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Composition optimization and characterizations of poly(L-lactic acid)/cellulose acetate blends films in solvent mixture system

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Abstract

A biomaterial was developed by blending a commercially available poly(*L*-lactic acid) (PLLA) with cellulose acetate (CA) using a solvent casting technique. PLLA and CA have great potential for the manufacture of environmentally friendly thin films packaging but there is very limited number of studies on their blend compatibility. This work aimed to evaluate the compatibility of PLLA and CA in a solution form. The solution blends of various PLLA/CA weight percentages (0-100 %w/w) were prepared in a chloroform/acetone mixture solvent. Both physical and spectroscopic techniques were employed to characterize the homogeneity, structural integrity and various physicochemical properties of the films. Results indicated that PLLA was partially compatible with CA and the optically transparent films were only observed in either the PLLA- or CA-rich blend. However, this limit could be further extended by partial hydrolysis of the two polymers through the addition of hydrochloric acid. By altering some experimental conditions, a wide range of PLLA/CA films with different properties were fabricated. Interestingly, the Scanning Electron

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Microscopy (SEM) micrographs of the acid-free 40/60 blend film revealed the spherical agglomerated PLLA particles throughout the CA domain. Such embedded particles reinforced the thin film, as confirmed by the increased tensile strength comparing to that of the neat PLLA and CA films. This suggested the possible intermolecular interactions between the two components. The PLLA/CA blend system thus demonstrated its potential use for a wide range of applications, particularly in the manufacture of novel active biodegradable packing.

Keywords: biodegradable polymers; poly(lactic acid), cellulose acetate, polymer blends, films

1. Introduction

Petroleum-based plastics are attractive man-made materials that are widely used in a wide range of applications due to their excellent properties such as low-cost, strong and light weight. Despite these advantages, they also cause serious environmental problems because of their long-lasting in nature. Therefore, there is a need to develop alternative source of materials that can be naturally decomposed to yield the non-toxic materials and can reduce greenhouse-gas emission (carbon dioxide) by replacing and reducing the uses of crude-oil [1,2]. Polymer blends and composites from renewable resources have attracted much interest from researchers as a promising material to replace the petroleum-based ones. Normally, polymer from renewable resource (PFRR) can be classified into three types; (1) natural polymers such as starch and cellulose, (2) synthetic polymers from natural monomers such as poly(lactic acid)(PLA), and (3) polymers from microbial fermentation such as Poly(hydroxybutyrate) (PHB). The properties of PFRR can also be improved through blending and polymer composited [3]. Among all renewable resource polymers, the aliphatic polyester, PLA, is one of the most outstanding candidates. It has been used in many fields including packaging [4-6], tissue engineering [7] and other biomedical applications [8-9]. PLA has great potential for the development of environmentally friendly packaging (e.g., trays, cups, bottle, film etc.) due to its unique characters such as impressive mechanical properties, suitable permeability to gas and water, tunability and importantly, its hydrolytic degradability, [10, 11]. McCarthy [12] showed that A-PLA exhibited slower soil degradation rate as compared to poly(butlyene-adipate-*co*-terephthalate) (PBSA). PLA was presumed to be biodegradable although the role of hydrolysis vs. enzymatic depolymerization in this process remains open to debate [13]. Composting conditions were found only in industrial units with a high temperature (above 50°C) and a high relative humidity (RH) to promote chain hydrolysis. Biodegradation of PLA has been reported to give no eco-toxicological effect [14]. However, application of PLA is still limited due to its stiffness and brittleness at room temperature [15]. This drawback could be overcome by blending PLA with other polymers

[16-17]. Cellulose and its derivatives have much recently attracted considerable interest as an eco-environmentally polymer, possessing a high potential to develop further as renewable bioplastics with good performance [17] and low cost. Cellulose acetate (CA) is the esterified derivative of cellulose which has a better mechanical strength, water absorbability and processability than cellulose. It has been applied for many industrial applications in the form of film and fiber due to its desirable physical properties such as good optical clearly, a comparatively high modulus, adequate flexural and tensile strengths as well as its biodegradability under appropriate conditions [18-21]. CA is thus, one of interesting candidates for the development of biodegradable materials. Since CA and PLA are quite different in their chemical structures blending of the two polymers together may generate a new polymeric system with superior properties. This could also lower the production cost and extend practical uses of PLA for a wider range of applications. N. Ogata studied the structure and physical properties of cellulose acetate/poly(L-lactide) blends using tetraisopropyl titanate (TP) as a compatibilizer then concluded that the addition of TP produces small PLLA crystallites and assists the hydrolysis of the blends, moreover, the young’s modulus of the blends is almost independent of the blend ratio [22].

The objective of this work aimed to evaluate the compatibility of PLLA and CA blended films, consisting of the biodegradable poly(lactic acid) (PLA, Fig.1a) and cellulose acetate (CA, Fig.1b) by using a solvent casting method. PLLA was used in this work because it was cheaper and more stable than PDLA. The effects of some experimental conditions, including the blend composition and acidication, on the compatibility and physicochemical properties of the blends were evaluated through the uses of both physical and analytical techniques. This study established another alternative choice for the manufacture of film applications with reasonable price, light weight but durable and as strong as the conventional ones.

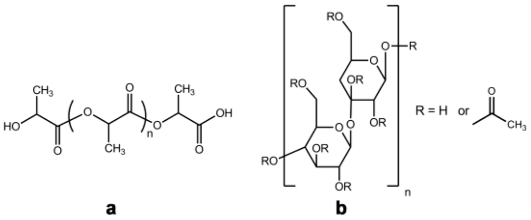


Fig. 1 Chemical structures of; (a) polylactic acid (PLA) and (b) cellulose acetate (CA).

2. Materials and Experiments

2.1 Materials

The Poly(*L*-lactic acid) (PLA) was supplied by Nature works, USA. The selected grade, PLA 4042D, is a semi crystalline extrusion material. Cellulose acetate (CA) (white powder; M_w = 30,000 Da; degree of acetyl substitution = 2.4; acetyl content = 39.7%) was purchased from Sigma-Aldrich (USA).

2.2 Preparation of PLLA/CA Blend Films

A solvent film casting technique was used to fabricate PLLA/CA blend films. Blend solutions (5% weight by volume) of different PLLA/CA mass percentages (i.e. 0/100, 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, 90/10 and 100/0) were prepared by dispersing appropriate amounts of PLLA and CA in a mixture of chloroform and acetone (70:30 percent by volume). The solutions were then casted onto a glass petri-dish, followed by drying at 50^{o}C for 48 h. The blend films are denoted accordingly to their PLLA/CA weight ratio. For example, the 20/80 sample is referred to the blend film containing 20% and 80% (by weight) of PLLA and CA, respectively. The effect of acid hydrolysis on the film formation was also evaluated by using a similar method to that mentioned above. However, in this case, a small portion of a hydrochloric acid (0.1 M) was added into the blend solution prior to casting onto a petri-dish. A final concentration of the acid in the blend solution was approximately 2.5% (v/v).

2.3 Characterization

Film Transparency

The UV-Vis spectrophotometer (Genesys20; Thermo) was used to measure the optical transparency of the blend film. The percent transmittance (%T) was measured at a wavelength of 600 nm.

Fourier Transform Infrared (FTIR) Spectroscopy

All infrared spectra were recorded in the range of 2400-4000 cm^{-1} using a Spectrum GX FTIR spectrometer (PerkinElmer). Each spectrum was acquired by accumulation of 32 scans with a resolution of 4 cm^{-1}. Background measurements were subtracted from the sample readings.

Thermal analysis

A DSC822E differential scanning calorimeter (Mettler Toledo) and a TGA/SDTA 851E thermogravimetric analyzer (Mettler Toledo) were used to measure the temperature transitions of PLLA, CA and their blends. All measurements were performed under nitrogen atmosphere with a scanning rate of 10^{o}Cmin^{-1}. Thermogravimetric Analysis (TGA) was carried out in the range from 25^{o}C to 600^{o}C. For differential scanning calorimetry (DSC) analysis, samples (3-5 mg) were sealed in aluminum crucibles and heated from 25^{o}C to 220^{o}C. The upper temperature limit for the DSC was selected based on the initial decomposition temperature as observed from the TGA.

Scanning Electron Microscopy (SEM)

Surface morphology and interior structure of the films was investigated by using a LEO 1450VP microscope. SEM images were acquired after gold sputtering at acceleration voltage of 15 kV and at 16 mm working distance.

Mechanical Properties

The tensile test for the blend films was performed at room temperature on the tensile testing machine (INSTRON-5566). The method used was adapted from the ASTM D638-03. The crosshead speed was 10 mm min^{-1} and the initial gauge length was 30 mm.

3. Results and Discussion

3.1 Characterizations

Film Transparency

From Fig.2 illustrates the optical transparency of the blend films containing different PLLA contents (0-100% w/w) casted in a chloroform/acetone solvent mixture. It can be seen that both CA (0/100) and PLLA (100/0) neat films are clear and transparence with no sign of macroscopically phase separation. This indicates that a mixture of chloroform and acetone (70:30 % by volume) is a good solvent for the two polymers. From the results, neat films of both acid-free and acid system show more transparency than the blend films. This is consistent with the lower %T values, as compared to the neat films (0/100 and 100/0), suggesting a partial compatibility existed in PLLA/CA blend system.

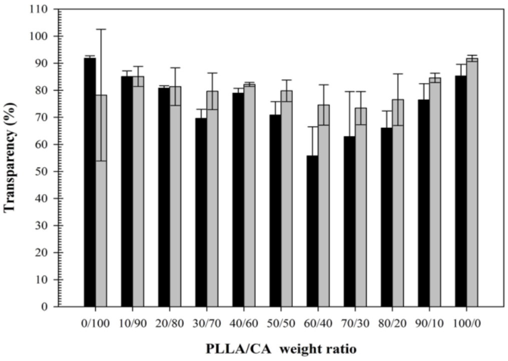


Fig. 2 Transparency (%) of the blend films prepared at different PLLA/CA weight percentages casted in a chloroform/acetone solvent mixture (70:30 % by volume) (black-bar) and hydrochloric acid/chloroform/acetone (light grey-bar).

However, the comparison between acid-free and acid system were interesting. When a small amount of hydrochloric acid was added into the blend solution, all of the resultant films display improved transparency with little or no phase separation, particularly for the cases of 30/70, 40/60, 50/50 and 60/40 films. It can explain that the acid induced hydrolysis scission in PLLA and CA structure resulting in the reduction of crystalline giving more transparency films.

Surface Morphology

Scanning Electron Microscopy (SEM) was used to investigate both surface and interior morphologies of the films. SEM images of the 0% (neat CA), 40% and 100% (neat PLLA) and blend films are presented in Fig.3.

As could be observed in Fig.3a-b, the 0/100 (neat CA) and 100/0 (neat PLLA) films in acid-free system display smooth surface with no sign of phase separation, confirming the absence of a microscopically phase separation. For the cases of the acid-free 40/60 blend film, a number of agglomerated particles were found on the films (Fig. 3c). These particles are spherical with uniform size and shape. The presence of such particles explains the decreased %T of the blend films comparing to either the 0/100 or 100/0. When a hydrochloric acid/chloroform/acetone was used as a casting solvent, the resultant 40/60 film shows no agglomerated particle on the surface (Fig. 3d). This illustrates a potential impact of the acid addition to improve their compatibility over a whole range of the blend composition.

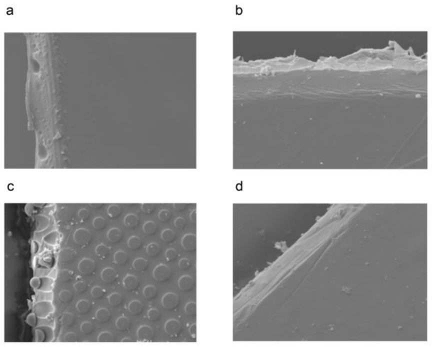
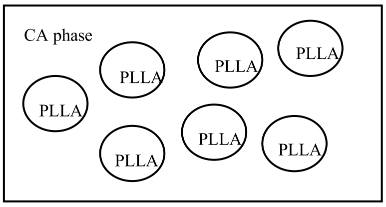


Fig. 3 SEM images of the neat CA (a) and neat PLLA films (b) casted in a chloroform/acetone solvent mixture. The 40/60 (PLLA/CA) blend films were casted in a chloroform/acetone (c) and hydrochloric acid/chloroform/ acetone (d). Images were taken at 1.0Kx magnifications.



Schematic 1 the formation of the blended film of 40/60 PLLA and CA without acid.

The micrographs of the acid-free 40/60 blend film revealed the spherical agglomerated PLLA particles throughout the CA domain, but the spherical agglomerated of 40/60 blend film in acid addition were not observed. It can explain that 40/60 PLLA/CA blend films in free acid is partially compatible blend as the droplet phase of PLLA particles dispersed in the continuous phase of CA solution shown in the schematic 1. The improvement of the mechanical property of the PLLA/CA blended film with the present of PLLA particle would explain that CA might form the “network-like” continuous structure with itself which is believed to contribute the enhanced mechanical properties. [23-24].

Thermal Properties

The transition temperatures of different films casted in a chloroform/acetone and hydrochloric acid/chloroform/acetone mixture solvents were determined from the second heating cycle as shown in Fig.4 (a) and (b), respectively. Thermal properties of all casted films were summarized in Table 1 and 2.

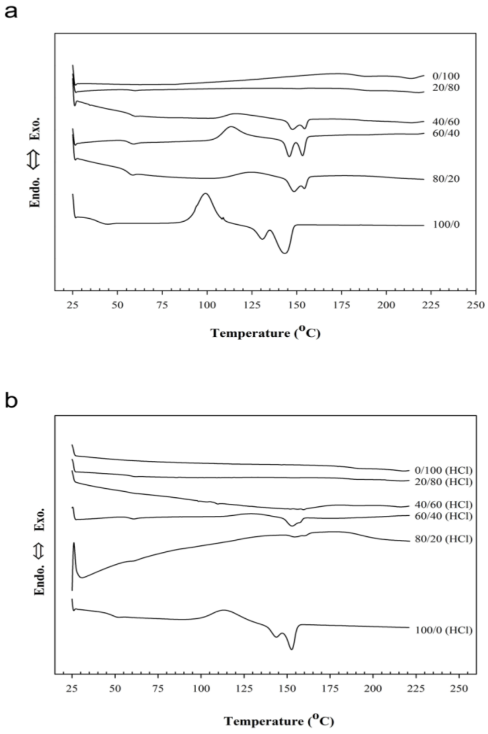


Fig. 4 DSC thermograms (2^{nd}- heating cycle) of the films casted in a mixture solvent of; (a) chloroform/acetone and (b) hydrochloric acid/chloroform/acetone.

TABLE 1 Summary of thermal properties of the films casted in a chloroform/acetone mixture solvent.

Films (PLLA/CA ratios)	Transition temperatures (^oC)				Degradation temperature (^oC)
	T_g	T_c	$T_{m,1}$	$T_{m,2}$	
0/100	N/A	N/A	188	214	364
20/80	56	N/A	189	219	357
40/60	58	116	148	155	358
60/40	56	113	146	153	358
80/20	55	125	149	154	365
100/0	38	99	131	135	369

TABLE 2 Summary of thermal properties of the films casted in a hydrochloric acid/chloroform/acetone mixture solvent.

Films (PLLA/CA ratios)	Transition temperatures (^oC)				Degradation temperature (^oC)
	T_g	T_c	$T_{m,1}$	$T_{m,2}$	
0/100	N/A	N/A	193.4	218.3	370
20/80	59	N/A	N/A	N/A	358
40/60	N/A	N/A	N/A	N/A	357
60/40	61	130	153	158	363
80/20	61	N/A	155	160	366
100/0	51	114	143	153	370

As can be observed in Fig.4, the 0/100 (neat CA) blend film displays relatively broad and weak endothermic peaks at around 188^{o}C and 214^{o}C, while those of the 100/0 (neat PLLA) film displays at lower temperatures of 131^{o}C and 135^{o}C. These results represented stronger intermolecular chain interactions of the former than the latter one. Interestingly, the neat PLLA film also shows signals of both the T_g and T_c at around 38^{o}C and 99^{o}C, respectively (see Fig.4), lower than the values reported earlier [25-27]. This illustrates a huge impact of casting solvent chosen on the physicochemical properties of the PLLA-based films. Blending of PLLA with CA dramatically increases all of its transition temperatures. For example, the T_g, T_c, $T_{m,1}$ and $T_{m,2}$ of the 40/60 blend film are around 58^{o}C, 116^{o}C, 148^{o}C and 155^{o}C, respectively, while that of the neat PLLA film are 38^{o}C, 99^{o}C, 131^{o}C and 135^{o}C, respectively (see Table 1). This confirms the extent of intermolecular interactions between PLLA and CA in both amorphous and crystalline domains. Interestingly, all blend films exhibit lower degradation temperature ($T_{d,max}$) values than that of the neat films (0/100 and 100/0). It is worth mentioning that the intermolecular forces between the two polymers are about one-tenth the strength of the covalent bond, thus the presence of these forces in the system may not necessarily increase the $T_{d,max}$ values of the blend films. The effect of acid addition on thermal properties of the casted films could be observed when comparing Fig.4 (a) and (b). For the neat PLLA (100/0) and CA (0/100) films, all the peaks in the DSC thermograms become broader and the transition temperatures (e.g., Tg, Tc and Tm) are found to shift towards higher temperature region (see Table 1 and Table 2). These results indicate that the hydroxyl and carboxyl free ends, formed during the acid hydrolysis of PLLA and CA, respectively, may enhance the molecular packing preferentially in the amorphous domain. Furthermore, these free ends of the two polymers perhaps, facilitate stronger intermolecular interactions between each other in the amorphous region of the blend. The higher % T and Tg values of the 40/60 blend films casted in the acid-containing solvent system, comparing to that in the acid-free system also supports this statement (Fig.1 and Table 1-2).

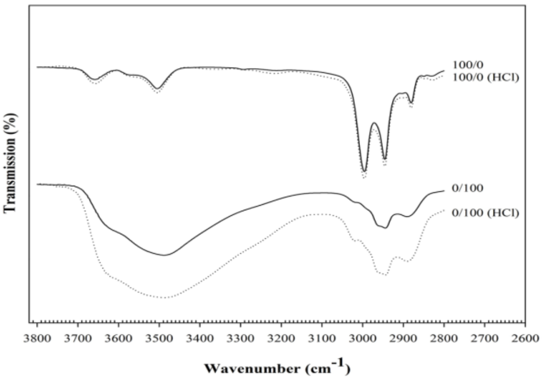


Fig. 5 FTIR-Spectra of the neat CA (0/100) and the neat PLLA (100/0) films casted in either a chloroform/acetone (solid lines) or a hydrochloric acid/chloroform/acetone (dashed lines) solvent mixture. Spectra were recorded in a region of 2800-3800 cm^{-1}.

FTIR Analysis

In Fig. 5 shows the FTIR spectra in a region of 2800-3800 cm^{-1} for the neat PLLA (100/0) and the neat CA (0/100) films casted in a mixture solvent either in the presence (dashed lines) or the absence (solid lines) of a hydrochloric acid addition. As seen in Fig.5 the 100/0 film (solid line) shows the bands between 3400-3700 cm^{-1}, corresponding to the vibrational stretching of the –OH groups. The presence of these bands indicates the extent of unreacted carboxylic acid groups after polyesterification reaction of the lactic acid to PLLA. The 100/0 film casted in an acidic mixture solvent also displays the –OH stretching bands, but they are slightly broader. One more time, the acid perhaps induces the hydrolytic scission of PLLA chains, leading to the formation of the carboxyl-terminated chain fragments that enhance the –OH vibrational signals as seen in Fig.5 (100/0, dashed line). As expected, the neat

CA (0/100) film shows a strong absorption band at 3100-3700 cm^{-1}, responsible for the cellulose –OH stretching on the pyronose ring (Fig.5, solid line). A decreasing in the band intensity of this vibrational mode should be observed as the degree of acetylation of CA is increased. Likewise, a 0/100 film casted in an acidic solvent system also display even broader asymmetric–H stretching band, as compared to the one casted in an unmodified solvent system.

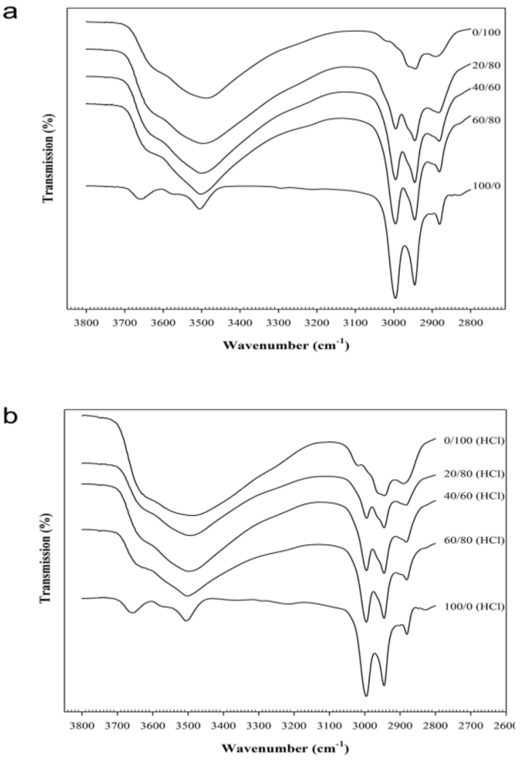


Fig. 6 FTIR-Spectra blend films with at different PLLA/CA mass percentages casted in; (a) chloroform/acetone and (b) hydrochloric acid /chloroform/acetone mixture solvent. All spectra were recorded in a region of 2800-3800 cm^{-1}

The results from FTIR suggests another possible phenomenon concerning the acid hydrolysis of the acetyl pendant groups on the CA backbone. The hydrolytic scission of the cellulose ester takes place when the hydroxyl groups (-OH) replace the acetyl groups (-COCH$_3$) on the cellulose ring [28]. This process, commonly known as a de-acetylation, would increase the hydroxyl moieties in the neat 0/100 film, explaining the broadening of the –OH absorption band as shown in Fig.5 (dashed line) and the enhanced hydrogen bonding formation. As noticed, all of the blend films, 20/80, 40/60 and 60/40, casted either in the absence (Fig.6a) or in the presence (Fig.6b) of the acid show strong absorption characteristic bands at around 2996, 2945 and 2882 cm^{-1}, corresponding to the C-H stretching of PLLA sample. This confirms the existence of PLLA in the blend films. From another point of view, the co-existence of CA in the films is also proven by the FTIR, as evidenced by the appearance of a broad –OH stretching band between 3100 cm^{-1}and 3800 cm^{-1} (Fig.5). In addition, the intermolecular interaction between PLLA and CA is more pronounced in the acidic casting solvent, possibly through the hydrogen-bonding formation, as confirmed by the even broader absorption band of the -OH groups for the 20/80, 40/60 and 60/40 films (Fig.6b), comparing to those acid-free addition (Fig.6a).

Mechanical Properties

The tensile mechanical properties of both the neat (0/100, 100/0) films and the blend

(10/90, 20/80, 30/70, 40/60, 50/50) films are shown in Fig.7. Their tensile strength is summarized in Table 3.

As seen in Fig.7, the tensile strengths of the films casted in the acid-free system are generally, higher than that casted in the acid addition system.

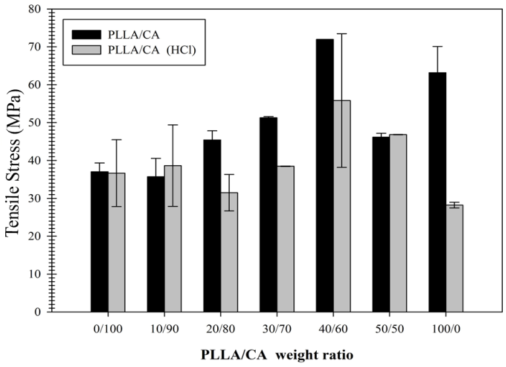


Fig. 7 Mechanical properties of the films containing at different PLLA/CA weight ratios casted in either; chloroform/acetone (black-bar) or hydrochloric acid/ chloroform/acetone (light grey-bar) mixture solvent.

TABLE 3 Mechanical properties of the films containing different PLLA/CA mass percentages casted in either chloroform/acetone or hydrochloric/chloroform/acetone mixture solvent.

Sample	Tensile stress* (MPa)	
	chloroform/Acetone	HCl/chloroform/Acetone
0/100 (neat CA)	37.02 ± 2.33	36.64 ± 8.81
10/90	35.69 ± 4.86	38.63 ± 10.76
20/80	45.42 ± 2.43	31.48 ± 4.82
30/70	51.28 ± 0.28	38.48 ± 0.05
40/60	**71.94 ± 0.01**	**55.80 ± 17.63**
50/50	46.15 ± 1.02	46.82 ± 0.04
100/0 (neat PLLA)	63.17 ± 6.93	28.22 ± 0.74

*Average value carried out in triplicate.

From the previous discussion in Fig.3, it is believed that the utility of a hydrochloric acid enhances the compatibility between the two polymers. However, this approach may also cause a side-effect in the way that the occurrence of a hydrolytic scission, induced by the acid addition, possibly reduces the polymer molecular weight and so, the tensile mechanical properties [22]. The considering tensile strength of the neat PLLA films casted from different mixture solvent systems. It was found that the composition ratio of PLLA/CA at 40/60 achieves a maximum tensile stress both in acid-free and acid system. Among all blend films, the 40/60 blended film in acid-free shown a maximum tensile strength of 71.94 MPa, higher than that of its parental components neat PLLA (63.17 MPa) and CA (37.02 MPa) films. This improved tensile strength may be associated with the appearance of the sub-micron particles in the 40/60 blend film observed from the SEM-micrograph (Fig.3C). These aggregates may reinforce and enhance the thermal properties without affecting the optical transparency of the blend film. In the other hand, the addition of acid reduces the mechanical strength of the neat PLLA, neat CA and blended films.

4. Conclusion

Overall results suggest that in the hydrochloric acid/chloroform/acetone solvent system can improve the compatible of PLLA/CA blend films. However, CA addition at the optimum ratio of 40/60 PLLA/CA can improve the tensile stress of the neat PLA films and neat CA films in both acid-free and acid-present systems. The optimal composition ratio of blend films is 40/60 of PLLA/CA in acid condition giving good compatibility, transparency, higher T_g with good tensile strength than neat PLLA and neat CA. Therefore, it is good sign to develop the PLLA/CA blend film for applying in widely useful film applications.

5. Acknowledgements

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