Compatibilization Method Applied to the Chitosan-Acid Poly(L-lactide) Solution

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ABSTRACT: We are testing the compatibilization of the chitosan/PLA blends by addition of diisocyanate and at studying the effect of several MDI concentrations (0.5 and 2.5% of the global blend mass, w/w). To evaluate the MDI efficiency as a compatibilizer of chitosan/PLA blends, we worked with the following methods: IRTF spectra with higher peak at 1558 cm^{-1} is due to the —NH bonds that exist in urea and urethane, thermal properties shows that the temperature of the endothermic peaks of the chitosan/PLA blends with MDI is very close to the temperature of pure chitosane and SEM micrography shows that MDI addition decreases the PLA particles size in the chitosan mixture; they also comply with the compatibilization theory. After that the mechanical properties have been characterized: we can notice that the MDI compatibilized chitosan/PLA blends have a higher Young's modulus than the noncompatibilized blends. we are showed that the use of 0.5% MDI is not enough sufficient to obtain a compatibilization, because a part of the MDI can be consumed by water. The addition of MDI increases the performance of the mechanical properties of the blends. Therefore, with this compatibilization, we could obtain some chitosan/PLA blends that would be water-resistant and that would also keep their mechanical properties. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 3083–3091, 2010

Key words: chitosan; PLA; compatibilization; MDI; blend

INTRODUCTION

Chitosan is a natural, nontoxic, edible, and biodegradable polymer. It is obtained by deacetylation of chitin, which is the second most abundant biopolymer that can be found in nature, just after cellulose.[1] In general, chitin can be found in the exoskeleton of arthropods such as insects, crabs, shrimps, lobsters, and some fungal cell walls.[2] It has potential as packaging polymer and, more precisely, as an edible packaging or coating thanks, to its film-forming ability, without using any additives.[3] Moreover, chitosan films have a good oxygen and carbon dioxide permeability, which is lower than the one of polyethylene films[4,5]; they also have good mechanical properties, which can be compared with those of many medium-strength commercial polymers.[5] Furthermore, chitosan has an antimicrobial activity against different microorganism groups, such as bacteria,[6–10] fungi,[10–13] and yeast.[10,12] Therefore, chitosan can be used to create edible coatings or films to extend foodstuffs' shelf life, such as fruits,[14–16] meat,[17,18] fish, and seafood.[19,20] These studies show that chitosan might act as an antimicrobial packaging, which seems to be a promising form of active food packaging.[21] Furthermore, with growing concerns about environment, the development of new biodegradable packaging materials, such as chitosan films, could be an interesting alternative to petroleum-based plastics.

Unfortunately, there are some limitations in these kinds of applications for chitosan, because it is highly moisture sensitive. One solution to overcome this drawback is to associate chitosan with a moisture-resistant polymer, while maintaining the product overall biodegradability. This association between polymers can result in blends or in multilayer products, for example, coatings or laminated films. Nevertheless, blending is an easier and a more effective way to achieve multiphase polymeric materials with the required properties.[22]

Adding chitosan to other biodegradable polymers, for example, poly(3-hydroxybutyric acid) (PHB)[23] and poly(ε-caprolactone) (PCL),[24,25] is a way to modify its water-sensitive properties. Another interesting possibility is to add chitosan to poly(lactic acid) (PLA): this kind of study has not been reported yet, as far as packaging applications are concerned.

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Moreover, the chitosan film has good barrier properties against gas and good mechanical properties. Thanks, to these qualities, several studies have been launched on the possible applications of chitosan, to preserve or to extend shelf life from some fresh products, such as fruits and vegetables, meat, and seafood. These studies show that it is possible to use chitosan as an active packaging material. However, there are some limitations. Indeed, it is steam sensitive due to its ability to form a big number of hydrogen bonds (two hydroxyl functions and one amine function in each motif repetition); it is also hard or brittle, and it needs to be associated to another polymer to overcome this kind of problem.

PLA belongs to the family of aliphatic polyesters, commonly derived from lactic acid, and which can be produced via fermentation processes[26] based on renewable resources such as starch. It is a thermoplastic, high-strength, high-modulus polymer, and it is considered as biodegradable and compostable.[27] As far as PLA availability on the market is concerned, at least six companies said they plan developing PLA.[28] Indeed, Cargil Dow (USA) produces annually about 140,000 metric tons of PLA.[26]

The reactive groups on the macromolecular chains of each constituent in a polymer blend can be used for the compatibilization process. However, most of the time, the intermolecular chemical reaction can occur only when adding a reagent during the blending process. In our case, chitosan has a lot of —OH and —NH$_2$ groups, whereas PLA has some —OH and —COOH groups. The approach proposed here, consists in compatibilizing the chitosan and PLA blends thanks, to a chemical reaction between these reactive groups.

The compatibilization between two incompatible polymers can be made through chemical reactions between their functional groups, to form an *in situ* compatibilizer. The compatibilizer[29–31] is an interfacial agent that (1) reduces the interfacial energy between the two phases, (2) reduces the particles size during the blending process, (3) gives stability to the mixture, and (4) increases the interfacial adhesion.

In the literature, some compatibilization works have been achieved on starch/PLA systems, using the 4,4′-Methylenebis(phenyl isocyanate) (MDI) to produce an *in situ* compatibilization.[29] The compatibilization by adding diisocyanate is based on the addition reaction between the isocyanate group and the PLA hydroxyl group that results in a urethane R—NH—CO—OH—R′ group.[28] The possible chemical reactions between the PLA and the diisocyanate are showed in Figure 1(A).[31] The chitosan can also react with the diisocyanate groups due to the presence of numerous hydroxyl and amine groups: the reactions are showed in Figure 1(B). It may therefore be possi-

ble that for PLA/chitosan blends, the diisocyanate acted as a coupling agent to bind PLA and chitosan with covalent bonds; this could enhance the interactions between the two polymers and reduce the size of PLA particles during the blending process.

Moreover, some authors[32] reported that using low-concentration MDI (0.5%, w/w) in PLA/native starch blends, could enhance the traction resistance and the elongation-at-break of the compatibilized blend, compared with noncompatibilized blends. On the other hand, the use of higher MDI concentrations (1 and 2%) does not enhance more these two mechanical characteristics.

This survey aims at testing the compatibilization of the chitosan/PLA blends by addition of diisocyanate and at studying the effect of several MDI concentrations (0.5 and 2.5% of the global blend mass, w/w).

To evaluate the MDI efficiency as a compatibilizer of chitosan/PLA blends, we worked with the following methods: IRTF spectra, thermal properties, and SEM micrography. After that the mechanical properties have been characterized: Young's modulus (E), break strength (σ_r), and elongation-at-break (ε_r).

MATERIALS AND METHODS

Materials

The chitosan used was a commercial material obtained from shrimp shell (Les Pêcheries Marinard, Québec, Canada). Its degree of deacetylation was 80–85%, determined by a colloidal method. The PLA (92% L-Lactide and 8% meso-lactide) was provided in pellets by Cargil Dow (Dow Cargill Manufacturing, Blair, Nebraska). The average molecular weight of 49,000 was determined by intrinsic viscosity measurements in chloroform at 25°C. The solvents were acetic acid and chloroform purchased from Aldrich.

Chitosan/PLA blend compatibilization

MDI was used as a compatibilizer because it had already been used in the PLA/starch blend[31,32] and also in our blend.[33] In a preliminary survey, the Toluene diisocyanate TDI was also tried to be use but it gives a brown coloration to the resulting films. The chitosan-g-PLA copolymers (synthesized with the direct grafting method (DG) and with the ROP method) cannot be used as compatibilizers in our survey, because they are insoluble. That is why the chitosan/PLA blend compatibilization is done as shown in Figure 2: The isocyanates react with the PLA (solubilized in chloroform) at 60°C during 1 h. The PLA solution, linked with the isocyanate groups, is dripped into the chitosan's solution (1% w/w). The chitosan/PLA solution is first heated at
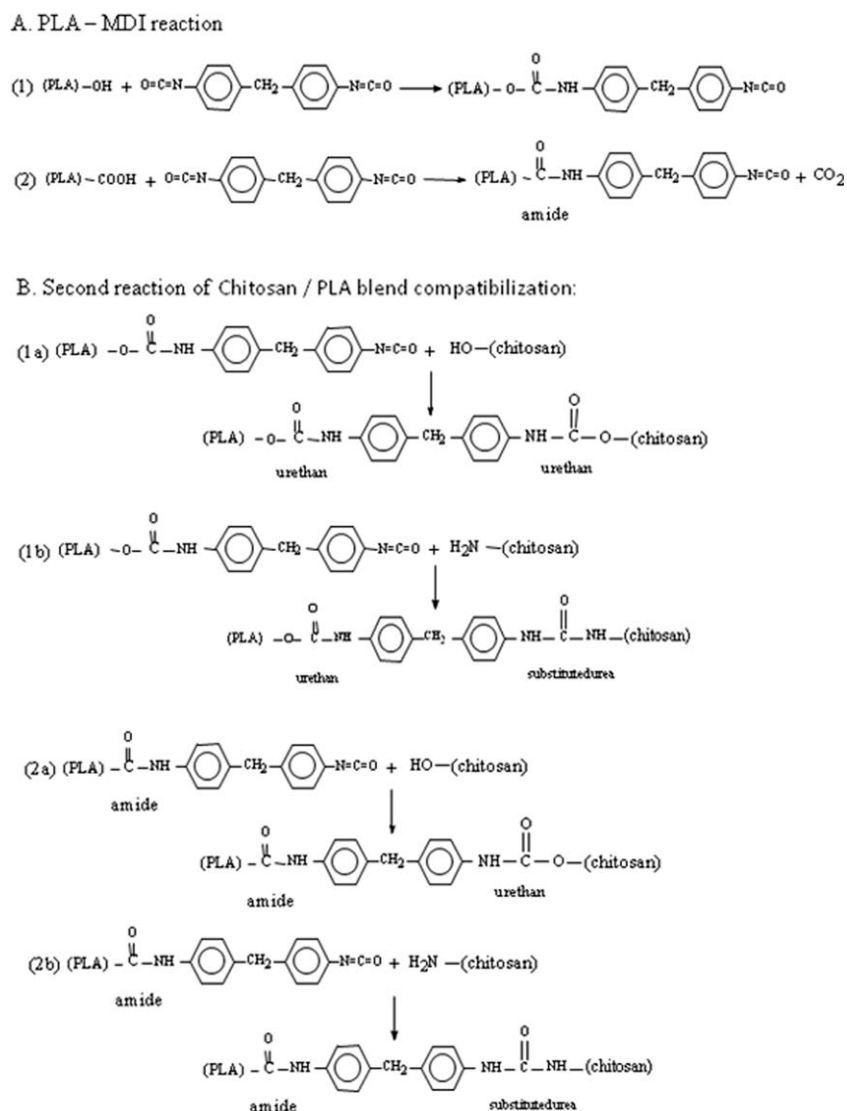
Figure 1 (A) Addition of 4,4'-méthylènebis(phénylisocyanate) (MDI) on the PLA and possible (B) Reactions leading to the compatibilization of the chitosan/PLA mixture with MDI.

80°C during 30 min, and then mixed during 2 h, until the solution becomes homogenous.

Sample analysis

Tensile testing

Tensile testing was carried out on a tensile testing machine (Adamel-Lhomargy, DY25, France), with a crosshead speed of 50 mm/min. Each sample's width and thickness were measured before testing. Ten samples from each blend composition were tested after a 6-week conditioning period at 50% HR (Humidity relative) and 23°C. Tensile strength (TS), Young's modulus (E), and elongation-at-break (EB) were obtained. TS can be calculated by dividing the ultimate strength by the cross-sectional area. EB can be calculated by dividing the elongation at the moment of rupture by the initial length of the sam-

ple and by multiplying it by 100. Young's modulus (E) can be obtained from the initial slope of the stress–strain curves.

Thermal analysis

The thermal characteristics of the blends were determined by using a differential scanning calorimeter method (DSC) (TA instrument-USA) cooled with a liquid nitrogen circulation. Samples (8–10 mg) were cut from a sample specimen after conditioning and placed in sealed aluminum pans. In DSC analysis, the method of Sakurai has been used with minor modifications. For each sample, the following thermal cycle was applied: a first scan was made from 30 to 190°C, and then kept 1 min at 190°C; afterward then the sample was cooled rapidly to 30°C; it has been kept 3 min at 30°C, and a second scan up to
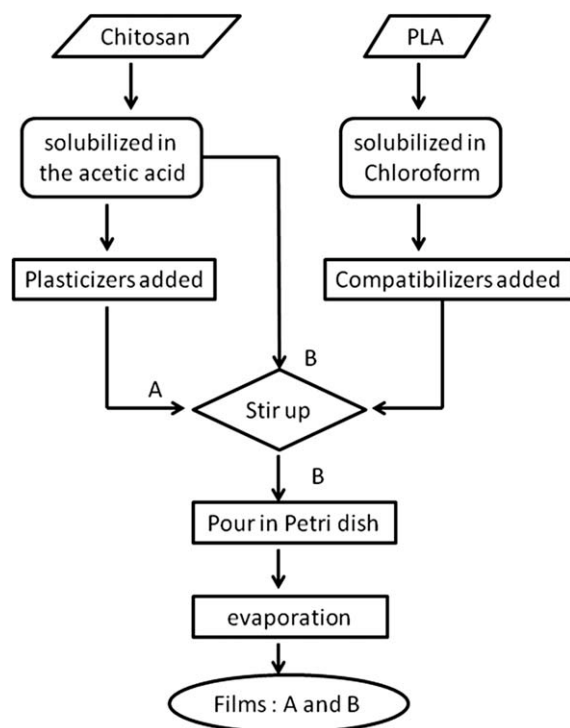
Figure 2 Manufacturing process of films by casting. (A) chitosan plasticized and (B) compatibilization of the chitosan/PLA mixture.

250°C was made again. The scanning rate was 10°C/min, and an empty pan was used as a reference.

FTIR spectrometry analysis

The samples were prepared in 0.50 mm-thick KBr pellets, obtained by mixing 3–5 mg of powder films (extra fine) with 200 mg of dried KBr. The FTIR spectra between 4000 and 400 cm^{-1} were recorded using a Nicolet 460 ESP FTIR spectrometer (Madison, WI). All spectra were obtained at ambient temperature with a resolution of 4 cm^{-1}, and 16 scans were carried out for each sample.

Scanning electron microscopy (SEM)

It is the most direct method to observe the demixing phenomenon, because it allows measuring precisely the dimensions from the different phases. However, this method is only efficient if there is enough contrast for the observation and therefore for the interpretation. Its principle is similar to optical microscopy with direct lighting. When the beam of electrons is directed on the sample, one part of the electrons interacts with the sample, whereas the other part is reflected. The resulting calculations give images that create a three-dimensional appearance from the surface structure of the studied sam-

ple. This technique has been used to study the chitosan-PLA compatibility in composite films.

The device we used is the SEM "JEOL JSM 5400 LV" (Japan). The micrographics have been obtained with a 3 kV accelerating voltage.[24]

RESULTS AND DISCUSSION

FTIR spectroscopy analysis

The chitosan/PLA blends compatibilized by MDI addition have been characterized with the infrared spectroscopy method. This method allows detecting the presence of hydrogen bonds and also some other interactions, by comparison between the blends' spectra, the chitosan spectrum, and the PLA spectrum. Figure 3 shows the chitosan IR spectra (spectrum A), the PLA spectrum (spectrum E), the 90/10 noncompatibilized chitosan/PLA blend (spectrum B), and the MDI 0.5 and 2.5% compatibilized chitosan/PLA blends (spectrum C and D, respectively). Figure 4 shows the same kinds of curves, but for composite films containing 20% of PLA.

Figures 3 and 4 show the absorption peaks that characterize pure chitosan and pure PLA, in the spectra of MDI-free chitosan/PLA blends. The bands of valence vibration $\nu_{C=O}$ from the —NH—CO—CH$_3$ group and from the deformation δ_{NH} that characterize the —NH—CO—CH$_3$ and —NH$_2$ groups, can be seen at, respectively, 1652 cm^{-1} and 1558 cm^{-1} [Figs. 2(B) and 3(B)]. In the chitosan/PLA blends spectra, which contain 0.5 and 2.5% of MDI, [Figs. 3(C) and 3(D)], there is no $\nu_{N=C=O}$ peak at 2266 cm^{-1} and this confirms a total chemical reaction between the
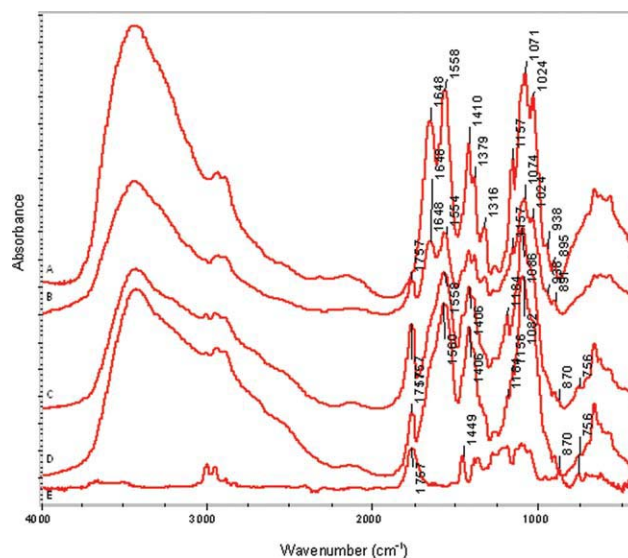

Figure 3 IRTF spectrum of pure chitosan films (A); of blend chit/PLA: 90/10 (B), 90/10 + 0.5% MDI (C), 90/10 + 2.5% MDI (D), and pure PLA (E). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 4 IRTF spectrum of pure chitosan films (A); of blend chit/PLA: 80/20 (B), 80/20 + 0.5% MDI (C), 80/20 + 2.5% MDI (D), and pure PLA (E). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
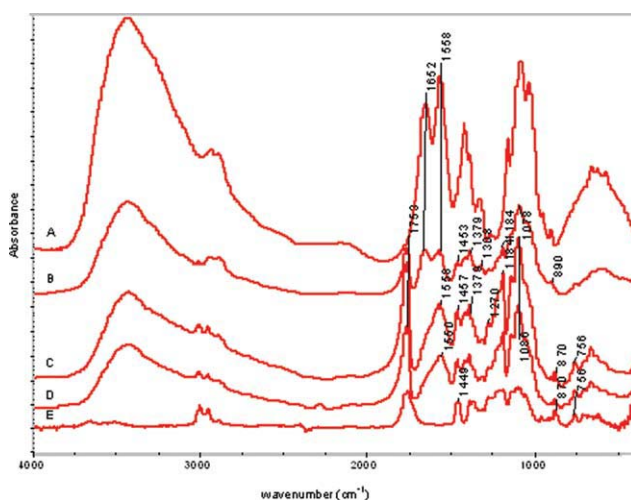
—NCO groups, the —OH groups (PLA and chitosan) and the —NH2 groups. More over, the higher peak at 1558 cm^{-1} is due to the —NH bonds that exist in urea and urethane. The peak levels at 1757 cm^{-1} ($\nu_{C=O}$ in esters and urethanes) and at 1652 cm^{-1} ($\nu_{C=O}$ in urea) are also higher: this is due to the formation of urethane and urea groups. Furthermore, MDI addition shows that the crystalline phase characteristic bands appear at 756 cm^{-1}; the PLA amorphous phase characteristic bands also appear at 870 cm^{-1}, even if the PLA quantity in the mixture is low (10%). All these results confirm that the specific interaction between PLA and chitosan occur at a higher level, when MDI is added.

The crystallinity index (CI) of the chitosan/PLA films has been calculated thanks, to the Cohn and Younes method[34] for the PLA and following the Focher method[35] for the chitosan. Table I summarizes the calculation of these crystallinity indexes for the chitosan/PLA films. We can see here that the PLA incorporation (without using any compatibilizer) decreases the chitosan's cristallinity. On the other hand, MDI addition increases the chitosan's cristallinity in the chitosan/PLA mixtures. As far as PLA is concerned, the crystallinity index of the compatibilized blends is higher than the one of pure PLA. We can also notice that the PLA crystallinity index is higher in the compatibilized blends than in the blends without MDI.

In blends containing MDI, the formation of urethane and urea bonds between MDI, PLA, and chitosan increases the interfacial adhesion and makes crystallization easier. These results comply with[31] that studied the PLA/starch blends, compatibilized with MDI.

SEM observation

Figure 5 shows SEM micrographics from the film surface for a chitosan/PLA mixture 80/20 (w/w) without MDI (A), with 0.5% MDI (B), and with 2.5% MDI (C). The different sizes of the PLA particles scattered in the chitosan matrice can be clearly seen. In the MDI-free mixture, the PLA particles size can vary a lot and their size is much bigger than in the mixture with 0.5% MDI. In the mixture with 2.5% MDI, PLA particles are quite invisible, even under a magnifying glass, because their sizes are very small. These results show that MDI addition decreases the PLA particles size in the chitosan mixture; they also comply with the compatibilization theory.[36] The SEM observation shows that the compatibilization is better achieved by using a 2.5% MDI concentration than a 0.5% MDI concentration.

The FTIR spectroscopy and the SEM results show that the interfacial adhesion between PLA and chitosan is enhanced thanks, to MDI addition. Besides, we can notice that the compatibilization with a 2.5% (w/w) MDI solution is better than with a 0.5% (w/w) MDI solution. Indeed, all the MDI introduced into the chitosan/PLA mixture cannot contribute to the compatibilization process because a part is used in a parasitic reaction that occurs with water. According to some authors,[31] MDI can react with water present in the material (here in our case, it is the aqueous solution of chitosan) following the mechanism showed in Figure 6. Therefore, a low-concentration (0.5%) MDI solution has may be not a sufficient concentration, because a part of the MDI is consumed by water. For this reason, MDI and the PLA have been first tried to force to react together, and after we added this mixture into the chitosan's solution. In so doing, we hope limiting the extension of the reaction between MDI and water.

As far as the application of these films on the food market is concerned, the parasitic reaction between MDI and water will be very useful. Indeed, thanks, to this reaction, there won't be any free isocyanates groups left in the film. Figures 3 and 4 confirm that,

TABLE I
Calculation of These Crystallinity Indexes for the Chitosan/PLA Films

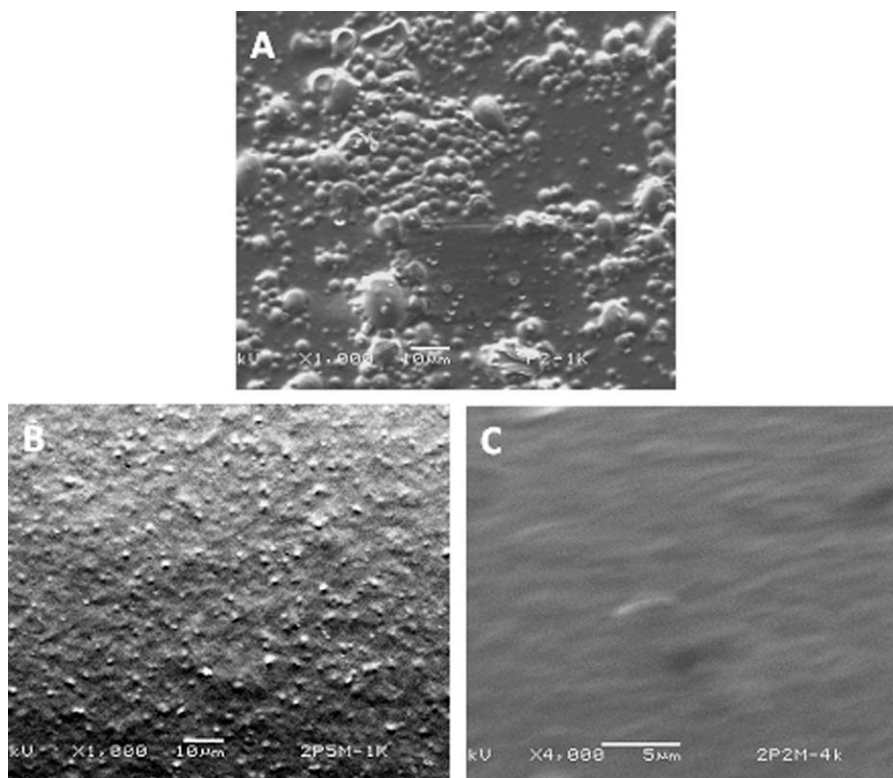| Chitosan/PLA blend Chit/PLA (w/w)	IC chitosane (A1379/A2900)	IC PLA (A756/A870)
100/0 (pure chitosane)	0.75	–
90/10	0.70	–
90/10 + MDI 0.5%	0.83	1.03
90/10 + MDI 2.5%	0.79	1.10
80/20	0.73	0.71
80/20 + MDI 0.5%	0.90	1.20
80/20 + MDI 2.5%	1.05	1.30
0/100 (PLA pur)	–	0.79

Figure 5 Micrographics from the film surface for a chitosan/PLA mixture: 20% of PLA: (A) without MDI, (B) with 0.5% MDI, and (C) with 2.5% MDI.

in the end products, the characteristic band of the isocyanate group (N=C=O), that is normally located at 2270 cm^{-1} does not appear.

Thermal properties obtained by a differential scanning calorimeter method (DSC)

Figure 7 shows the DSC thermograms obtained after the first sweep. Pure PLA shows a glass transition temperature T_g at 58°C. The chitosan/PLA blends with and without MDI show a slightly higher PLA T_g value than the pure PLA T_g (Table II). Pure PLA shows a melting peak at 154°C, with an enthalpy of fusion of 15.3 J/mol (% of cristallinity = 16.5%). The pure chitosan and the blends show a high endothermic peak due to water evaporation, water that is still present in the material. The temperature of the endothermic peaks of the MDI-free chitosan/PLA
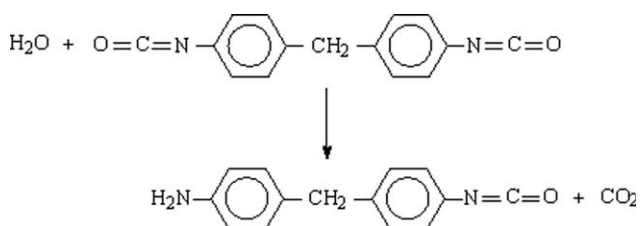
blends is lower than the one of pure chitosan; the temperature of the endothermic peaks of the chitosan/PLA blends with MDI is very close to the temperature of pure chitosane. The enthalpy of vaporization is showed in Table II and is linked to the material's moisture.[37] The values of $\Delta H_{\text{vaporization}}$

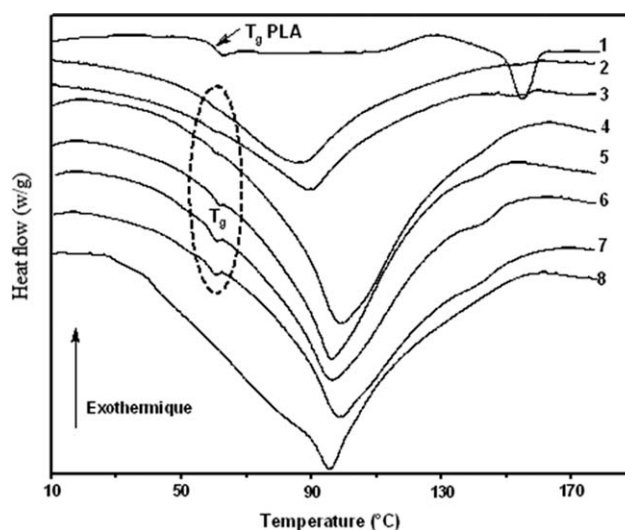**Figure 6** Reaction parasitizes between the MDI and water.

Figure 7 DSC thermograms obtained after the first sweep for blends of chit/PLA: (1) 0/100 or pure PLA, (2) 90/10, (3) 80/20, (4) 90/10 + 0.5% MDI, (5) 90/10 + 2.5% MDI, (6) 80/20 + 0.5% MDI, (7) 80/20 + 2.5% MDI, and (8) 100/0 or pure chitosan.

TABLE II
Thermal Analysis of Blend of Chitosane/PLA With and Without MDI

Chit/PLA (w/w)	Pic endo (°C)	ΔH evaporation (J/g)	T_g exp. (°C)	T_g theoretical (°C)[a]	T_{deg} (°C)
100/0 (pure chit)	96	422.0	206	–	286
90/10	87	419.2	59, 197	185	260
90/10 + 0.5% MDI	96	381.4	59, 195	185	271, 293
90/10 + 2.5% MDI	96	341.5	59, 193	185	281, 295
80/20	90	387.5	59, 193	167	260
80/20 + 0.5% MDI	96	368.4	59, 182	167	267, 295
80/20 + 2.5% MDI	99	361.2	59, 182	167	271, 298
0/100 (pure PLA)	154	–	58	–	–

[a] Obtained by the equation of Fox, introduced by Gordon et al. (1977).
$1/T_g = w_A/T_{gA} + w_B/T_{gB}$, w_i is the mass fraction of phase i and T_g in K.

clearly show that PLA incorporation, especially for the blends containing MDI, decreases the chitosan's ability to absorb water. This is because a part of its —OH and —NH$_2$ groups has already reacted with the MDI isocyanate groups and/or is linked by hydrogen bonds with the PLA —OH groups. This result confirms that the *in situ* compatibilization using MDI really occurred between chitosan and PLA.

Figure 8 shows the DSC thermograms obtained after the second sweep. The chitosan/PLA (90/10 and 80/20) blends without MDI show a low endothermic peak at 154°C that is linked to the PLA; on the contrary, in the blends with MDI, this peak does not exist, except for the chitosan/PLA blend 90/10 with 0.5% MDI, which indicates a phase separation between PLA and chitosan.

The curve Nbr 8 in Figure 8 shows that pure chitosan has a unique T_g at 206°C, whereas the PLA T_g can be found at 58°C (Nbr 1). The chitosan/PLA blends have two separate T_g due to the related polymers. The PLA T_g in composite films occurs at 59°C, very close to the pure PLA T_g, and does not change with the MDI use, whatever the composition of the mixture. On the other hand, in blends, the chitosan's T_g depends on PLA quantity, this means that there is a partial miscibility between PLA and chitosan. Moreover, if we use the equation of Fox for the blends of miscible polymers, the T_g of the chitosan/PLA blends 90/10 and 80/20 must be theoretically found, respectively, at 185°C and at 167°C. Table II shows that the chitosan's T_g in the MDI compatibilized blends is close to the theoretical value of the miscible mixture. These results confirm that MDI
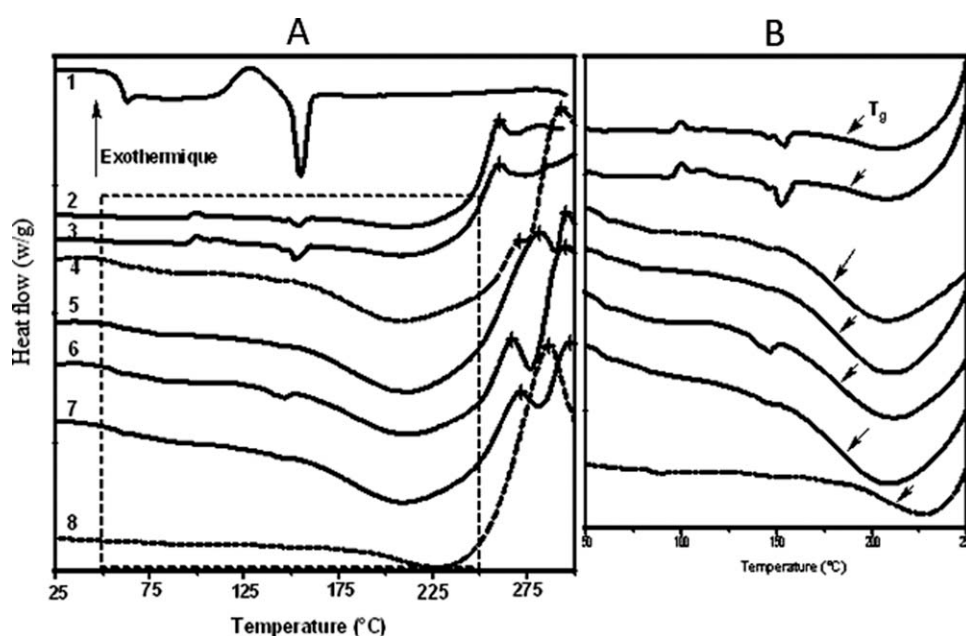

Figure 8 (A) DSC thermograms obtained after the first sweep for blends of chit/PLA: (1) 0/100 or pure PLA, (2) 90/10, (3) 80/20, (4) 90/10 + 0.5% MDI, (5) 90/10 + 2.5% MDI, (6) 80/20 + 0.5% MDI, (7) 80/20 + 2.5% MDI, (8) 100/0 or pure chitosan. (B) Zoom of part of A to observe evolution of T_g depending on blend chit/LPA.

addition increases the compatibility between PLA and chitosan and that they comply with the previous FTIR spectroscopy and SEM observations.

Figure 8 (A,B) also shows the thermal degradation peaks for the films but not for the PLA. PLA shows a better thermal stability than chitosan. Pure chitosan films show a thermal degradation peak at 286°C. This result complies with Ref. 38. The mixture with PLA, but without MDI, decreases the chitosan's resistance to thermal degradation: this is indicated by a lowering of the thermal degradation peak at 260°C. MDI addition causes thermal degradation temperature to increase. Besides, for the chitosan/PLA blends with MDI, we can see two thermal degradation peaks. We assume that the first peak can be linked to the degradation of urethane and/or urea bonds and the second peak can be linked to the degradation of the chitosan's main chain.
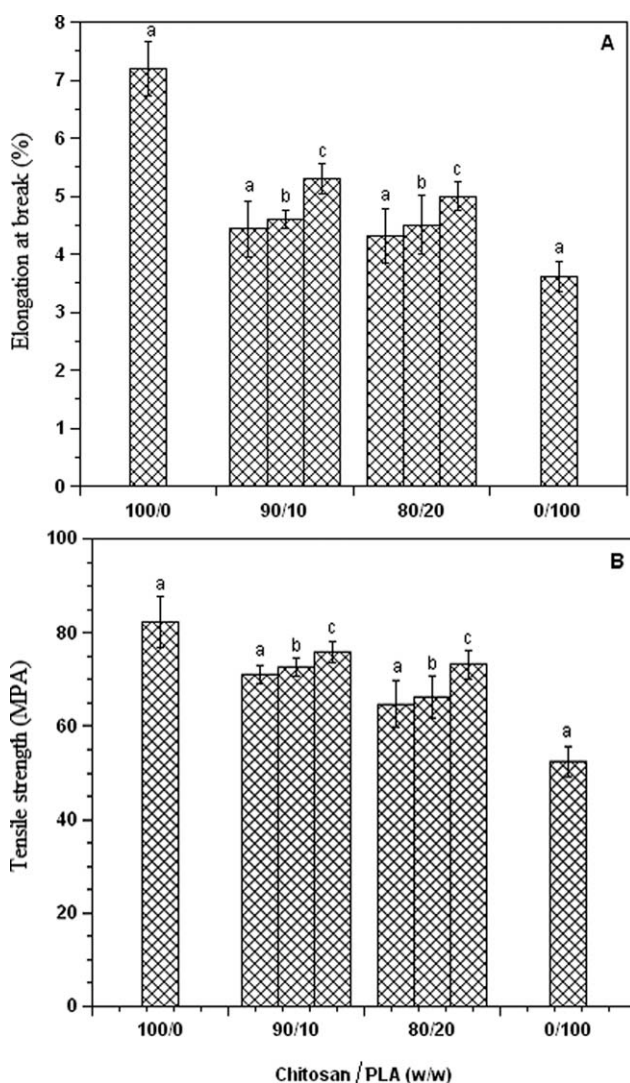

Figure 10 Comparison between experimental and calculated Young's modulus of blend chitosane/PLA without MDI (●) and Compatibilizers with 0.5% (Δ) and 2.5% (◇) of MDI compared with theoretical modules for the compatible mixture.

Mechanical properties

Figure 9(A) shows the percentage of elongation-at-break for the films obtained. MDI addition has a positive effect on the elasticity of the mixture. Indeed, the elongation-at-break of the compatibilized films with 2.5% MDI is higher than the one of the MDI-free films. The break strength of the chitosan/PLA blends with MDI [Fig. 9(B)] are also higher than those of the MDI-free blends, whatever the PLA quantity.

Figure 10 draws a comparison between experimental and calculated Young's modulus. The calculations have been computed with the parallel, the serial, and the Davies models, according to the PLA volume fraction. On this figure, we can notice that the MDI compatibilized chitosan/PLA blends have a higher Young's modulus than the noncompatibilized blends. On the other hand, the result is only significant for the chitosan/PLA blend 80/20 with 2.5% of MDI. For the chitosan/PLA mixture 90/10, there is no significant effect, this is probably due to the low PLA quantity. Moreover, we can notice that the Young's modulus values in the blends with 2.5% MDI are closer from the lowest limit (serial model): this shows that the PLA and the chitosan are more compatible, thanks, to the reactions with MDI. Again, these results show that the compatibilization from the chitosan/PLA mixture is efficient with a 2.5% (w/w) MDI concentration.

CONCLUSIONS

The FTIR spectroscopy analysis shows that specific interactions exist between the chitosan and the PLA

Figure 9 Elongation-at-break (A) and tensile strength (B) of blend of chitosane/PLA witout MDI (a) and Compatibilizers with 0.5% (b) 2.5% (c) of MDI.
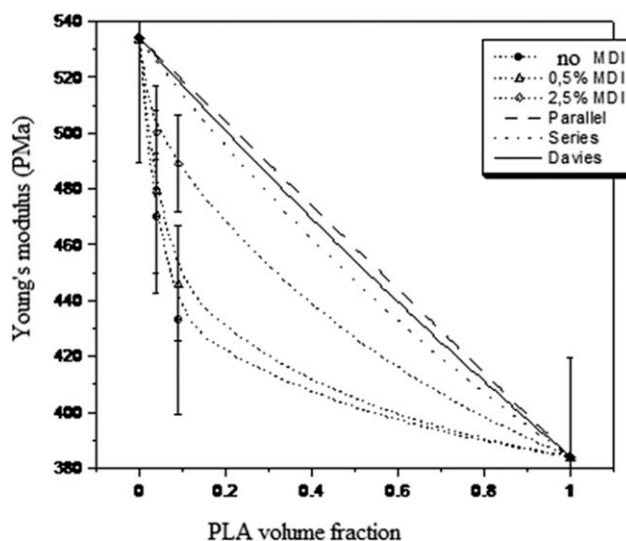
in the MDI compatibilized chitosan/PLA blends. Moreover, the films morphology, observed with the SEM microscopy, shows that the MDI chitosan/PLA blends are more homogenous and that the PLA particles incorporated in the chitosan's matrice are smaller. Finally, the DSC analysis also shows that MDI can be used as a compatibilizer for the chitosan/PLA blend. This is indicated by the chitosan's T_g lowering, which comes closer to the theoretical T_g value of a miscible mixture.

Besides, this survey shows that an addition of 2.5% MDI solution is more efficient to compatibilize the chitosan/PLA blend that a 0.5% MDI solution. It seems that the use of 0.5% MDI is not enough sufficient to obtain a compatibilization, because a part of the MDI can be consumed by water. The addition of MDI increases the performance of the mechanical properties of the blends. Therefore, with this compatibilization, we could obtain some chitosan/PLA blends that would be water-resistant and that would also keep their mechanical properties.

To improve compatibility between chitosan, some chemical modifications are interesting techniques to make the chitosan compatible with other polymers. Among the possible solutions, the copolymerization method by grafting may be one of the best methods to combine synthetic polymers with chitosan. Polymer grafting on the chitosan's chains can be studied, like Ring Opening Polymerization method (ROP), to synthesize chitin-grafted-PLA copolymers.

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