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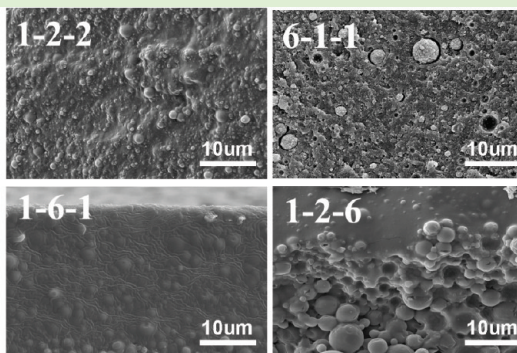
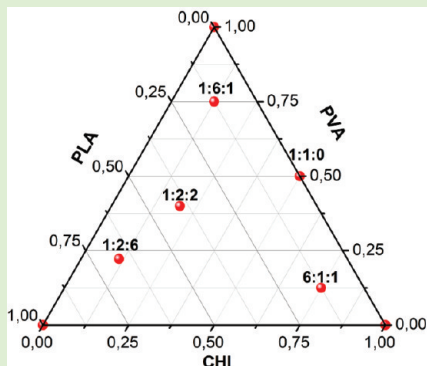
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Compatible Ternary Blends of Chitosan/poly(vinyl alcohol)/poly(lactic acid) Produced by Oil-in-Water Emulsion Processing

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ABSTRACT:



Ternary compatible blends of chitosan, poly(vinyl alcohol), and poly(lactic acid) were prepared by an oil-in-water (O/W) emulsion process. Solutions of chitosan in aqueous acetic acid, poly(vinyl alcohol) (PVA) in water, and poly(lactic acid) (PLA) in chloroform were blended with a high-shear mixer. PVA was used as an emulsifier to stabilize the emulsion and to reduce the interfacial tension between the solid polymers in the blends produced. It proved to work very well because the emulsions were stable for periods of days or weeks and compatible blends were obtained when PVA was added. This effect was attributed to a synergistic effect of PVA and chitosan because the binary blends PVA/PLA and chitosan/PLA were completely incompatible. The blends were characterized by scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermal mechanical analysis (TMA), stress–strain tests, and Fourier transform infrared spectroscopy (FTIR). The results indicated that despite the fact that the system contained distinct phases some degree of molecular miscibility occurred when the three components were present in the blend.

INTRODUCTION

Natural and synthetic biodegradable and biocompatible polymers are of great interest, especially for biomedical applications, where bioactive materials with antifungal and antibacterial activity are growing in importance. Chitosan, a mucopolysaccharide, is produced by alkaline N-deacetylation from chitin, which, with cellulose, is one of the most abundant polymers found in nature.^{1,2} Besides its biodegradability and biocompatibility, chitosan is reported to be an active polymer with antimicrobial and antifungal activities.^{1–6} Therefore, many efforts have been made to produce new polymer systems incorporating chitosan as a bioactive material. In general, chitosan is processed from an aqueous solution in the presence of organic acids, such as acetic and formic.

Polymer blending is an interesting way of preparing polymeric materials with new properties. Poly(lactic acid) (PLA) is prominent among the polymers that are biodegradable and biocompatible, being produced on an industrial scale at relatively little cost.

PLA is produced from renewable resources and has properties similar to most petroleum-based materials, such as polyethylene, polypropylene, and poly(ethylene terephthalate) (PET).^{7,8} It is commonly processed by extrusion or injection molding.⁷

Chitosan, like other polysaccharides such as cellulose, cannot be processed by melting, so that solution blending is the processing technique of choice. It is highly desirable to develop melt processable blends of chitosan with polymers such as PLA and other biodegradable and biocompatible polymers. Attempts to produce blends of PLA with chitosan by melt processing have led to composite systems, where chitosan is the filler.⁹ This occurs because chitosan decomposes instead of melting, owing to the strong intermolecular hydrogen bonding.

Solution blending is a processing technique in which a common solvent is used to dissolve the polymers. However, when very different polymers have to be mixed, no common solvent exists and emulsion blending becomes an interesting possibility.¹⁰ Emulsion blending can present technical challenges, depending on the system. Important factors are the stability of the emulsion during storage and during solvent evaporation and the size of the dispersed phase.^{10,11}

When polymers of very different polarities are blended, such as chitosan and PLA, it is necessary to use a compatibilizer to reduce

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the interfacial tension between the polymers to decrease the particle size of the dispersed phase and to enhance the interaction between the distinct phases so that a compatible blend can be achieved. Sébastien et al.¹² described a chitosan/PLA blend produced by casting an emulsion of a water solution of chitosan with PLA dissolved in chloroform using PEG 400 as plasticizer and found that the system showed very poor compatibility, making it necessary to use a compatibilizer to improve the interfacial adhesion of these polymers. One alternative is to use a polymer that can interact with both of the polymers to be mixed, thus decreasing the interfacial tension between the components.

Polyvinyl alcohol is an interesting candidate compatibilizing polymer for PLA and chitosan because it forms compatible or miscible blends with chitosan, depending on their molecular weight and degree of substitution and can be obtained with several degrees of hydrolysis, which can be used to control its hydrophobicity. PVA is water-soluble, biodegradable, nontoxic, and biocompatible and has been used for biomaterial applications.^{13–15} PVA can also act as an emulsifier and stabilize the emulsion during emulsion blending, which is of fundamental importance for the subsequent performance of the polymer blend and is the object of research.^{10,11}

In this Article, we describe a ternary blend of chitosan/poly(vinyl alcohol)/PLA, processed via an oil-in-water (O/W) emulsion. The blends were prepared by mixing solutions of chitosan in aqueous acetic acid, poly(vinyl alcohol) (PVA) in water, and PLA in chloroform in a high shear mixer (Ultra-Turrax). The blend films were produced by casting and drying the emulsion in poly(tetrafluorethylene) dishes. The films were characterized by scanning electron microscopy (SEM), differential scanning calorimetry (DSC), Fourier transform infrared (FTIR) spectroscopy, stress-strain tests, and thermal mechanical analysis (TMA).

■ EXPERIMENTAL SECTION

Materials. The polymers used were: chitosan derived from crab shell with 74% deacetylation and $M_v = 32\,740$ g/mol, supplied by Galena Química, Brazil, PVA from Aldrich (80% hydrolyzed, $M_w = 9000$ – $10\,000$ g/mol), and PLA L 9000 from Biomer, with $M_w = 187\,000$ g/mol and polydispersity index of 1.5.

Emulsion Preparation. Chitosan was dissolved in water with 1% w/w glacial acetic acid. This solution was passed through a paper filter to remove insoluble substances. The weight loss due to filtration was <1% with respect to the initial dry weight of chitosan. PVA was dissolved in cold water and filtered through paper filter. PLA was dissolved in chloroform by stirring overnight. A clear transparent solution was obtained.

To prepare the oil-in-water emulsion, two immiscible solutions were used. An emulsion may be water-in-oil (W/O) or oil-in-water (O/W). In an O/W emulsion, the “oil” (chloroform solution in our case) is the inner discontinuous phase, which is dispersed in the outer (water) phase, whereas a W/O emulsion consists of droplets of aqueous phase dispersed in an oily phase. The properties of the corresponding emulsion are substantially determined by the outer phase so that W/O emulsions seem oily and O/W emulsions behave more like aqueous solutions. The majority of our experiments were performed in the O/W regime, with the exception of the blend with the highest proportion of PLA. To prepare the emulsion, an aqueous solution of chitosan in 1% acetic acid and PVA in pure water was mixed in a beaker with the PLA solution in chloroform, with a high-shear mixer (Ultra-Turrax) at 22 000 rpm for 60 s. The Ultra-Turrax mixer (Figure 3) enables an emulsion to be prepared with smaller droplets than in conventional mixing. The stability

of the emulsion was checked by inspecting the mixture under a light microscope at $400\times$ magnification, immediately after preparation and after 30, 60, and 120 min. In general, the emulsions were used immediately after preparation. However, most of the ternary blend emulsions proved to be stable for more than 2 weeks when examined under the light microscope. Conversely, the binary blends with PLA (CH/PLA and PVA/PLA) were stable for only a few hours.

Blend Preparation. In a preliminary test, the emulsions were spread in poly(tetrafluorethylene) Petri dishes and left to dry at room temperature or at 40°C . However, this procedure yielded unrepeatable results with phase separation. The chloroform droplets coalesced during drying, giving rise to brittle and heterogeneous films. To avoid this effect, the emulsion produced with the Ultra-Turrax was poured in a beaker and stirred with a magnetic stirrer at room temperature ($\sim 25^\circ\text{C}$) for 2 h. During this procedure, there was a loss of $\sim 40\%$ of the volume of emulsion due to evaporation of solvent, mostly chloroform. The resulting emulsion was spread in the Petri dishes and dried at 40°C in an oven. The emulsion stability was checked during stirring under a light microscope at $400\times$ magnification.

Blend Characterization. *Fourier Transform Infrared Spectroscopy.* Attenuated total reflection (ATR) infrared spectra were recorded from a Nicolet Nexus 470 spectrophotometer equipped with a Nicolet Specular-ATR module with zinc selenide crystal (45°), 4 cm^{-1} resolution, and 64 scans.

Differential Scanning Calorimetry. The DSC experiments were performed in a Shimadzu DSC-50 calorimeter with a liquid nitrogen cooling accessory and nitrogen as carrier gas, flowing at ca. $20\text{ cm}^3/\text{min}$. The instrument was previously calibrated (temperature and heat flow) with a high-purity indium sample at a heating rate of $20^\circ\text{C}/\text{min}$. The samples consisted of circular pieces cut from the films to give a total of 6 to 7 mg. The temperature program in all experiments was the same: heating at $20^\circ\text{C}/\text{min}$ from room temperature to 200°C , followed by cooling at $8^\circ\text{C}/\text{min}$. Two runs were performed with each sample, and the data were taken from the second run.

Thermomechanical Analysis. Thermomechanical tests were carried out in a Shimadzu TMA-50 thermomechanical analyzer with a silicon probe applying a load of 1.6 g during the analysis. The temperature was raised from room temperature ($\sim 23^\circ\text{C}$) to 190°C at a heating rate of $10^\circ\text{C}/\text{min}$ in a nitrogen atmosphere.

Stress–Strain Curves. The stress–strain curves were obtained in a dynamic mechanical thermal analyzer DMA Q800 from TA Instruments. The measurements were performed in the isothermal mode at room temperature at a constant loading rate ($0.5\text{ N}/\text{min}$) in the loading range of 0–18 N. The test pieces were $20 \times 1.5 \times 0.01\text{ mm}$.

Scanning Electron Microscopy. The morphology of samples was examined with liquid-nitrogen-cryofractured surfaces of the blends with a Philips XL30 FEG SEM. The samples were sputter-coated with gold after drying in a vacuum oven at 40°C overnight.

■ RESULTS AND DISCUSSION

Emulsion Preparation. The process used to prepare the ternary blends of chitosan/PVA/PLA by the emulsion blending method is outlined in Figure 1.

The step of solvent evaporation and emulsion concentration during the 2 h period of stirring at 25°C not only increased the emulsion stability but also enabled recovery of the organic solvent (CHCl_3), preventing its discharge into the atmosphere and allowing its reuse.

The compositions of the blends studied are plotted in the ternary diagram in Figure 2. Blend compositions are indicated by the relative proportions of their components in the order CH/PVA/PLA. Two of the binary blends, CH/PLA (1:1) and PVA/

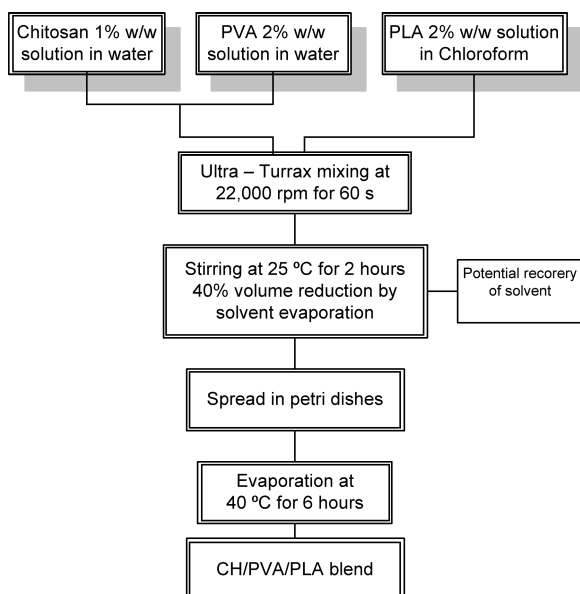


Figure 1. Flowchart of blend preparation.

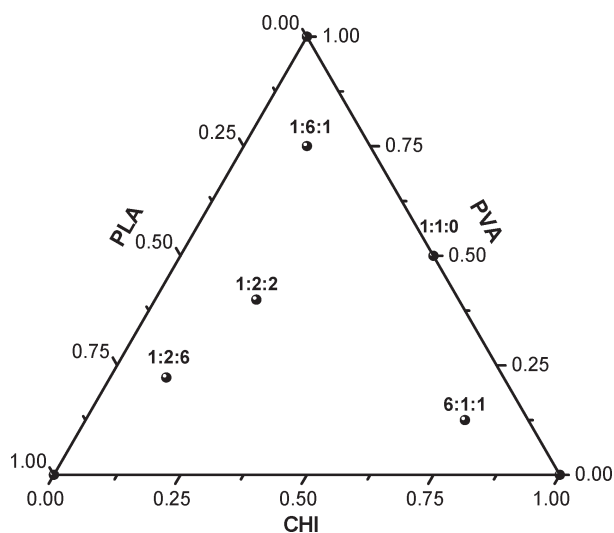


Figure 2. Ternary phase diagram for the blends of CH/PVA/PLA indicated in dry weight proportions.

PLA (1:1), are not shown on the ternary diagram because they were extremely fragile and difficult to handle. All prepared ternary blends were strong and easily handled, with the exception of the zone where $\text{PLA} > 0.75$, in the bottom left-hand corner of the diagram in Figure 2. Materials with these compositions were extremely brittle, making them impossible to handle or characterize, as were the binary blends CH/PLA and PVA/PLA (1:1).

Figure 3 shows the solutions prior to mixing and the emulsion formed after mixing with the Ultra-Turrax. The resulting emulsion was analyzed by light microscopy under $400\times$ magnification. The droplet size was from 1 to $30\ \mu\text{m}$, as shown in Figure 4, before concentration by solvent evaporation.

The stability of the emulsion was monitored by light microscopy at $400\times$, and it was found that the system was stable for at least 1 week. Micrographs of the “stable” emulsions of 1:2:2 CH/PVA/PLA, taken immediately after preparation and up to 3 days later, are reproduced in Figure 4.

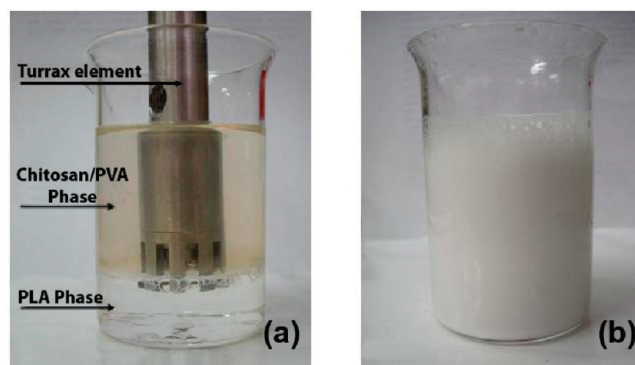


Figure 3. Photographs of (a) solutions of chitosan and PVA in water (top phase) and PLA in chloroform (bottom phase) with the immersed Ultra-Turrax and (b) the emulsion formed after mixing.

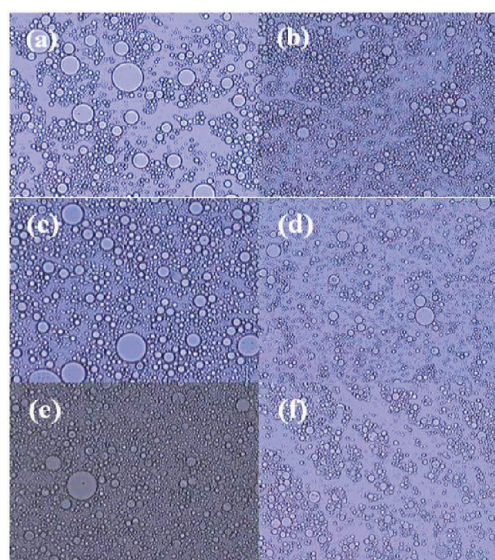


Figure 4. Micrographs of emulsion of CH/PVA/PLA 1:2:2 by weight at $400\times$ magnification after various storage times: (a) $t = 0$, (b) $t = 60$ min, (c) $t = 120$ min, (d) $t = 180$ min, (e) $t = 1440$ min, and (f) $t = 4323$ min.

Blend Film Preparation by Casting. The drying of the emulsion immediately after its preparation gave rise to inhomogeneous films with bubbles and signs of phase separation. Several tests were performed with the objective of producing a more homogeneous film. Those tests included evaporating the film in steps at several temperatures and controlling the vapor saturation by covering the film in the initial steps of drying. These trials resulted in some improvement in homogeneity and decrease in bubble formation. However, the best result was produced when the emulsion was stirred and concentrated by evaporation at $25\ ^\circ\text{C}$ for 2 h, leading to a fall of around 30–40% in the volume. In this step, most but not all of the chloroform was eliminated. If the evaporation was prolonged, then PLA precipitation occurred. The stability of the resulting emulsion was superior to that of the initial emulsion, even during long-term storage. This procedure selectively removed the more volatile chloroform yielding a stable (on a time scale of days to weeks) emulsion of PLA in the aqueous medium. An additional advantage is the possibility of recovering most of the chloroform prior to film processing.

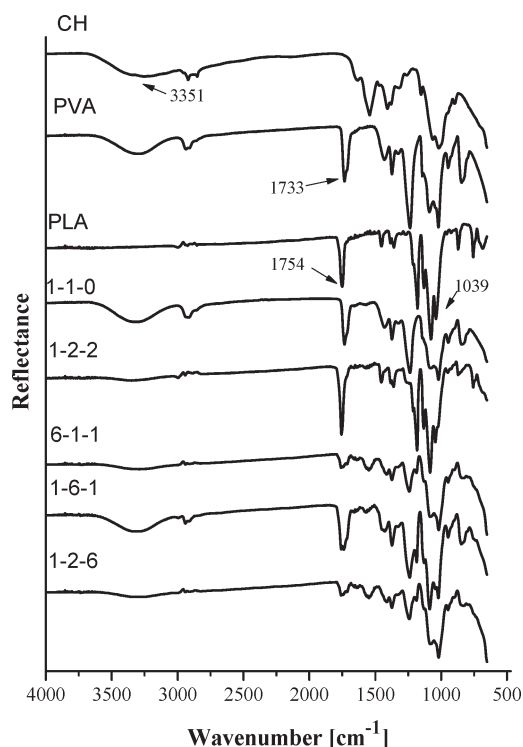


Figure 5. FTIR spectra of CH, PVA, PLA, and CH/PVA/PLA blends collected in the ATR mode.

Blend Characterization. *Fourier Transform Infrared Spectroscopy.* The FTIR spectra of CH, PVA, PLA, and the blends of various compositions are shown in Figure 5.

FTIR spectroscopy is a powerful technique to investigate polymer blend miscibility. When chemical groups interact at the molecular level, influencing their immediate environment, changes are seen in FTIR spectra such as the shifting of absorption bands. Such changes can be an indication of miscibility at the molecular level. Figure 5 shows FTIR spectra of CH, PVA, PLA, and their blends. Two important changes in the spectra of the blends were observed: a decrease in the intensity of the —NH and —OH absorption bands at $3355\text{--}3300\text{ cm}^{-1}$ of the chitosan and PVA spectra and shifting of the PVA and PLA peaks. Figure 6 shows in more detail the regions of the ester group bands of PVA and PLA ($\sim 1750\text{ cm}^{-1}$) and the spectra between 800 and 1400 cm^{-1} , where important peak shifting was observed.

The FTIR spectrum of chitosan shows, at 896 and 1153 cm^{-1} , peaks due to the saccharide structure, at 1262 cm^{-1} , a peak due to O—H deformation, at 1378 cm^{-1} , a peak assigned to —CH_3 , and the characteristic peaks of —NH and —OH groups at $3255\text{--}3360\text{ cm}^{-1}$.¹⁶ PVA showed absorption bands at 3300 , 2942 , 1733 , 1428 , 1376 , 1236 , 1090 , and 844 cm^{-1} attributed to —OH axial stretching, CH_2 stretching, ester band (20% unhydrolyzed acetate groups), H—OH deformation, CH—O deformation, CH wagging, C—O stretching, and C—C deformation, respectively, in agreement with the literature.¹² The peak at 1733 cm^{-1} of the ester band of PVA, which also appears at the same wavelength in the binary blend CH/PVA, is shifted to higher wavenumbers in the ternary blends, indicating specific interactions of PVA and PLA, which appears only in the ternary blends.

PLA showed absorption bands at 1754 , $1451/1360$, 1180 , 1076 , and 1039 cm^{-1} , which were assigned to C=O stretching

in —CO—O— (ester band), —CH_3 angular deformation, C—O—C symmetric stretching, C—O—C asymmetric stretching, and —C—O— stretching, respectively. The peak at 1754 cm^{-1} (carbonyl stretching) of PLA shifted to 1758 cm^{-1} in the blends 6:1:1 and 1:6:1, owing to the interaction of PLA with chitosan and PVA. The peak at 1039 cm^{-1} of PLA, due to —C—O— stretching in —O—C=O , shifted to 1045 cm^{-1} in the blend 1:2:2, owing to molecular interactions between the components. The peak at 1077 cm^{-1} of PLA also shifted to 1083 cm^{-1} in the ternary polymer blends.

The most appreciable change observed in the FTIR was in the peaks at $3355\text{--}3300\text{ cm}^{-1}$ for —OH and —NH stretching of PVA and chitosan. These peaks were reduced in the ternary polymer blends, except in the blend 1:6:1, which consisted mainly of PVA. This result indicates new molecular interactions of the —OH groups, suggesting that these groups were in a new chemical environment, possibly exposed to fewer hydrogen bonding interactions, which lead to a reduction in the peak intensity. This effect was observed only when all three components were mixed, indicating specific interactions caused by the addition of PVA and not observed in the binary blends. The weakening of the —OH and —NH peaks, at $3355\text{--}3300\text{ cm}^{-1}$ supports the assumption that the system should not be described as two completely separated phases with no or very little interaction but has a system in which the PLA and the hydrogen-bonding polymers PVA and CH are interacting closely.

Because the binary blend CH/PLA was incompatible, the effect of PVA as compatibilizer is notable. One interesting finding is that the blend PVA/PLA is also incompatible. These results show that there is probably a synergistic effect when all three components are present that is fundamental for the blend compatibilization.

Differential Scanning Calorimetry. The second heating stage was used to determine the thermal transitions of the isolated polymers and of the blends. It is hard to detect the glass-transition temperature (T_g) of CH, owing to the strong hydrogen-bonding between the polysaccharide macromolecular chains. DSC traces for CH, PVA, PLA, and the 1:2:2 blend are shown in Figure 7. The DSC data for T_g and T_m of PVA, PLA, and the blends are presented in Table 1. The T_g values of PVA and PLA were 68 and 58 , respectively. In the binary blend, CH/PVA, the T_g of PVA is decreased because of the miscibility of CH and PVA. The same effect occurred in the ternary blends, and one single value of T_g , close to that of PLA, was observed. However, it should be noted that the values of T_g for PVA and PLA are relatively close ($10\text{ }^\circ\text{C}$ difference), which could make it hard to identify individual values in the blends.

The melting points of PVA and PLA were 190 and $167\text{ }^\circ\text{C}$, respectively. For the blend CH/PVA, the melting point was decreased to a value close to that of PLA because of the miscibility between CH and PVA.¹³ Apart from blend 1:2:2, the other blends showed a single value of T_m due to the overlap of the peaks for PVA and PLA. The melting point of PVA/PLA in the chitosan-rich blend (6:1:1) showed the lowest value, an indication of miscibility due to the synergistic effects of the three components. The PLA-rich blend (1:2:6) showed a melting point near that of the pure polymers, indicating that increasing the proportion of PLA decreases the miscibility. For the PVA-rich blend (1:6:1), a relatively low value of T_m was observed, attesting to a good level of miscibility. The intermediate composition blend (1:2:2) exhibited two melting points, at 150 and $170\text{ }^\circ\text{C}$, one probably corresponding to PLA and the other to

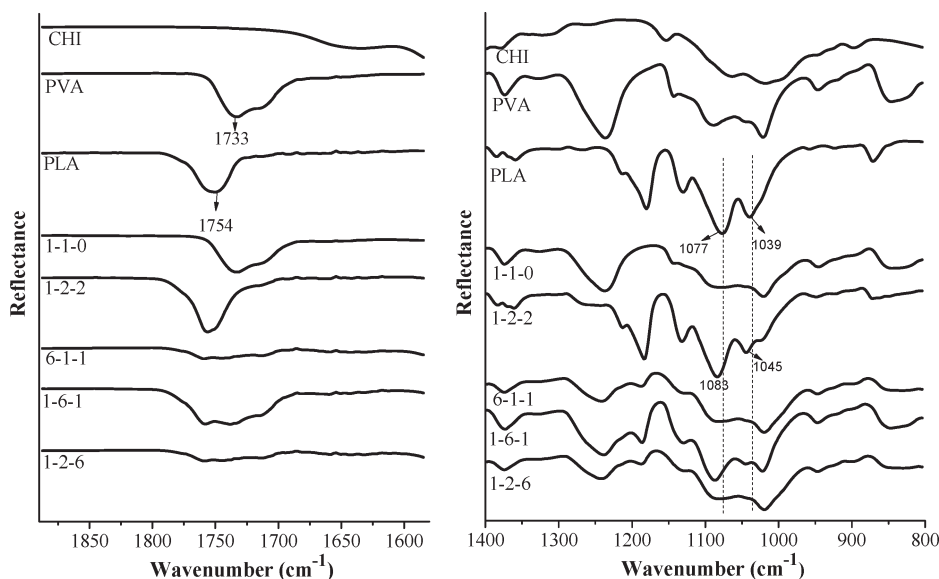


Figure 6. Expanded FTIR spectra of CH, PVA, PLA, and the CH/PVA/PLA blends collected in the ATR mode in the region of 1750 cm^{-1} and from 800 to 1400 cm^{-1} .

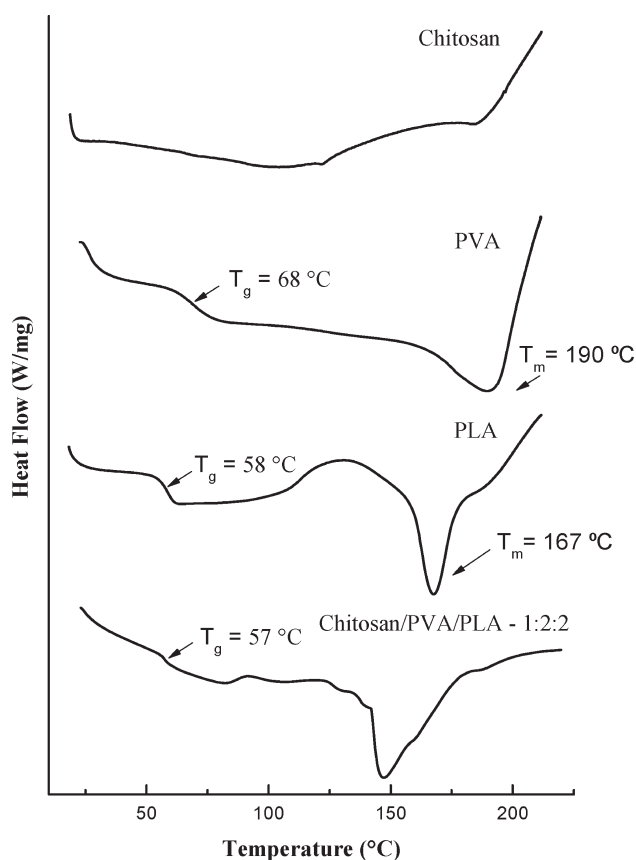


Figure 7. DSC curves of CH, PVA, and PLA and of the CH/PVA/PLA (1:2:2) obtained in the second heating scan.

PVA, each depressed by $\sim 20^\circ\text{C}$. This result also indicates some miscibility because the melting points of the pure components were depressed. These results showed the compatibilization of the three-component system, which is not observed in the binary blends.

Table 1. Glass-Transition Temperature, T_g , and Softening Points Measured by TMA (T_g or T_m)

blend mass ration CH/PVA/PLA	DSC		TMA	
	T_g ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	low softening point T_g ($^\circ\text{C}$)	high softening point T_m ($^\circ\text{C}$)
1:0:0				
0:1:0	68	190	57	187
0:0:1	58	167	47	155
1:1:0	56	170	60	
1:2:2	57	150/170	42	
6:1:1	55	145		
1:6:1	59	156	57	160
1:2:6	58	167	59	

Thermomechanical Analysis. In TMA, a probe is lowered onto the surface of a sample while the temperature is increased at a predetermined rate. The technique is based on the measurement of the deformation of the sample under very low load as the temperature is increased, and two main modes of deformation can be used, defined by the probe/sample contact area and the applied load: (i) expansion, when there is a large contact area and a low force is applied, and (ii) penetration, with a small contact area and high load.^{17,18} In general, a combination of expansion/penetration is observed. Here TMA was used to determine the glass-transition temperature,^{17,19,20} the softening temperature,^{17,18,20} and the crystalline melting point. These transition temperatures were taken as the temperature at which the rate or direction of probe deflection changes suddenly. Apart from T_g , it is possible to determine the softening temperature, which may coincide with T_g , T_m , or with other mechanisms because TMA combines thermal and mechanical events.

TMA curves of CH, PVA, PLA, and of the blends are shown in Figure 8. The glass-transition temperature, melting temperature, an softening point data determined from TMA curves are given

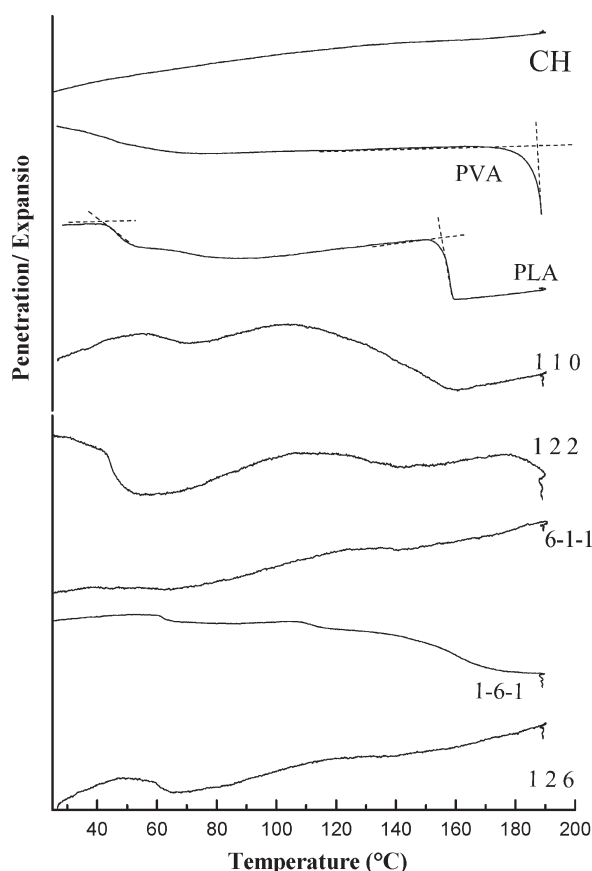


Figure 8. TMA curves for CH, PVA, PLA, and CH/PVA/PLA blends recorded from room temperature to 190 °C.

in Table 1. Because thermal transitions in TMA are characterized only by an inflection in the baseline, the criteria used to attribute the event to the glass transition or melting point were the temperature range (lower temperature for T_g and higher for T_m) and the proximity to the T_g and T_m determined by DSC. CH shows a continuous expansion profile as the temperature is increased, without thermal transitions. For PVA, an inflection point was detected at 57 °C, which is 10 °C below the DSC value for T_g and complete penetration, which is correlated with the melting temperature, occurred at 187 °C, which is very close to the temperature detected by DSC.

PLA shows both T_g and T_m very clearly at 47 and 155 °C, respectively. Those values are lower than those observed by DSC, which were 58 and 167 °C, respectively.

The blends showed more complex TMA profiles, but in general only one low softening temperature was detected, which represented the glass-transition temperature of PVA and PLA. Complete penetration at higher temperature was observed only for the PVA-rich blend (1:6:1) at 160 °C.

Stress–Strain Behavior. This test was performed on the ternary and CH/PVA blends. For the binary blends PVA/PLA and CH/PLA tensile tests were impossible because these blends disintegrated after preparation, making them impossible to handle. The results of tensile stress tests performed in the DMA equipment operating in tension mode are presented in Figure 9.

The data for tensile strength at break and tensile modulus are presented in Table 2.

Chitosan shows typical brittle behavior and displays the highest tensile modulus (4.5 GPa). PVA and PLA display tough

behavior but break before reaching their yield points. PVA has a lower modulus than PLA, showing tough behavior with the highest area under the stress–strain curve. The blends show a behavior more like that of chitosan, with higher tensile moduli than PLA and PVA and brittle behavior. This behavior was observed even in the blend 1:2:2, which contains only 20% chitosan. The behavior of the binary blend CH/PVA shows that chitosan is the component dominating the mechanical behavior. The results for the ternary blends confirm that the system is compatible because the mechanical properties, in particular, the modulus, are effectively higher. Despite the low proportion of chitosan, the moduli for the blends are of the same order as that of chitosan. One indication that PVA has a synergic effect on the system is the fact that although PVA is the component with the lowest modulus, the ternary blends showed high moduli, becoming more like the brittle chitosan. The 1–6–1 blend showed properties very close to that of PVA, owing to the high proportion of PVA in this blend, and can be considered to be a miscible blend of chitosan/PVA with finely dispersed phase of PLA. The blend 1–2–6 was extremely fragile and brittle, making any stress–strain measurement impossible. This blend was clearly incompatible, representing a limit to the increase in PLA concentration.

Scanning Electron Microscopy. Figure 10A–H shows SEM images of brittle fracture surfaces of CH, PVA, PLA and blend films. The pure polymers CH, PVA, and PLA show homogeneous flat surfaces. The binary blend CH/PVA shows a homogeneous surface with a (micro) wave pattern of fibrils. The brittle fracture surfaces of the ternary blends show two clear distinct phases, a globular phase in a continuous matrix. The globular phase is the PLA, whereas the matrix is composed mostly of CH/PVA. The PLA-rich blend (1:2:6) is more heterogeneous, showing PLA globules of very varied size and holes due to low adhesion between the phases. The SEM analysis shows that among the blends, this is the blend with the lowest level of compatibility, corroborating the DSC and FTIR data.

The blends 1:2:2, 6:1:1, and 1:6:1 show rough surfaces, with globules that could represent the PLA phase. The CH-rich blend, 6:1:1, with 75 wt % chitosan, also shows some holes due to low adhesion between the components, but its properties are consistent with a compatible blend. It is notable that this blend, in which the PVA content is low (12.5 wt %), is compatible, showing that lower concentrations of PVA are also effective as a compatibilizer.

The blends 1:2:2 and 1:6:1 also show the PLA globules, but there is no evidence of debonding, which leads to the conclusion that these are compatible blends. Of these two blends, 1:6:1 shows a very high level of compatibility, the matrix appearing similar to the CH/PVA matrix, with the characteristic fibril wave pattern. The blend 1:2:2, with 40% of PLA and 20% of chitosan, was also compatible and is of great interest for its high proportion of PLA and chitosan. Using the SEM observations to order the blends from least to most compatible, we find 1:2:6 < 6:1:1 < 1:2:2 < 1:6:1. This order is in reasonable agreement with the data from DSC and FTIR observations.

These results confirm the importance of PVA, not only to stabilize the emulsion but especially as a blend compatibilizer. The results of DSC, stress–strain tests, and FTIR suggest a synergistic effect when PVA and chitosan are both present. It should be stressed that for the binary blends of chitosan–PLA or PVA–PLA, the films are extremely fragile and difficult to handle. Their mechanical properties were not determined because of the

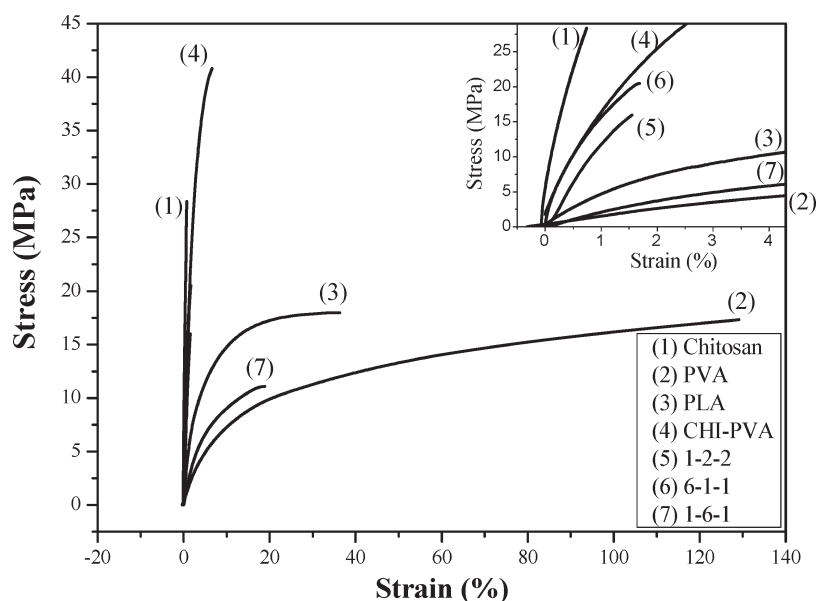


Figure 9. Stress–strain curves for CH, PVA, and PLA and for the blends CH/PVA 1:1 and CH/PVA/PLA 1:2:2 and 6:1:1.

Table 2. Tensile Strength at Break and Tensile Modulus of Pure Polymers and Its Blends (CH-PVA-PLA) Measured by DMA

	breaking strength (MPa)	tensile modulus (GPa) ^a
chitosan	>28	4.52
PVA	>17	0.15
PLA	18.0	0.50
1:1:0	40.8	1.64
1:2:2	16.0	1.20
6:1:1	20.5	1.70
1:6:1	11.0	0.20
1:2:6		

^a Modulus taken at 1% deformation except for chitosan which was obtained at 0.5% deformation.

extreme fragility of the films produced from these binary blends. One possible explanation for the synergistic effect was the fact that chitosan forms a miscible blend with PVA, making the final ternary immiscible blend in reality a binary blend between the chitosan/PVA miscible blend and PLA, rendering a distinct new system. The binary blend chitosan/PVA is a complex system which, depending on the characteristics of the individual polymers, has been described as a partially miscible system.¹³ This is attributed to the fact that chitosan in general has a wide molar mass distribution and a heterogeneous distribution of the acetyl groups on the chain backbone. These characteristics probably force portions of chitosan chains out of the chitosan/PVA phase so that they have to interact with the PLA phase, increasing the interfacial adhesion between the PLA and chitosan/PVA phases.

The level of compatibilization observed opens the way to potential new applications of PLA-chitosan blends in which their biodegradability, biocompatibility, and nontoxic characteristics are retained.

CONCLUSIONS

Blends of chitosan, PLA, and PVA were prepared successfully by O/W emulsion processing of PLA, PVA, and chitosan. PVA

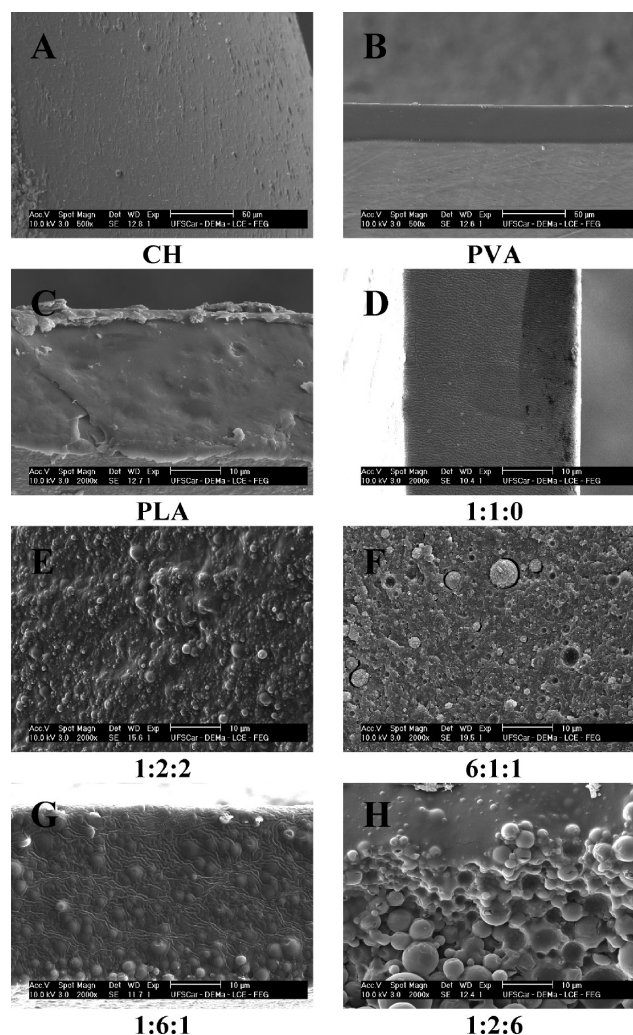


Figure 10. SEM micrographs of the cryofractured surfaces of (A) chitosan, (B) PVA, and (C) PLA and the blends CH/PVA/PLA: (D) 1:1:0, (E) 1:2:2, (F) 6:1:1, (G) 1:6:1, and (H) 1:2:6.

was used as a compatibilizing agent for PLA and chitosan. The blends produced were biodegradable and biocompatible because all raw materials were biodegradable, nontoxic, and biocompatible. An Ultra-Turrax mixer was used to produce stable emulsions of the polymers dissolved in appropriate solvents, viz aqueous media for chitosan and PVA and chloroform for PLA. The emulsion produced was of the O/W type, in which the dispersed phase was the PLA chloroform solution. Stabilization of the emulsion was highly dependent on the presence of PVA and on an evaporation step prior to the film casting. This evaporation allowed concentration of the polymer solution and enabled the majority of the chloroform used to be recovered. The blends were characterized by thermal analysis (DSC and TMA), by FTIR spectroscopy, and by SEM. DSC measurements show depression of the melting temperatures of PVA and PLA and of the glass temperature of PVA in the blends.

The FTIR absorption characteristic bands of the three polymers changed in the blends. Two important changes were seen, the depression of the peaks due to -NH and -OH absorption of PVA and chitosan in the region $3355\text{--}3300\text{ cm}^{-1}$ and shifts of the carbonyl peaks of PLA, indicating that some degree of compatibility had been achieved. The stress-strain mechanical tests show that the ternary blends behave more like chitosan than the other components, exhibiting a brittle behavior and tensile modulus of the same order, whereas PVA and PLA behave as tough materials, confirming that the ternary blends are compatible because of the addition of PVA. Except for the PLA-rich blend, which is incompatible, the other blends showed a very good level of compatibility, especially the blends CH/PVA/PLA 1:2:2 and 1:6:1, which showed a very high level of adhesion between phases and are promising candidates for the development of new materials composed of PLA and chitosan, with the antifungal and antibacterial activity. The blends produced are good candidates for such applications because they combine easy processing with the hydrophobic properties of PLA and the functional properties of chitosan.

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