technique is a combinatorial approach using transmission spectrophotometry, 96-well plates, and a multi-wavelength plate reader. It has permitted the phase diagrams to be mapped out to identify the optically clear, apparently miscible regions in our binary and ternary solvent blends.¹⁸

About 7 wt % solutions of individual polymers are dissolved in chloroform (used as the solvent) and then pipetted into the 96-wells with the desired compositions. Samples were left to evaporate slowly at 21 °C (± 2 °C) for 24 h, followed by drying in vacuum at 40 °C for 24 h to remove residual solvent, this produced films with a thickness of approximately 100 μm . The blended films in the 96-well plates then had their percent transmittance (%T) measured using a plate reader. Each film was defined as opaque, semi-translucent, translucent, or optically clear on the basis of visual examination with the boundaries corresponding to %T at 450 nm (an optimal wavelength for this polymer solution) of < 30%, 31–45%, 46–75%, and > 75%, respectively. This transmittance data was used to plot the binary and ternary phase diagrams. The regions are presented with various colors, ranging from black (opaque film), gray to light gray (semi-translucent and translucent film) to white (clear film), as shown in Figure 2. The appearance of the clear, translucent, and opaque films is shown in the Supporting Information Figure S1.

Sample Preparations

PLA (PLLA1, PLLA2, PLLA3, and PDLLA) pellets were first vacuumed for 24 h to eliminate any moisture before use. Binary blends of PLA/PCL, PLA/CAB, and PCL/CAB and ternary blends of PLLA1/PCL/CAB, PLLA2/PCL/CAB, PLLA3/PCL/CAB, and PDLLA/PCL/CAB (229 samples for each blend) at the desired compositions were prepared using the preparation method described in the rapid screening method. The results are presented in the form of binary and ternary phase diagrams.

Sample Characterization

A Mettler Model DAC1 Differential Scanning Calorimeter (DSC) with sub-ambient operation was used to analyze thermal properties of the samples. The samples were conducted under different conditions depending on the polymer used. Generally,

%T	0-30 opaque	31-45 semi-translucent	46-75 translucent	76-100 clear

Figure 2. Shading diagram represents the clarity of the film prepared by a rapid screening method.

Table I. Coleman–Painter’s Miscibility Prediction of Binary Blends Using Calculated Critical Solubility Parameter Difference, $(\Delta\delta)^{\circ\text{Crit}}$ ²⁰

Polymer blends	$\Delta\delta$	Interaction types	$\Delta\delta^{\circ\text{Crit}}$	Miscibility
PLLA or PDLLA with PCL	1.8	Dispersive forces only	≤ 0.1	No
		Weak	0.5	No
		Dipole–Dipole	1.0	No
PLLA or PDLLA with CAB	0.1	Weak to moderate	1.5	Yes
		Moderate	2.0	Yes
PCL with CAB	1.7	Weak to moderate	1.5	No
		Moderate	2.0	Yes

$\Delta\delta$ and $\Delta\delta^{\circ\text{Crit}}$ are in unit of $(\text{cal cm}^{-3})^{0.5}$.

the procedure was to cool down from 25°C to −100°C (20°C/min), and then heat from −100°C to 220°C (10°C/min) under a nitrogen atmosphere. FTIR (Perkin Elmer Spectrum GX, 4000–400 cm^{-1}) was used to identify the structure of all polymers and to observe the shifting of spectra of certain functional groups present in the blends. The morphology of blended films was analyzed using Leo Model 1455VP SEM. Panalytical Model X’Pert Powder XRD, a multipurpose X-ray diffractometer, was used to analyze the distance between polymer segments and the electron intensity in the crystal cell. The atomic planes of a crystal cause an incident beam of X-rays (Cu K α , 1.54 Å) to interfere with one another when they leave the crystal. Sample powders of homopolymers and solution-blended films were examined by recording the radial scans of intensity versus scattering angle (2θ). To calculate the distance between polymer segments (d spacing), the Bragg’s law equation was applied, $n\lambda = 2d \sin(\theta)$, where, n is integer, λ is wavelength (1.54 Å), d is the distance between polymer segments, and θ is the scattering angle.

RESULTS AND DISCUSSION

Binary Blends Based on PLA (PLLA, PDLLA)

Three different molecular weights of the crystallizable PLLA (PLLA1, PLLA2, and PLLA3) and an amorphous PDLLA were selected to blend with low molecular weight PCL and CAB. The first selected criterion for these pairs was that they must be biodegradable and be able to improve the mechanical properties of PLA. The second selected criterion for a selection of polymer pairs is a predictive model from Coleman *et al.*²⁰ PCL—a flexible and biodegradable polymer—was the most obvious choice selected to blend with PLA in order to improve the processing and mechanical properties. CAB, a well-known and environmentally degradable polymer in the field of blending, was the other selected polymer. It contains hydroxyl groups that can promote hydrogen bonding and helps to increase interactions between polymer pairs.

The Coleman–Painter’s approach uses a term called the critical solubility parameter difference, $(\Delta\delta)^{\circ\text{Crit}}$, which comes from the solubility parameter (δ), which is calculated from eq. (1). Where F_i is the sum of molar attraction constants and V is the

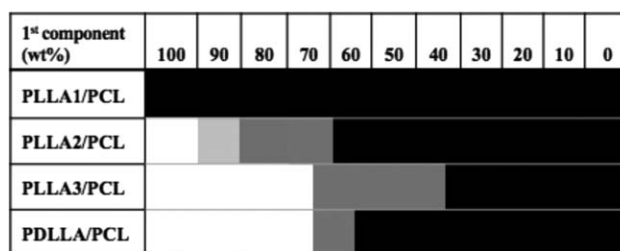
molar volume of the groups presented in the repeat unit of the polymer.

$$\delta = \sum_V^{F_i} \quad (1)$$

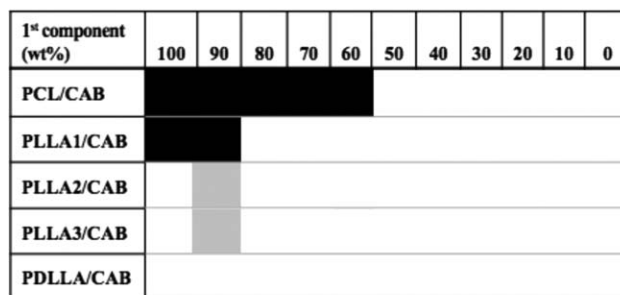
In this work, $\Delta\delta^{\circ\text{Crit}}$ term is used as the miscibility guidelines to predict miscibility of binary blends. If the solubility parameter difference between two polymers ($\Delta\delta$) is lower than $(\Delta\delta)^{\circ\text{Crit}}$ then the polymer pairs are predicted to be miscible with each other, but if higher, then the pairs are predicted to be immiscible. Table I shows the $\Delta\delta$ for the polymer pairs, as well as the possible interaction types with their corresponding $(\Delta\delta)^{\circ\text{Crit}}$. The results show the possibility of PLA (PLLA and PDLLA) to be miscible with CAB but immiscible with PCL. PCL is predicted to be miscible with CAB when moderate interactions between molecular chains occur. Therefore, PCL and CAB meet the second selection criteria and were selected to blend with PLA, even though PLA and PCL are not compatible, as reported by many other researchers.^{14,15,21–23}

The combined knowledge of binary blend behavior and solubility parameter difference (calculated by Coleman–Painter model) provides an apparent miscibility between each polymer pairs. However, this is not the only factor that influences the morphology in the blend and optical clarity is an important aspect to observe also. The binary blends of PLLA (PLLA1, PLLA2, PLLA3)/PCL, PDLLA/PCL, PLLA (PLLA1, PLLA2, PLLA3)/CAB, PDLLA/CAB, and PCL/CAB were experimentally fabricated using the rapid screening method. The transmittance of each blend was calculated from the plate reader output and represented by the binary shading diagram as a function of compositions used (ranged from 100 to 0 wt %), as shown in Figure 3.

Figure 3(a) indicates that the blends containing the higher molecular weight PLLA (PLLA2, PLLA3) and amorphous



a. PLA/PCL blends



b. PCL/CAB and PLA/CAB blends

Figure 3. Optical clarity shading diagram of binary blends: (a) PLA/PCL blends and (b) PCL/CAB and PLA/CAB blends, using rapid screening method.

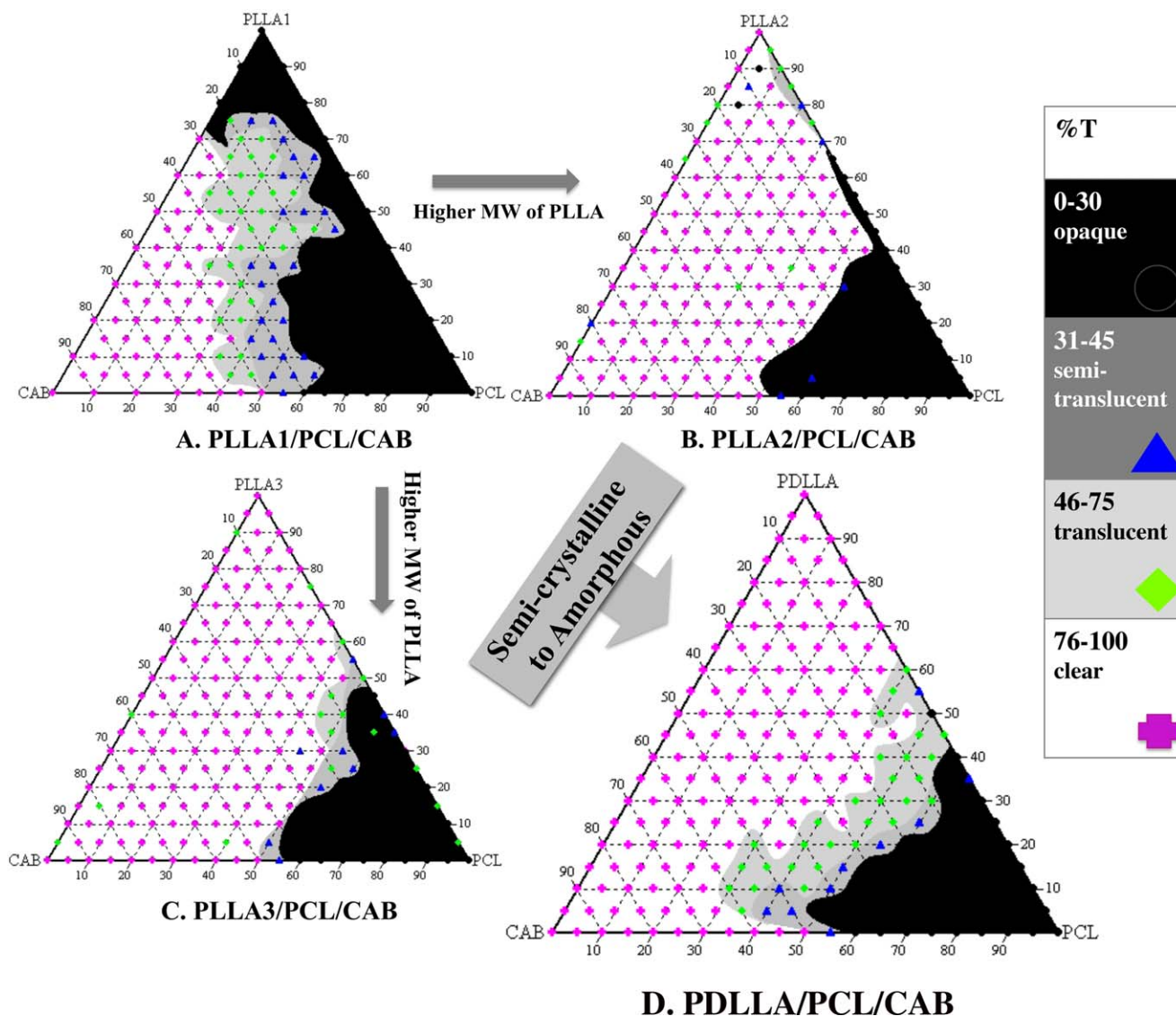


Figure 4. The ternary phase diagram of PLA/PCL/CAB blends showing the effect of the molecular weight of PLA (PLLA1, PLLA2, and PLLA3) and stereo-regularity (PDLLA). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PDLLA produce more optical clear regions in the polymer pairs of PLA/PCL than the low molecular weight PLLA1. Surprisingly, the semi-crystalline PLLA2 and PLLA3 show comparable phase regions with the amorphous PDLLA in their blends. In addition, the blended films of higher molecular weight PLLA (PLLA2, PLLA3) and PDLLA with CAB [Figure 3(b)] show more optical clarity than low molecular weight PLLA1 and PCL with CAB. Other points to note are PLA generates more extended optical clear regions in the blends with CAB than it does with PCL. This means that the presence of PDLLA, PLLA2, and PLLA3 can disturb the crystallization of the blends (an indicator of apparent miscibility between polymer pairs).

The results from both the Coleman and Painter approach and the binary blends optical clarity provide a useful first step in understanding the ternary blends of PLLA/PCL/CAB and PDLLA/PCL/CAB. The presence of a third component is capable of mediating the imbalance in solubility parameters (exemplified in Table I), but the position of the interface between completely

miscible and incompletely miscible regions cannot be predicted with certainty. In addition, it is important to note that the binary blend results confirm that the similarities in refractive indices of the polymer used in our blends (PCL = 1.52, CAB = 1.48 and PLA = 1.44)²⁴ are not responsible for optical clarity.

Ternary Blends of PDLLA/PCL/CAB and PLLA/PCL/CAB

Ternary blends of different stereo-regular PLA (PLLA and PDLLA) with three different molecular weights of PLLA (PLLA1, PLLA2, and PLLA3) were blended with PCL and CAB, these blend's optical clarity was studied and the results are shown in ternary phase diagrams in Figure 4. Figure 4(A) shows the blend of low molecular weight of PLLA (PLLA1), Figure 4(B,C) represents the blends of higher molecular weight PLA (L-isomer) (PLLA2 and PLLA3), while Figure 4(D) shows the blend of amorphous PLA (DL-isomer). It is clear that the blends using higher molecular weights of PLA [PLLA2 [Figure 4(B)] and PLLA3 [Figure 4(C)]] and amorphous PDLLA [Figure

Table II. Film Samples from Ternary Phase Diagrams Shown Together with SEM Images of PLLA1, PLLA3, or PDLLA Blended with PCL and CAB at Three Different Compositions

Sample codes	Ternary blends	Loading (wt %)	Film clarity	SEM image (5 k×)		
SBF1	PLLA1/PCL/CAB		Clear			
SBF2	PLLA3/PCL/CAB	40/10/50	Clear			
SBF3	PDLLA/PCL/CAB		Clear			
SBF4	PLLA1/PCL/CAB		Translucent			
SBF5	PLLA3/PCL/CAB	40/25/35	Clear			
SBF6	PDLLA/PCL/CAB		Clear			
SBF7	PLLA1/PCL/CAB		Opaque			
SBF8	PLLA3/PCL/CAB	40/45/15	Translucent			
SBF9	PDLLA/PCL/CAB		Translucent			

4(D)] produce more extended optical clear regions than low molecular weight PLLA1 [Figure 4(A)]. All blends show the loss of optical transparency when high amounts of PCL were used (> 50 wt % the bottom right hand corner of each triangle plot). The optically clear region (white area) in the blends of PLLA2 and PLLA3 are wider than that of PDLLA blend, as the blend of PDLLA produces an extended translucent area (light gray area). However, the opaque regions of the high molecular weight PLLA and PDLLA blends are similar.

As the blends of PLLA2 and PLLA3 show similar optical phase regions (from the ternary phase diagrams in Figure 4), only the PLLA3 blend was chosen to represent the high molecular weight L-isomer PLLA for further investigation. Three different compositions with a constant loading of PLA (40 wt %) (PLLA1/PCL/CAB, PLLA3/PCL/CAB, and PDLLA/PCL/CAB blends; 40/10/50, 40/25/35, and 40/45/15), were chosen and their morphology via SEM, miscibility by DSC and FTIR and crystallinity by means of XRD was examined. The sample details are shown in Table II along with the SEM images. Phase homogeneity and a finely dispersed matrix can be observed in all clear blend films, as in PLLA3/PCL/CAB blends (SBF2 and 5) and PDLLA/PCL/CAB blends (SBF3 and 6). Whereas, the phase separation between polymers can be observed in the opaque (SBF7) and translucent

(SBF4) blended films of PLLA1/PCL/CAB. The lack of clarity in certain blends may be caused by the greater crystallinity present in low molecular weight PLLA1 and PCL when compared to the high molecular weight PLLA3 and amorphous PDLLA blends.

Capability of a mixture to form a single phase over certain ranges of temperature, pressure, and composition is defined as a miscible mixture from the definition of miscibility by international union of pure and applied chemistry (IUPAC).²⁵ However, this is based on thermodynamic theory and researchers have looked for simple experimental ways in which to predict miscibility. In terms of thermal observations, a change in glass transition temperature (T_g) of the blend is one of the most useful ways to measure the miscibility of the binary blends and if the two polymer blends (binary) are miscible, a single glass transition (a change in amorphous regions) will be observed.^{26,27} In addition, FTIR spectroscopy has proved to have popular analytical tool for studying intermolecular interactions of polymer blends. Such interactions between polar groups of two miscible polymers lead to small frequency shifts of absorption bands of involved groups.²⁸

In three polymer blends (ternary), a single T_g is unlikely, as all three components do not have to be miscible. It is more likely, that the T_g s of the components will shift toward one another.

Table III. Thermal Properties of Ternary Blends Analyzed by DSC Technique

Blends	Observed T_g (°C)	T_m (PCL) (°C)	ΔH_f (PCL) (°C)	%X (PCL)	T_m (PLA) (°C)	ΔH_f (PLA) (°C)	%X (PLA)	Clarity ^a
SBF1	102	59	4.73	3	162	18.53	20	C
SBF2	-50/40/80	62	4.40	3	150	8.05	9	C
SBF3	-50/37/75	54	1.35	1	-	-	-	C
SBF4	-50/100	57	23.19	17	162	19.00	20	T
SBF5	-50/105	58	16.04	12	150	4.40	5	C
SBF6	-50/-20/100	57	17.84	13	-	-	-	C
SBF7	-55	56	53.30	38	160	22.21	24	O
SBF8	45/110	60	43.77	31	149	13.13	14	T
SBF9	None	59	46.80	34	-	-	-	T

^aClarity: C = clear, T = translucent, and O = opaque.

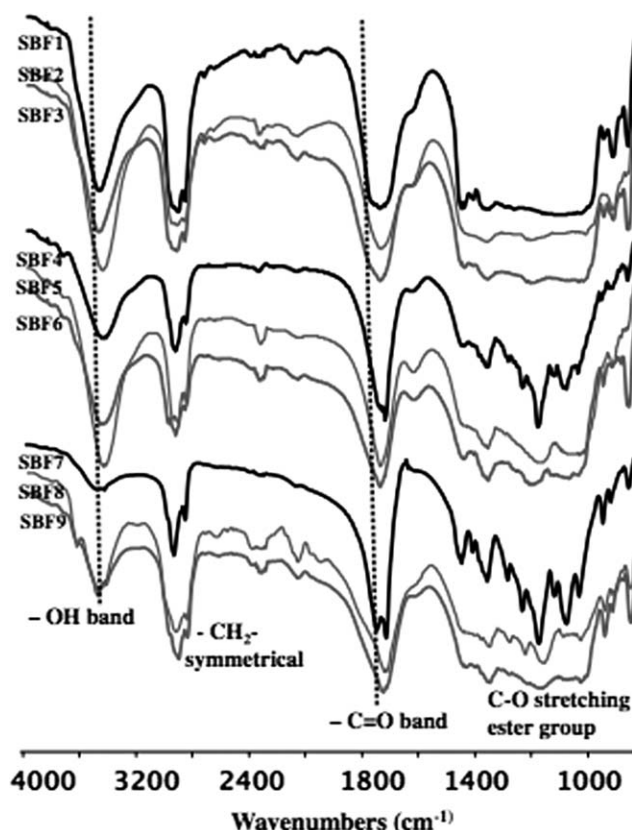


Figure 5. FTIR spectra of PLA/PCL/CAB blends with different molecular weight and stereo-regularity of PLA at three different compositions.

Table III shows the thermal properties and percent crystallinity of PLA/PCL/CAB blends (SBF1-9, sample details shown in Table II) analyzed by DSC. The T_g of the homopolymers of PLLA1, PLLA3, PDLLA were observed at 55, 62, and 60 °C, respectively, while PCL and CAB is at -55 and 115 °C, respectively. Unfortunately, the T_g of PLA shows at the same temperature as the melting point (T_m) of PCL, which is observed at approximately 60 °C, therefore, it is not possible to monitor.

From Table III, the first results column is the observed T_g of the blends. The general trend is that the clear blends tend to present more observable T_g peaks because the T_g s are shifted toward each other from the homopolymers when a more disordered structure occurs in an amorphous region. This indicates that the blends have some degree of molecular mixing at the interface between the two or three polymeric phases present in the blends. Thus, there is apparent miscibility found in the blends of PLLA3 and PDLLA at certain compositions. In addition, the percentage of crystallinity of PCL and PLA in SBF2, 3, and 6 can be seen in the range of 1–20% but their blends are still clear. For the only one opaque blend SBF7 (40/45/15 PLLA1/PCL/CAB), one T_g can be observed at -55 °C, which is expected to be the T_g of PCL and its percent crystallinity of PCL and PLLA1 are 38% and 24%, respectively. This blend with the shorter chain PLA (PLLA1) is mostly an immiscible blend as it also shows phase separations between PCL and PLLA1 (% crystallinity ca. 60% in total). Another important point that can be observed from this DSC data is

the comparable properties between the blends of higher molecular weight L-isomer of PLA (PLLA3) and low molecular weight DL-isomer of PLA (PDLLA).

Furthermore, if the blends are immiscible the FTIR spectrum of the blends is simply the spectrum of the two or three homopolymers, while a shift in FTIR spectrum describes as a miscible blend.^{28–30} Figure 5 shows the FTIR spectra of the PLA/PCL/CAB blends (SBF1-9, sample details shown in Table II). A shift in FTIR spectrum can be observed in the blends of PLLA3/PCL/CAB and PDLLA/PCL/CAB (SBF2, 3, 5, 6, 8, and 9), as they give an interaction spectrum with frequency shifts and intensity changes in the absorption bands; -OH band (3500–3600 cm^{-1}), -C=O stretching bands (1700–1750 cm^{-1}), and -CH₂- symmetrical stretching band (2886 cm^{-1}) and their peaks are similar. It should be noted that the change in the -OH band may be also result from the interaction of CAB molecules, not only the interaction between the polymer pairs. While, the blends of PLLA1 (SBF1, 4 and 7), especially the opaque blend of SBF7 (40/45/15 PLLA1/PCL/CAB) show simply the spectrum sum of all homopolymers indicating that they are most likely to be immiscible blends. However, it is difficult to see the changes in the FTIR spectra absorption bands, so we focused on the change in spectral variation of the carbonyl stretching vibration region (-C=O band), which relates to the intermolecular packing of homopolymers and can be used to observe the miscibility of the blends.¹⁰

Figure 6 shows the carbonyl stretching vibration of PLA/PCL/CAB blends at 40/10/50. A peak with higher wavenumber of -C=O band can be observed in the PLLA1 blend due to the close intermolecular packing of PLLA1 (self-aggregation). Whereas, the peaks with a lower wavenumber can be seen in PLLA3 and PDLLA blends due to the loose intermolecular packing (freedom movement) of PLLA3 and PDLLA.

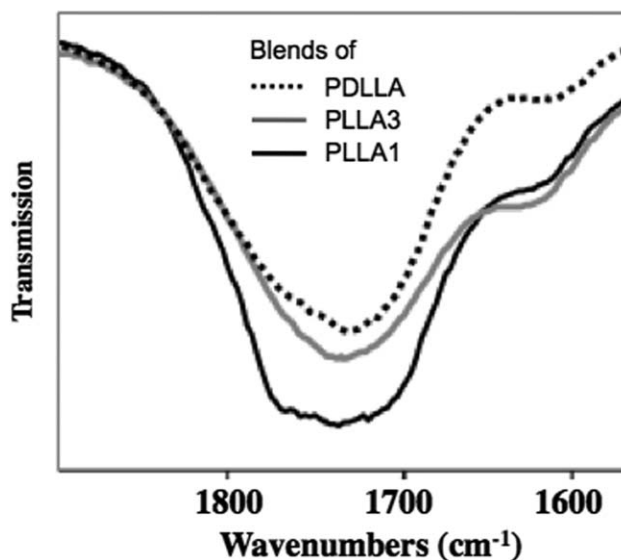


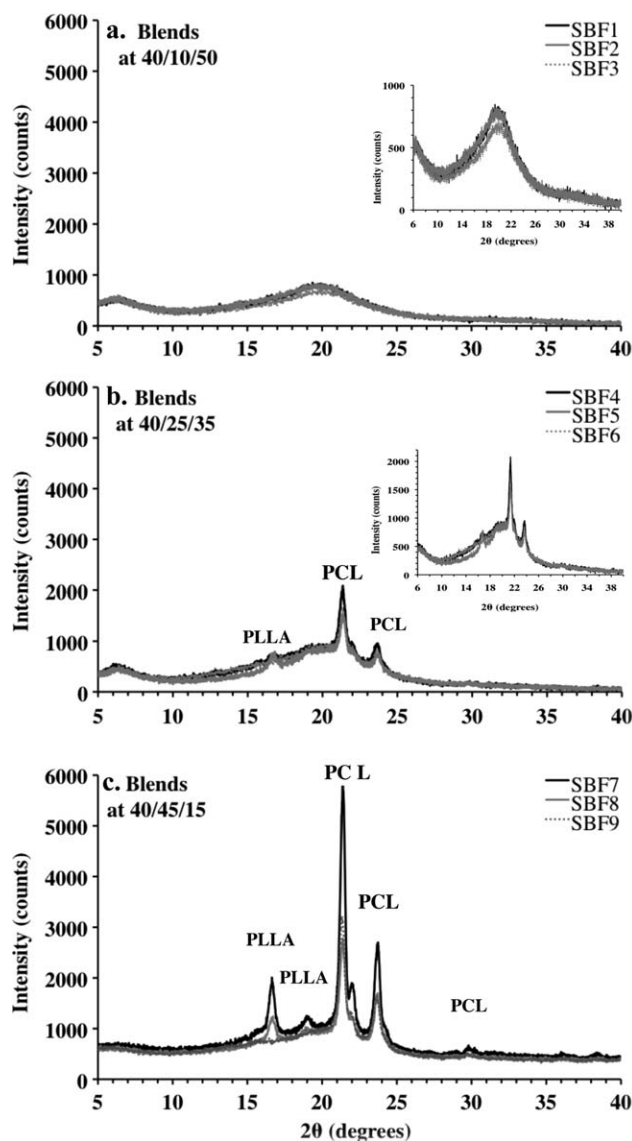
Figure 6. FTIR spectra revealing carbonyl stretching vibration of PLA/PCL/CAB blends at 40/10/50.

Table IV. X-ray Incidence Angle (2θ) and Lattice Inter-Planar Spacing of the Crystal (d -spacing) of Homopolymers

Homopolymers	2θ (degrees)/ d -spacing (\AA)
PLLA1, PLLA3 ^a	14.50/6.08, 16.50/5.37 (1st), 18.80/4.71 (2nd), 22.07/4.02
PCL	15.40/5.90, 21.41/4.15 (1st), 21.76/3.98, 23.70/3.75 (2nd), 29.64/3.01 (3rd)
CAB	Broad peak at 14–30/6.32–2.98
PDLLA	Broad peak 12–27/7.37–3.30

^aPeak intensities of PLLA3 are weaker than that of PLLA1. 1st and 2nd refer to the strongest peaks.

This confirms that the blends of PDLLA and PLLA3 with high loading of CAB show similar behavior in blend miscibility, while the blend of PLLA1 is most likely to be less miscible.

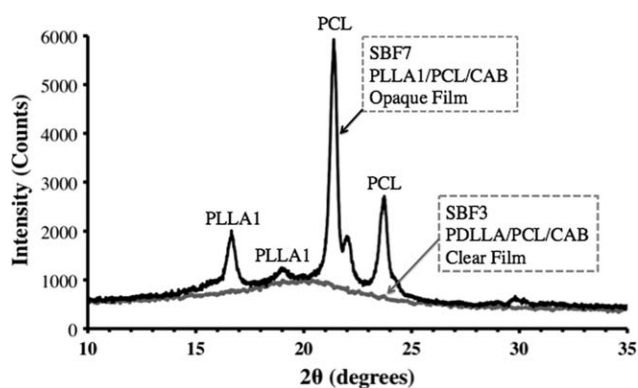
**Figure 7.** XRD patterns of PLA/PCL/CAB blends with different molecular weights and stereo-regularities of PLA at three compositions.

In summary, the results seen from the DSC and FTIR are all in agreement with the results from the optical clarity. They show that the clarity, miscibility, and crystallinity of the PLLA3 and PDLLA blends are similar but different from the PLLA1 blends. In addition, the results combined suggest that these blends under these certain conditions are either miscible or immiscible as stated depending on the composition, molecular weight, and stereo-regularity of the polymers.

In our previous work, we concluded that the nature of the non-transparent regions is influenced by crystallization.¹⁸ Therefore, in this work the study of the nature and extent of crystallinity from the different stereo-regularity of PLA blends was further observed by XRD.

Table IV shows the values of X-ray incidence angle (2θ) and lattice inter-planar spacing of the crystal (d -spacing) of the homopolymers as observed by the XRD technique. Figure 7 shows the XRD patterns of PLLA1/PCL/CAB (SBF1, 4, 7), PLLA3/PCL/CAB (SBF2, 5, 8), and PDLLA/PCL/CAB (SBF3, 6, 9) at the same scale of intensity. They show that the differences in peak intensities (from low to high) depend on the compositions of the blends as: 40/10/50 (a) < 40/25/35 (b) < 40/45/15 (c). All clear blends (40/10/50 PLLA1/PCL/CAB (SBF1), PLLA3/PCL/CAB (SBF2), and PDLLA/PCL/CAB (SBF3)) show broad peaks with low intensities, as they have low homopolymer crystallinity percentage, as also seen in the DSC results (Table III). Whereas, both translucent and opaque blends (SBF4–9) show tall narrow crystalline peak of PCL ($2\theta = 21.4^\circ$ and 23.8°) and short crystalline peak of PLLA ($2\theta = 16.7^\circ$). The degree of crystallinity (X_c) of PCL is higher than that of PLLA when compared at the same composition. The higher the loading of PCL the more X_c can be observed, the X_c of PCL in PLLA3/PCL/CAB blends is a similar value to that of the PDLLA/PCL/CAB blends. Figure 8 is a direct comparison of a clear and opaque blends, it highlights the differences that the stereo-regularity of PLA (PLLA1 and PDLLA) and PCL content have on the film clarity.

In summary the blended film clarity, which will be clear, translucent, or opaque, seems to depend on the following factors: (1) the crystallinity of PCL more than that of PLA, (2) the stereo-regularity of PLA, where amorphous PDLLA can promote more clarity than semi-crystalline PLLA. However, using

**Figure 8.** XRD patterns of a clear film of 40/10/50 PDLLA/PCL/CAB blend and an opaque film of 40/45/15 PLLA1/PCL/CAB blend.

a high molecular weight semi-crystalline PLLA3 and an amorphous PDLLA show similar film clarity.

CONCLUSIONS

In our previous work, a novel rapid screening method was employed to assess the apparent miscibility in PLLA/PCL/CAB solvent blends. It was observed that the moderating effect of CAB drives the position of the phase boundaries in blends of PLLA and PCL. In this work, we extended to study the effect of stereo-regularity of PLA (semi-crystalline PLLA and amorphous PDLLA) and higher molecular weight of PLLA had on the ternary blends phase boundaries. The rapid screening method was again used to enable the ready identification of optically clear and apparently miscible regions. The PDLLA/PCL/CAB blend showed similarities in regions of phase separation with the PLLA3/PCL/CAB and PLLA2/PCL/CAB blends. These blends show good miscibility and clarity except when using high amounts of PCL. The PLLA1/PCL/CAB blend on the other hand presents a large opaque region, due to the phase separation and immiscibility caused by the crystal structure of PCL and PLLA1. Whether the blend is opaque or clear depends upon the competition between recrystallization and intermixing. Amorphous polymers and higher molecular weight polymers favor intermolecular (communal) mixing, leading to more miscible blends (PDLLA, PLLA2, and PLLA3 blends), whereas the propensity to self-aggregate (crystallize) dominates in the shorter polymer chains, which have higher value of mobility and degrees of freedom, leading to greater immiscibility (PLLA1 blend). The use of XRD and DSC indicated that PCL had the greatest tendency to crystallize and thus dominates creating the opaque regions of the phase diagrams, especially with a rich PCL containing blend.

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