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Preparation of extruded polyethylene/chitosan blends compatibilized with polyethylene-*graft*-maleic anhydride

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ABSTRACT

Novel films of polyethylene and chitosan were obtained using extrusion. These polymers have interesting properties, and processing them with methods that are of high use in the industry, such as the extrusion method, can have a significant effect on the potential applications of these materials. The individual materials were thermally characterized; after this, extruded films of low density polyethylene and chitosan mixtures were prepared with the addition of polyethylene-graft-maleic anhydride as a compatibilizer for the blends, and glycerol, as a plasticizer for chitosan. The use of compatibilizer and plasticizer agents improved the processability and compatibility of the mixtures, as well as their mechanical properties, as revealed by mechanical property measurements and scanning electron microscopy. It was possible to prepare blends with a maximum chitosan content of 20 wt%. The material stiffness increased with the increase of chitosan in the sample. FTIR studies revealed the existence of an interaction between the compatibilizer and chitosan.

1. Introduction

Although polyethylene is one of the most widely used polymers (Dostál, Kasparkova, Zatloukal, Muras, & Simek, 2008), the use of synthetic polymers leads to environmental pollution (Bonhommea et al., 2003) associated with the waste generated by plastic products. Currently, these materials are widely used in containers or other types of disposable wraps for substances or articles, and these are discarded into the environment after use.

The mixture of natural and synthetic polymers is a simple and practical way of producing new materials with useful properties (Correlo et al., 2005; Ermolovich & Makarevich, 2006; Omura, Tsukegi, Shirai, Nishida, & Endo, 2006; Raghavan & Emekalam, 2001). Films formed by blending two or more polymers usually possess physical and mechanical properties differently from those of the initial components. Furthermore, because synthetic polymers are easily obtained and have low production costs, the mixture of natural and synthetic polymers may improve the cost–performance ratio of the resulting films.

Waste biodegradable polymeric materials are capable of degradation when exposed to natural factors and water-soluble chemical reagents. A large group of these materials is based on biopolymers belonging to polysaccharides, as well as on their composites with synthetic thermoplastics (Bourtoom & Chinnan, 2008; Fukushima, Abbate, Tabuani, Gennari, & Camino, 2009; Schlemmer, Sales, & Resck, 2009; Wu, 2005).

Chitosan is one of the polysaccharides more commonly found in nature and its films have great potential to be used as packaging material due to their antimicrobial activity, nontoxicity and biodegradability (Harish Prashanth & Tharanathan, 2007; Li, Zivanovic, Davidson, & Kit, 2010; Nair & Laurencin, 2007; Pillai, Paul, & Sharma, 2009; Shih, Shieh, & Twu, 2009; Sindhu & Abraham, 2008; Zhong, Wu, Reinhart-King, & Chu, 2010). Several studies have reported the preparation of chitosan blends with thermoplastics, but the blends reported in those papers were prepared primarily by solvent evaporation method (Feng & Dong, 2006; Kuo, Sahu, & Yu, 2006) which is associated with atmospheric pollution.

The major disadvantage of incorporating natural polymer into synthetic polymer is their compatibility. Natural polymers are hydrophilic whereas synthetic polymers are hydrophobic in nature. The resultant blend of these two types of polymers is generally immiscible (Mir, Yasin, Halley, Siddiqi, & Nicholson, 2011). The interfacial compatibility between chitosan and the thermoplastic

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matrix is a critical requirement for obtaining good mechanical properties in these composites. Several research groups have proposed the use of compatibilizers as alternatives to improve the interface of immiscible blends. Polymers grafted with maleic anhydride have been used as compatibilizers for immiscible binary mixtures, showing good results (Akopova, Vladimirov, Zhorin, & Zelenetskii, 2009; Del Castillo-Castro, Castillo-Ortega, Herrera-Franco, & Rodríguez Félix, 2011; Zelenetskii et al., 2003).

This work aims to prepare and characterize mixtures of low density polyethylene, one of the most widely used synthetic polymers, and chitosan, a biodegradable polymer, by an extrusion technique. The compatibilization effect of polyethylene-*graft*-maleic anhydride in the mixture was analyzed as a function of thermal, mechanical and morphological properties.

The novelty of this work is the use of a new method for the preparation of the films, which is of great importance in the industrial field. This new method may improve the potential applications of this material. Moreover, there is only one report of the use of this method (Martínez-Camacho et al., 2013) in the technical literature and the preparation conditions and the results achieved are different than those reported in our study.

Table 1
Concentration of each component used in the preparation of PE/chitosan blends.

Code	Concentration in composites			
	PE (wt%)	Chitosan (wt%)	PEgMA (wt%)	Glycerol (g/g chitosan)
A1	100	0	0	0
A2	95	5	0	0
A3	90	5	5	0
B1	90	5	5	2
B2	85	10	5	2
B3	80	15	5	2
B4	75	20	5	2
B5	65	30	5	2
C1	85	5	10	2
C2	80	5	15	2
C3	75	5	20	2

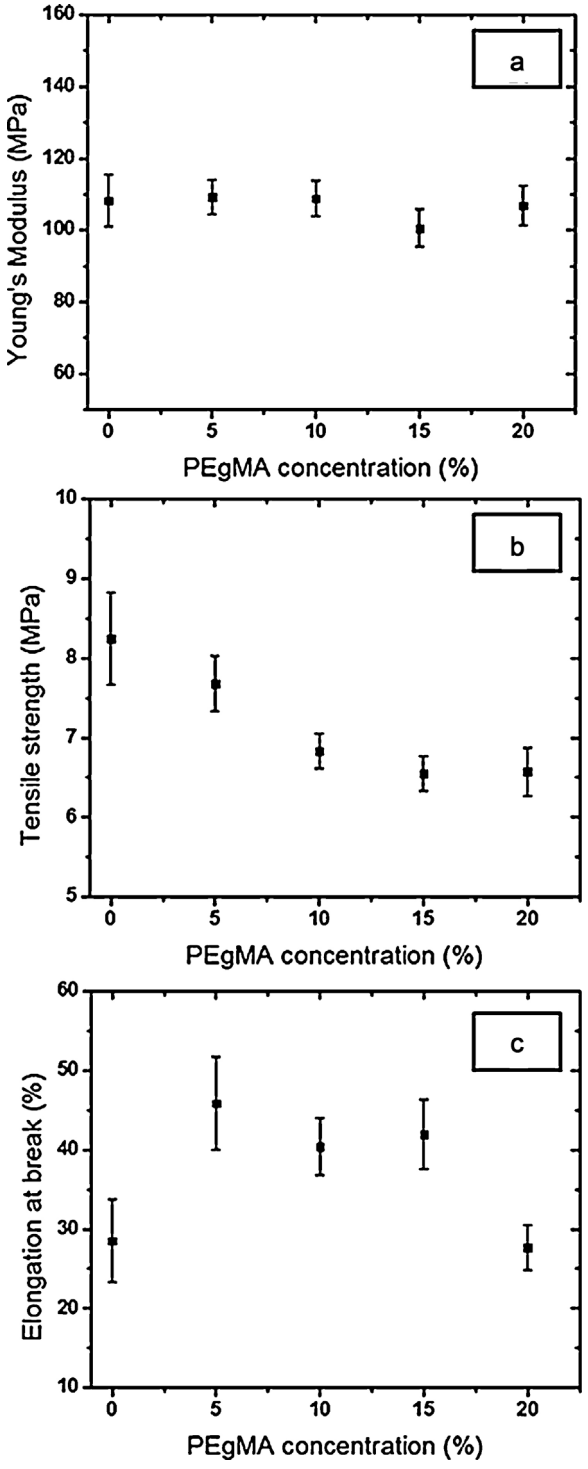

Fig. 1. (a) Young's modulus, (b) tensile strength and (c) elongation at break of A2, B1, C1, C2, C3 films vs. PEgMA concentration.

2. Experimental

2.1. Materials

Chitosan of medium molecular weight (molecular weight of 190,000–310,000 Da, and 75–85% deacetylated),

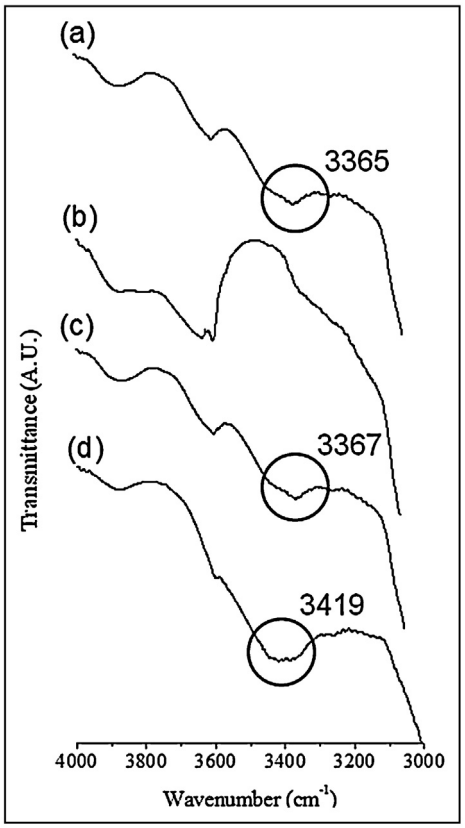

Fig. 2. FTIR spectra from 4000 to 3000 cm^{-1} of (a) chitosan, (b) PE, (c) A2 and (d) A3.

polyethylene-*graft*-maleic anhydride (PEgMA, with 3.5% maleic anhydride) and glycerol were obtained from Sigma–Aldrich. Commercial grade low density polyethylene (PE) (melt flow rate 2.0 g/10 min with 2.16 kg standard die at 190 °C), was obtained from Qatar Petrochemical Company (QAPCO). PE was milled and chitosan was dried at 110 °C for 24 h before usage, PEgMA and glycerol were used as received.

2.2. Film preparation

The PE/chitosan mixtures were prepared using glycerol as a plasticizer for chitosan and PEgMA as a compatibilizer for the blend. Glycerol was selected as a plasticizer because of its plasticizing power, nontoxicity and thermal stability (Ermolovich & Makarevich, 2006).

The polymeric blends were prepared in two stages: (1) mixing chitosan with the plasticizer to obtain a homogeneous mass and (2) mixing plasticized chitosan with PE and PEgMA. Both stages were carried out by mechanical agitation for 30 min. The blends were then extruded in an Atlas laboratory mixer-extruder, with a speed of 40 rpm. The temperatures were controlled at 130 and 140 °C for the rotor and the head respectively, except for the pure PE film. In this case, the temperatures were controlled at 115 and 125 °C. Table 1 indicates the concentration of each component on each prepared blend. The optimal content of PEgMA was determined by mechanical properties analysis in PE films with 5 wt% chitosan and 5, 10, 15 and 20 wt% of compatibilizer. The glycerol/chitosan weight ratio in the compositions was kept constant, 2 g of glycerol per gram of chitosan.

2.3. FT-IR spectroscopy

FT-IR spectroscopy of the blends was performed with an FTIR Perkin-Elmer 1600 spectrophotometer. The spectrum was scanned from 4000 cm^{-1} to 370 cm^{-1}. An average of 32 scans was recorded. Approximately 5 mg of dry sample was directly embedded into a KBr pellet and measured in transmittance mode. This test was done to identify possible polymer–polymer interactions by means of displacements in the characteristic absorption bands of both polymers.

2.4. Thermal analysis

The thermal behavior of the obtained films was studied by thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) using equipment of simultaneous DSC-TGA, TA

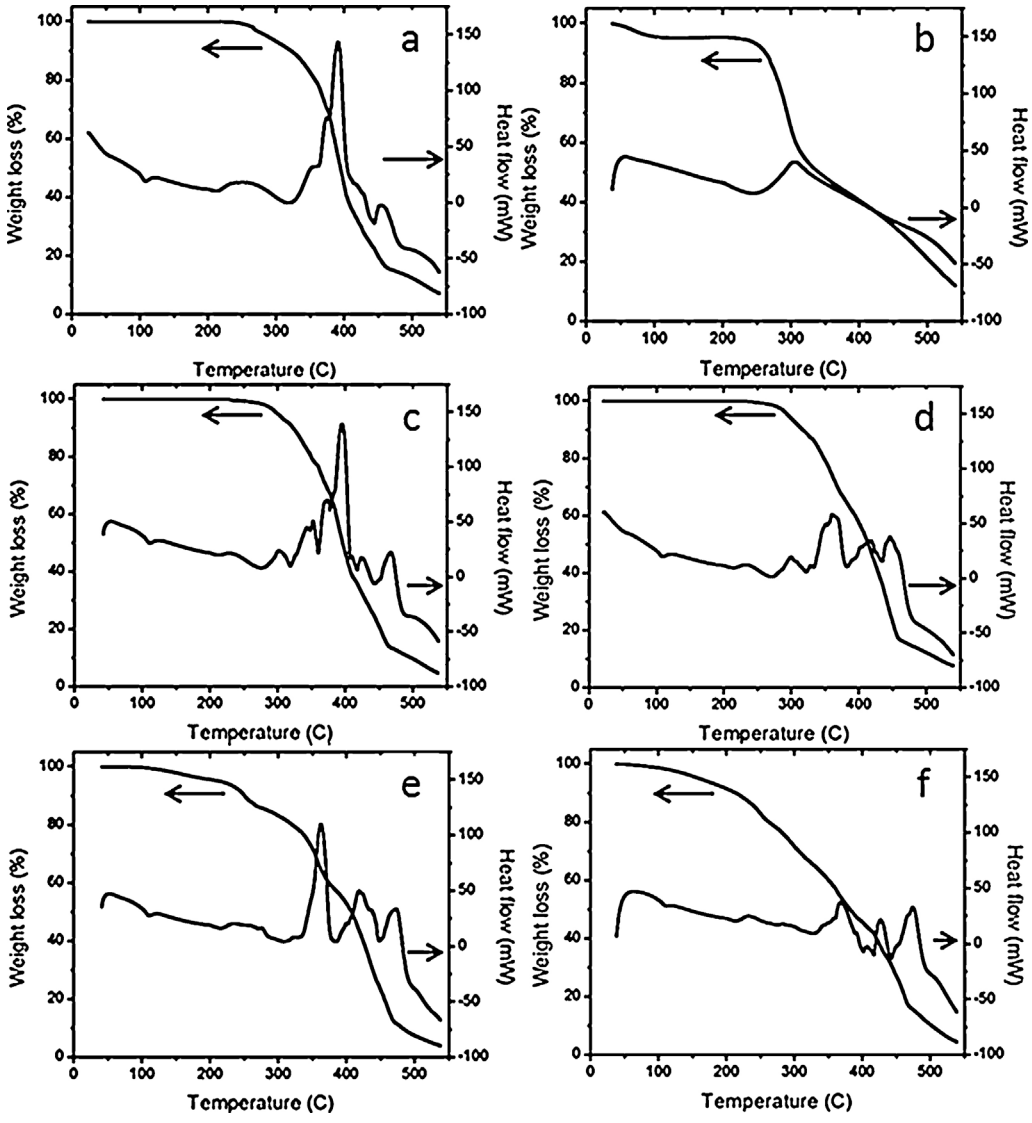

Fig. 3. TGA and DSC curves for (a) A1, (b) chitosan, (c) A2, (d) A3, (e) B1 and (f) B4.

Instruments model SDT 2960; approximately 6 mg of sample was placed in the aluminum pan at a heating rate of 10 °C/min from room temperature to 550 °C under air flow of 23 mL/min.

2.5. Mechanical analysis

The mechanical properties of the composite films were measured in a tensile loading mode with a United SSTM-5KN universal testing machine equipped with a load cell of 5 kN at a cross-head speed of 10 mm/min. At least eight specimens from each film were tested, and the average values were reported. The thickness of the film was measured with a Mitutoyo micrometer.

2.6. SEM imaging

A typical specimen from each composition was selected, and the morphology of its surface and cross-section was studied with a JEOL 5410LV scanning electron microscope (SEM). The samples were gold-sputtered before the SEM examination.

3. Results and discussion

3.1. Determination of content of compatiblizer in the films

To determine the effect of the compatibilizer content on the deformation and strength properties of the films extruded from the PE/PEgMA/chitosan ternary blends, content of chitosan in films was fixed at 5 wt%. The deformation and strength characteristics as a function of the compatibilizer concentration are shown in Fig. 1. It is seen that, with increasing content of the compatibilizer, the tensile strength of the films is mildly affected (a reduction of approximately a 20%) and Young' modulus is not affected by the PEgMA concentration in the films. However, when 5 wt% PEgMA (B1) was added to the composite, an improvement of approximately 60% in its ductility was observed when compared to the behavior of the film without PEgMA (A2). Considering the poor mechanical properties of PEgMA, it may be assumed that this enhancement in ductility could be attributed to an improvement in the interfacial compatibility produced by the presence of the coupling agent in the ternary blends. This positive behavior is almost constant in the 5–15 wt% PEgMA range (B1, C1, C2), however, the ductility of films with a 20 wt% content of PEgMA (C3) decreases compared to that of the blends with 5 wt% PEgMA (B1). This result suggests that the effect of the PEgMA on the ductility of the system is important and only a 5 wt% is necessary in the blend. Moreover, the considerable improvement of the ductility has no significant effect on the strength or stiffness of the ternary blend.

3.2. Films preparation

Using PEgMA as a compatibilizer and glycerol as a plasticizer it was possible to extrude films with chitosan compositions in the range of 5–20 wt%. The films showed good processability and homogeneity; at 30 wt%, it was not possible to obtain films in the extruder, only small film fragments. The results obtained in this part are considered an important contribution in this field because films with 20 wt% of chitosan content were obtained, whereas in the work published (Martínez-Camacho et al., 2013), where the authors also prepared extruded films of PE and chitosan, they achieved a maximum content of 5 wt% chitosan in films.

3.3. Infrared spectroscopy (FT-IR)

FTIR spectra showed the characteristic bands of the individual polymers, the stretching of the OH group of chitosan appeared at

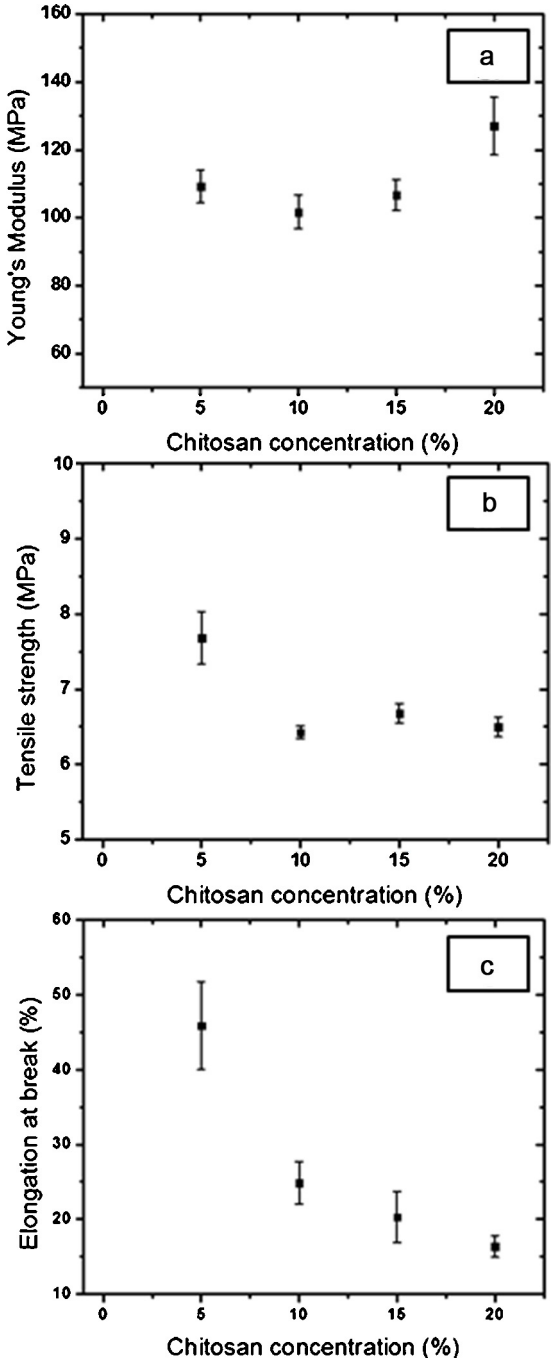

Fig. 4. (a) Young's modulus, (b) tensile strength and (c) Elongation at break of B1–B4 films vs. chitosan concentration.

3365 cm^{-1}; the characteristic peaks of PE: (1) hydrocarbon stretching peak around 2800–3000 cm^{-1}, (2) methylene scissoring peak at 1467 cm^{-1}, and (3) methylene rocking band at 722 cm^{-1} (Del Castillo-Castro et al., 2011). The A2 spectrum depicted the spectral contributions of PE and those of chitosan. It is important to note that no new band or peak shifts appeared with respect to the individual spectra of the components; this indicated the lack of any chemical or physical interactions. The spectrum of the composite containing PEgMA (A3) was also dominated by the characteristic signals of PE and chitosan. To further analyze this, the spectral region from 4000 to 3000 cm^{-1} is presented in Fig. 2. After the addition of PEgMA, the peak related to the stretching of the OH group of chitosan (Fig. 2(a)) appears at 3419 cm^{-1} (Fig. 2(d)), this peak shift can be attributed to

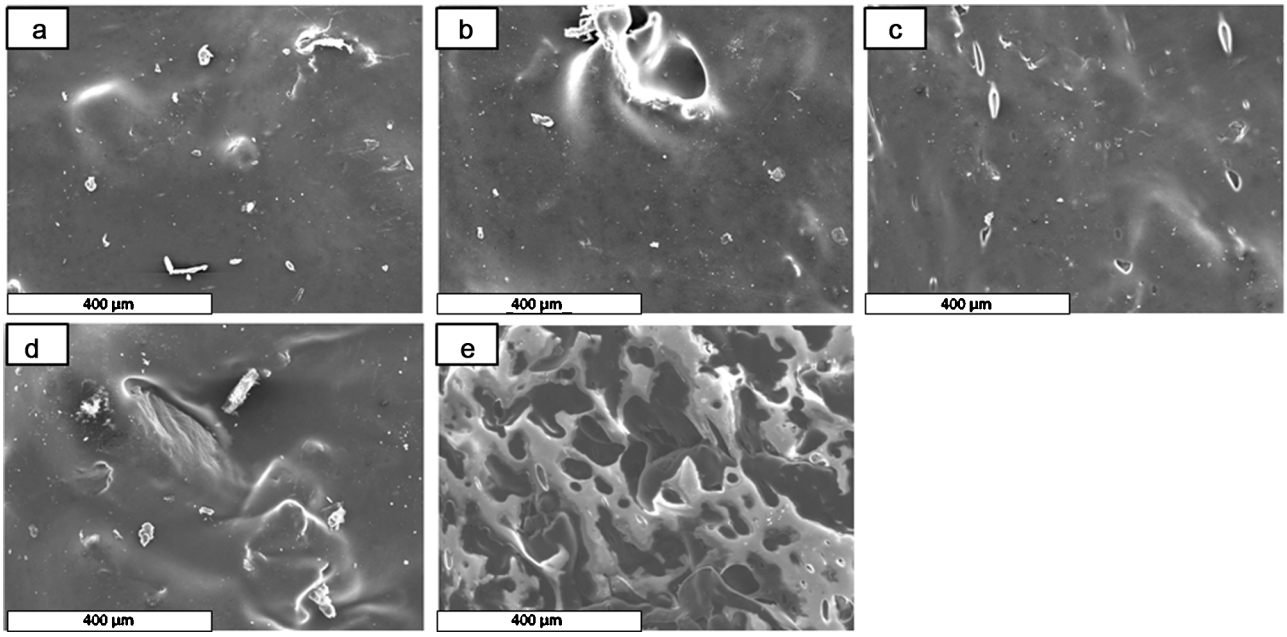

Fig. 5. SEM micrographs of the surface of (a) B1, (b) B2, (c) B3, (d) B4 and (e) B5 films.

the existence of some intermolecular interaction between chitosan and PEgMA.

3.4. Thermal analysis

Fig. 3(a–f) shows the weight loss and heat flow of the A1 film, chitosan and the composites A2, A3, B1 and B4 against temperature, respectively. The melting point (Tm) of PE was observed at approximately 110 °C. The Tm of PE was not affected by the presence of chitosan, glycerol or PEgMA. The start of the thermal degradation of PE was detected at 250 °C; as for chitosan, a certain loss of water was observed (ca. 4%), and its thermal degradation started at 230 °C. The addition of PEgMA slightly improves the thermal stability of the film, Fig. 3(d), which is also an indication of an improvement in the miscibility of PE and chitosan. The thermally stable materials show resistance to weight loss up to processing temperatures. The thermal degradation of the films plasticized by glycerol, Fig. 3(e and f), started at 125 °C; this can be attributed to a glycerol loss. When the

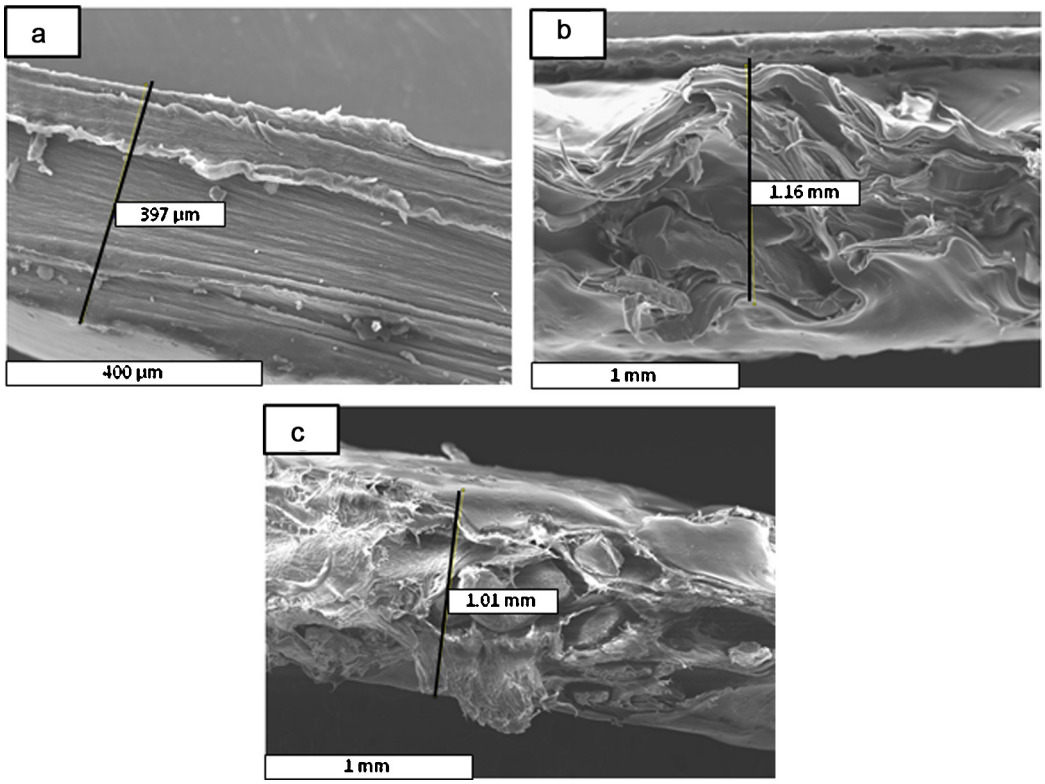

Fig. 6. SEM micrographs of the failure surface of (a) A1, (b) A2 and (c) B1 films.

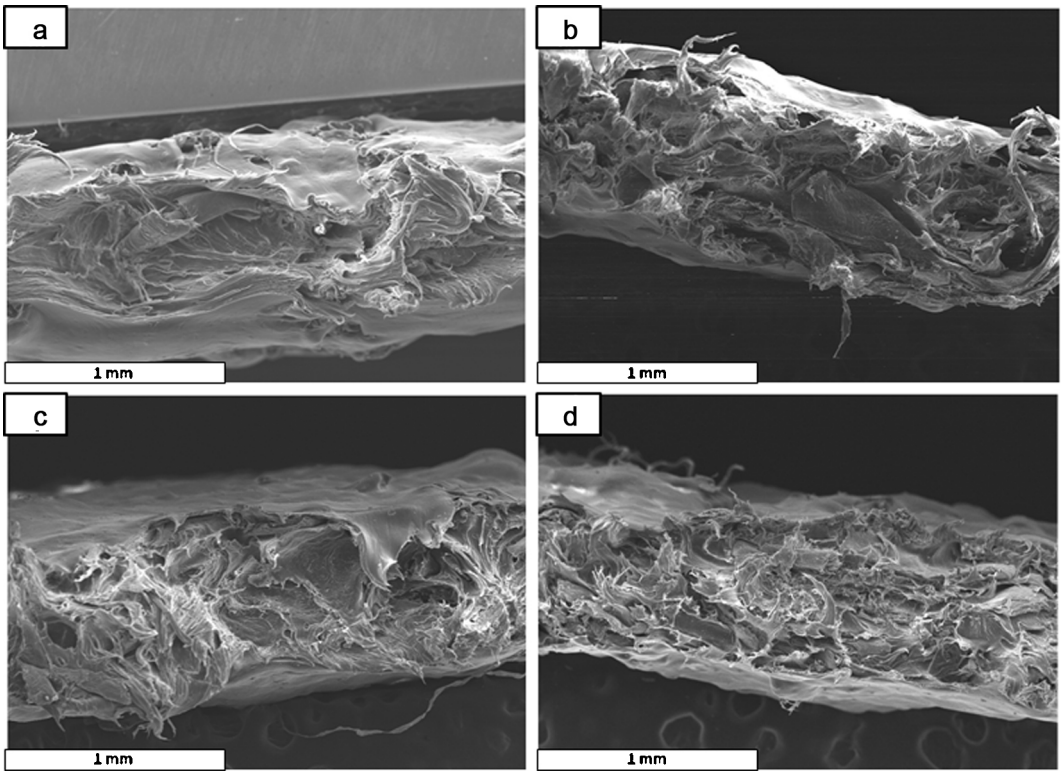

Fig. 7. SEM micrographs of the failure surface of films with different content of chitosan (a) B1, (b) B2, (c) B3, (d) B4 films.

blend is exposed to the processing temperatures (140 °C), approximately a 5% weight loss can be observed; nevertheless, this loss is not significant and does not affect the plasticization of chitosan.

3.5. Study of mechanical properties

Fig. 4 presents Young' modulus, tensile strength, and elongation at break of B1–B4 films as a function of the chitosan concentration. It can be observed that Young' modulus increases with large chitosan content, in this case, above 15%. This is typical behavior for thermoplastic materials blended with brittle materials such as chitosan.

Tensile strength as well as elongation at break shows a decreasing trend with increased chitosan content. However, the tensile strength decreases approximately 13% and remains constant even for 20 wt% chitosan weight content. The elongation at break shows a notorious decrease of approximately 60%. As chitosan is a brittle material, an increase in chitosan content should result in a decrease in ductility (Singh, Bhunia, Rajor, & Choudhary, 2011).

Apparently, tensile loading caused the ternary blends to fail at the interface between PE and the chitosan particles. Similar values of tensile strength and elongation at break of PE films with 15 wt% chitosan obtained by compression molding were reported by Mir et al. (2011).

3.6. Scanning electronic microscopy analysis

Fig. 5 shows the morphology of the surface of the extruded films. There were small qualitative differences in the surface of the films, the particles of chitosan were slightly more noticeable as the chitosan content increased, ranging from 5 to 20 wt%. Chitosan particles coated by PE can be observed, and this indicates a good interaction between PE matrix and chitosan, possibly because of a better dispersion of the chitosan particles in the PE matrix. In Fig. 5(e), the two phases are clearly observed. The results of the morphologic characterization corroborated the important role played by PEgMA in the compatibilization of the extruded samples of PE and chitosan blend films and on the mechanical properties, especially the ductility of the films.

Fig. 6 shows the morphology of the failure surface of the specimens loaded in a tensile mode. Fig. 6(a) depicts the typical tensile failure surface of PE (A1). Fig. 6(b) and (c) shows the presence of chitosan in PE (5 wt%) and the differences in the failure surface features. In the case of Fig. 6(b), there seems to be considerable PE tearing and the chitosan particles are not clearly distinguished. In the case of Fig. 6(c), the presence of the PEgMA compatibilizer shows a more homogeneous surface and chitosan particle distribution. The distribution of chitosan is responsible for the differences in the cross-section sizes of the films as revealed by the dissimilarity in their ductility. Also, the cross-section of Fig. 6(b) indicated a weak adhesion between phases that resulted in a separation of both materials. In contrast, the micrographs of the specimens that contained 5 wt% PEgMA (B1) (Fig. 6(c)), revealed the presence of chitosan agglomerates with matrix polymer still coating them after failure; this, thereby, indicated good adhesion between the chitosan particles and the thermoplastic matrix. Additionally, the effect of PEgMA in the compatibilization effect can be observed in the tensile failure surfaces of films containing 10, 15 and 20 wt% chitosan (see Fig. 7(b–d) respectively).

4. Conclusions

The addition of chitosan, a biodegradable polysaccharide, in low density polyethylene decreases the fluidity of the melt polymer. The addition of a compatibilizer into this blend, polyethylene with grafted maleic anhydride, allows easy processing of the polyethylene/chitosan mixtures into films in standard extrusion equipment.

In this manner it was possible to obtain films with a maximum content of 20 wt% chitosan.

The use of an anhydride-based coupling agent, extensively used to compatibilize polymer blends, was effectively extended to improve the mechanical properties of chitosan composites.

The processability and the changes in the mechanical properties of the composites with PEgMA were interpreted as a consequence of the compatibilization effect of the coupling agent.

Improvement in the mechanical properties, especially the deformation at break of the compatibilized films, makes these compositions suitable to be the basis for preparation of biodegradable film polymeric materials and other biodegradable items intended for short-term application.

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References

Akopova, T. A., Vladimirov, L. V., Zhorin, V. A., & Zelenetskii, A. N. (2009). State synthesis of amphiphilic chitosan polyethylene systems by the maleinization of both components. *Polymer Science Series B*, *51*, 3–4.

Bonhommea, S., Cuer, A., Delort, A. M., Lemaire, J., Sancelme, M., & Scott, G. (2003). Environmental biodegradation of polyethylene. *Polymer Degradation and Stability*, *81*, 441–452.

Bourtoom, T., & Chinnan, M. S. (2008). Preparation and properties of rice starch-chitosan blend biodegradable film. *LWT – Food Science and Technology*, *41*, 1633–1641.

Correlo, V. M., Boesel, L. F., Bhattacharya, M., Mano, J. F., Neves, N. M., & Reis, R. L. (2005). Properties of melt processed chitosan and aliphatic polyester blends. *Materials Science and Engineering: A*, *403*, 57–68.

Del Castillo-Castro, T., Castillo-Ortega, M. M., Herrera-Franco, P. J., & Rodríguez Félix, D. E. (2011). Compatibilization of polyethylene/polyaniline blends with polyethylene-graft-maleic anhydride. *Journal of Applied Polymer Science*, *119*, 2895–2901.

Dostál, J., Kasparkova, V., Zatloukal, M., Muras, J., & Simek, L. (2008). Influence of the repeated extrusion on the degradation of polyethylene. *European Polymer Journal*, *44*, 2652–2658.

Ermolovich, O. A., & Makarevich, A. V. (2006). Effect of compatibilizer additives on the technological and performance characteristics of biodegradable materials based on starch-filled polyethylene. *Russian Journal of Applied Chemistry*, *9*, 1526–1531.

Feng, H., & Dong, C. M. (2006). Preparation, characterization, and self-assembled properties of biodegradable chitosan-poly(l-lactide) hybrid amphiphiles. *Biomacromolecules*, *11*, 3069–3075.

Fukushima, K., Abbate, C., Tabuani, D., Gennari, M., & Camino, G. (2009). Biodegradation of poly(lactic acid) and its nanocomposites. *Polymer Degradation and Stability*, *94*, 1646–1655.

Harish Prashanth, K. V., & Tharanathan, R. N. (2007). Chitin/chitosan: Modifications and their unlimited application potential, an overview. *Trends in Food Science & Technology*, *18*, 117–131.

Kuo, P. C., Sahu, D., & Yu, H. H. (2006). Properties and biodegradability of chitosan/nylon 11 blending films. *Polymer Degradation and Stability*, *91*, 3097–3102.

Li, J., Zivanovic, S., Davidson, P. M., & Kit, K. (2010). Characterization and comparison of chitosan/PVP and chitosan/PEO blend films. *Carbohydrate Polymers*, *79*, 786–791.

Martínez-Camacho, A. P., Cortez-Rocha, M. O., Graciano-Verdugo, A. Z., Rodríguez-Félix, F., Castillo-Ortega, M. M., Burgos-Hernández, A., et al. (2013). Extruded films of blended chitosan, low density polyethylene and ethylene acrylic acid. *Carbohydrate Polymers*, *91*, 666–674.

Mir, S., Yasin, T., Halley, P. J., Siddiqi, H. M., & Nicholson, T. (2011). Thermal, rheological, mechanical and morphological behavior of HDPE/chitosan blend. *Carbohydrate Polymers*, *83*, 414–421.

Nair, L. S., & Laurencin, C. T. (2007). Biodegradable polymers as biomaterials. *Progress in Polymer Science*, *32*, 762–798.

Omura, M., Tsukegi, T., Shirai, Y., Nishida, H., & Endo, T. (2006). Thermal degradation behavior of poly(lactic acid) in a blend with polyethylene. *Industrial and Engineering Chemistry Research*, *45*, 2949–2953.

Pillai, C. K. S., Paul, W., & Sharma, C. P. (2009). Chitin and chitosan polymers: Chemistry, solubility and fiber formation. *Progress in Polymer Science*, *34*, 641–678.

Raghavan, D., & Emekalam, A. (2001). Characterization of starch/polyethylene and starch/polyethylene/poly(lactic acid) composites. *Polymer Degradation and Stability*, *72*, 509–517.

Schlemmer, D., Sales, M. J. A., & Resck, I. S. I. S. (2009). Degradation of different polystyrene/thermoplastic starch blends buried in soil. *Carbohydrate Polymers*, *75*, 58–62.

Shih, C. M., Shieh, Y. T., & Twu, Y. K. (2009). Preparation and characterization of cellulose/chitosan blend films. *Carbohydrate Polymers*, *78*, 169–174.

Sindhu, M., & Abraham, T. E. (2008). Characterisation of ferulic acid incorporated starch–chitosan blend films. *Food Hydrocolloids*, *22*, 826–835.

Singh, G., Bhunia, H., Rajor, A., & Choudhary, V. (2011). Thermal properties and degradation characteristics of polylactide, linear low density polyethylene, and their Blends. *Polymer Bulletin*, *66*, 939–953.

Wu, C. S. (2005). A comparison of the structure, thermal properties, and biodegradability of polycaprolactone/chitosan and acrylic acid grafted polycaprolactone/chitosan. *Polymer*, *46*, 147–155.

Zelenetskii, A. N., Volkov, V. P., Artemeva, N. Y., Sizova, M. D., Nikolskaya, V. P., & Egorova, N. A. (2003). Functionalization of polyolefins by reactive processing. *Central European Journal of Chemistry*, *3*, 277–290.

Zhong, C., Wu, J., Reinhart-King, C. A., & Chu, C. C. (2010). Synthesis, characterization and cytotoxicity of photo-crosslinked maleic chitosan–polyethylene glycol diacrylate hybrid hydrogels. *Acta Biomateria*, *6*, 3908–3918.