Polym. Bull. (2012) 69:561–577
DOI 10.1007/s00289-012-0750-x

ORIGINAL PAPER

Analysis of the influence of composition and processing parameters on the mechanical properties of biodegradable starch/pectin blends

**Francys K. V. Moreira · José M. Marconcini ·
Luiz H. C. Mattoso**

Received: 28 November 2011 / Revised: 6 March 2012 / Accepted: 25 March 2012 /

Abstract The selection of the composition and processing conditions for carbohydrate-based blends is of fundamental importance for many applications and plays a role in determining the mechanical behavior of these biodegradable materials. In this study, starch/pectin (PEC) blends were obtained via melt technique and an investigation of the effects of composition and processing parameters on their mechanical properties was performed. The blends were prepared by adopting an experimental design and were characterized by uniaxial tensile tests, scanning electron microscopy, and phase imaging atomic force microscopy. The starch:PEC mass ratio showed the maximum influence on the tensile properties, which were independent on the processing parameters. It was suggested that as the degree of methyl esterification of PEC decreased, the modulus and tensile strength of the blends increased, and this effect was observed up to 50 wt% starch. AFM revealed the immiscibility between the polymers and this phenomenon was associated to the mechanical behavior of the blends.

Keywords Biodegradable polymers · Starch/pectin blends · Melt processing · Mechanical properties · Experimental design

Introduction

Carbohydrate polymers have attracted tremendous interest in many areas of materials science. Their biodegradability and the possibility of controlling their

---

F. K. V. Moreira
Programa de Pós-Graduação em Ciência e Engenharia de Materiais, PPG-CEM, Universidade Federal de São Carlos, São Carlos, SP 13565-905, Brazil

F. K. V. Moreira · J. M. Marconcini · L. H. C. Mattoso (✉)
Laboratório Nacional de Nanotecnologia para o Agronegócio, LNNA, Embrapa Instrumentação, CNPDIA, Rua XV de Novembro, 1452, São Carlos, SP 13560-970, Brazil
e-mail: mattoso@cnpdia.embrapa.br

physical properties have been the subject of considerable research and may offer the feasibility in several applications, as shown in reviews about biomaterials [1], edible coatings [2], multilayers [3], and electrochemical devices [4].

Pectin (PEC) is an important family of carbohydrates with biocompatibility and gelling properties. It is a "smooth" backbone of α-1,4-linked D-galacturonic acid units (homogalacturonan, HG) partially methyl esterified. The degree of methyl esterification (DM) plays important roles in determining the physical and biochemical properties of PECs, and it has been used to categorize them into two groups, namely, high-methoxyl (HM) PECs (DM is >50 %) or low-methoxyl (LM) PECs (DM is <50 %) [5]. Schols and Voragen [6] have established that pure HG is the predominant form in PECs, but it also occurs interrupted by the insertion of 1,2-linked L-rhamnose in adjacent or alternative positions, forming "hairy" regions (rhamnogalacturonan, RG), which exhibits side chains of either D-galactose (galactan) or L-arabinose (arabinan), or both (arabinogalactan). This complex carbohydrate has been widely used because of its edible and non-toxic features and has also inspired recent studies aimed at developing new technologies, including drug delivery systems [7] and electrochemical devices [8]. Bergman et al. [9] also investigated PEC because of its inhibitory effect on malignant cell proliferation.

Over the last decades researchers in the field of polymer engineering has investigated new biodegradable plastic, including several processing routes for PEC-based films. The majority of these studies have focused on blending PECs with other biodegradable polymers as for example sodium alginate [10], poly(vinyl alcohol) [11], cationic [12], and high amylose [13] starches and chitosan [14]. Among them starch is very attractive to blending with PECs due to its low cost, non-abrasive, and chemical features. Starch is a backbone of D-glucose, naturally occurring in two forms: amylose, a few branched polymer with α-1,4-linkages and amylopectin, a highly branched polymer with α-1,4-linked chains connected by α-1,6-linkages. Thermomechanical plasticization of starch by conventional melt techniques produces thermoplastic starch (TPS) and it can be combined with other biodegradable polymers to yield blends with the benefits of low cost and the advantage of using eco-friendly materials [15].

Several composition–structure–property relationships have been identified as the key factors affecting the mechanical properties of starch/PEC blends. Glycerol and urea were reported as efficient plasticizers for HM PEC/starch cast films, providing flexibility and elongations of 1–3 %, whereas the addition of high amylose (~70 %) starch causes reverse effect, but it decreases the tack properties of the films [16]. These behaviors are similar to those observed in extruded TPS/HM PEC blends, which showed suitable mechanical properties (strength 2–13 MPa, elongation 6–30 %, and modulus $\sim 10^3$ MPa) for packaging applications [17, 18].

Despite the fact that many structural features have been reported in the literature, there are still many unanswered questions that should be further elucidated. These questions encompass a wide range of other matters such as the occurrence of miscibility between starch and PEC that is still unclear, as well as little information about the microstructure, thermal stability, and phase morphology of their blends. In addition, most starch/PEC blends described in the literature were composed of high amylose starch and the entire diagram of composition in terms of mechanical properties has not been previously reported. Then, it seems interesting to study starch/PEC blends made up of inexpensive high amylopectin starches including corn starch (~28 wt% amylose), and likewise to investigate the properties of blends containing this kind of polymer. Moreover, in the literature there have been few studies focusing on the melt processing of fully carbohydrate blends using different conditions taking into account the mutual dependence among parameters. As explained in detail by Wu and Hamada [19], the one-factor-at-a-time methodology used to study the influence of parameters on a response is insufficient mainly because it fails to detect the dependence among them. In the case of starch/PEC blends prepared via melt techniques, it is much important to better understand how the composition (polymer mass ratio, plasticizer content, and DM) may depend on the processing parameters (temperature, shear rate, and time) to reflect on the mechanical properties of the blends. In this context, design of experiment methodology has emerged as an important tool that enables investigating the effect of several parameters simultaneously with more information per reduced number of experiments, the computation of the interactions among parameters, and the facile detection of the optimized conditions [20].

The main objective of this study was to analyze simultaneously the influence of the blend composition (polymer mass ratio, DM, and glycerol) and processing (shear rate and time) parameters on the mechanical properties of starch/PEC blends obtained via melt processing. To conduct our analysis the design of experiment methodology was employed, which enabled us to investigate important composition–structure–property relationships, thus eliminating laborious, time-consuming experiments.

Experimental

Materials

Three commercial polymers were used in this study. Corn starch (~28 wt% amylose) was kindly supplied by Corn Products, Brazil. Citrus PECs were LM and HM samples purchased from CPKelco, Brazil. These samples had a DM of 8.4 and 74 %, respectively, according to manufacturer's instructions, and a weight-average molecular weights (M_w) of 170,000 and 130,000 g mol^{-1}, respectively, as determined by gel permeation chromatography (GPC). The water was deionized and filtered using a Milli-Q purification system. Glycerol (>99 %) and stearic acid (>99 %) were purchased from Synth, Brazil.

Preparation of starch/PEC films by casting

Aqueous solutions of the individual polymers (1 % w/w) were mixed to obtain the 0.25 and 0.75 starch:PEC mass ratios, followed by stirring for 30 min at 25 °C. The final solutions were casted on Teflon substrates and dried by evaporation at 35 °C during 24 h. The blend films with thickness of 30 ± 4 μm were conditioned in a humidity chamber at 50 ± 3 % for 3 days before characterizations.

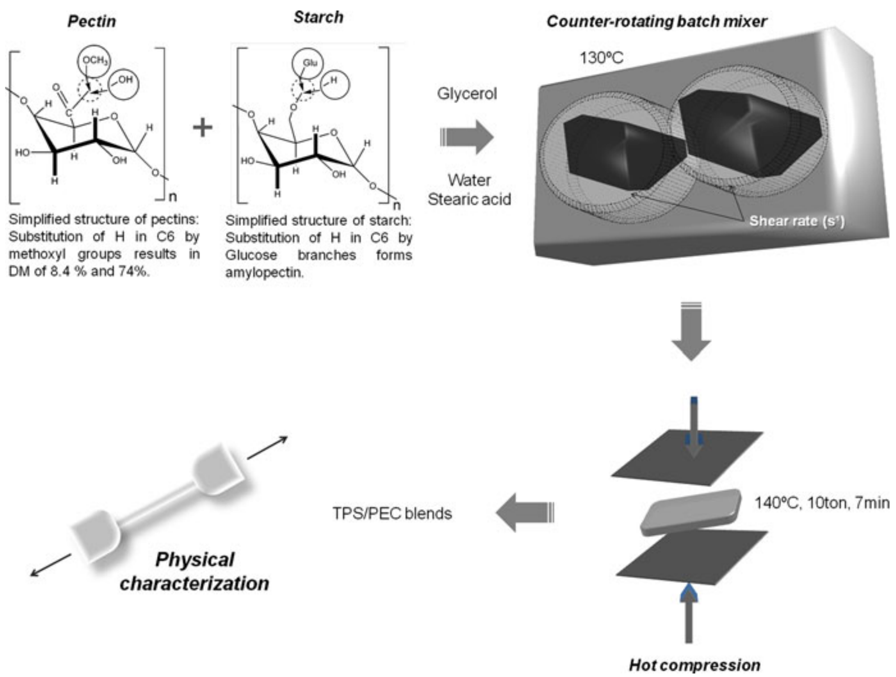


Fig. 1 Schematic illustration for thermoplastic corn starch/citrus PEC experiments

Melt processing of starch/PEC (TPS/PEC) blends

Blend formulations were prepared with starch:PEC mass ratios of 25:75 and 75:25 (w w^{-1}), using either LM or HM PECs. The evaluated glycerol concentrations were 30 and 40 wt%. Deionized water and stearic acid were added at 20 and 1 wt%, respectively. All these processing agents were used on a dry mass basis of the polymers in the formulations.

A batch mixer Rheomix OS4 coupled to a torque rheometer Haake (Thermo Fisher Scientific Inc, Germany) was used to yield TPS/PEC blends. The procedure, schematically represented in Fig. 1, can be summarized as follows: powder starch, PEC, and stearic acid were premixed for 5 min followed by adding appropriate amounts of glycerol and deionized water to complete the formulations. Then, the formulations were processed into the counter-rotating mixer equipped with roller-typed rotors operating at either 43.4 or 116.2 s^{-1} average shear rates. All formulations were evaluated after 4 and 6 min of mixing because longer times caused degradation of PECs [21]. After processing, the resulting samples were converted in pellets and then molded by compression at 140 °C and 10 ton pressure for 7 min.

All materials were saturated with water on 3-day incubation in a humidity chamber at 50 ± 3 % and temperature at 25 ± 5 °C before characterizations. No exudation of plasticizer was observed in the samples during the time of conditioning.

Uniaxial tensile tests

The properties such as tensile strength (σ_T), elastic modulus (E), and elongation at break (ε_B) were determined following the ASTM D638 standard (2008). The tests were performed on specimen type II, using a universal testing machine EMIC DL-3000 (EMIC Equipamentos e Sistemas de Ensaio LTDA, PR, Brazil) with a 50 kgf load cell and a crosshead speed of $50\ \text{mm min}^{-1}$. Each formulation was characterized in triplicate.

Scanning electron microscopy (SEM)

The brittle fracture surfaces of the samples were prepared in liquid nitrogen to investigate the blend morphologies. After fixation on proper supports and coating with gold, the samples were analyzed on a DSM 960 electron microscope (Carl Zeiss SMT GmbH, Germany). The micrographs were registered by using an accelerating voltage of 20 kV and the secondary electron mode.

Atomic force microscopy (AFM)

The phase morphology of the blends was determined by AFM using a Dimension V microscope (Digital Instruments/Veeco, CA, USA). Tapping mode phase images were performed side-by-side at scan speed of 0.5 Hz. In phase imaging, the phase lag of the cantilever oscillation, relative to the signal sent to the piezodriver of the cantilever, was simultaneously monitored by the Quadrex Module and recorded by the Dimension V. The sample surface was imaged using a silicon tip with radius of 10 nm and opening angle at 22°. The force constant was 5.6 N/m and the resonance frequency was 192.7 kHz. All measurements were carried out at 25 °C.

Experimental design

The melt processing of the TPS/PEC blends under multivariate conditions was investigated according to the design of experiments methodology. The parameters (1) starch:PEC mass ratio 0.25 (−) and 0.75 (+), (2) DM of 8.4 (−) and 74 % (+), (3) glycerol concentration of 30 (−) and 40 wt% (+), (4) average shear rate of 43.4 (−) and 116.2 s^{-1} (+), and (5) mixing time of 4 (−) and 6 min (+) were arranged with basis on a 2^{5-1} fractional factorial design, yielding 16 experiments or samples. The elastic modulus (E), tensile strength (σ_T), and elongation at break (ε_B) were the measured responses, as displayed in Table 1.

Based on such design the principal and binary factors were computed. Their statistical significances were judged by the visual graphical method involving the half-normal plots and by applying the Tukey's test at significance level of 95 %. Details about the statistical procedures used in factorial design as well as in the construction of half-normal plots can be found elsewhere in literature [17]. All calculations were performed using the software Origin 6.0 (OriginLab, USA).

Table 1 Design matrix and mechanical properties data for biodegradable TPS/PEC blends experiments

Samples	Variables					Mechanical properties		
	1	2	3	4	5	σ_T (MPa)	E (MPa)	ε_B (%)
1	−	−	−	−	+	3.6 ± 0.2	128.6 ± 1.7	5.2 ± 0.6
2	+	−	−	−	−	2.1 ± 0.4	38.3 ± 2.7	21.0 ± 1.4
3	−	+	−	−	−	2.7 ± 0.5	127.8 ± 25.0	7.6 ± 1.1
4	+	+	−	−	+	1.6 ± 0.3	33.2 ± 1.3	15.4 ± 4.0
5	−	−	+	−	−	2.4 ± 0.2	49.7 ± 2.5	10.4 ± 0.6
6	+	−	+	−	+	1.1 ± 0.1	10.0 ± 0.4	32.8 ± 4.9
7	−	+	+	−	+	2.6 ± 0.2	62.2 ± 4.7	10.2 ± 1.2
8	+	+	+	−	−	1.0 ± 0.2	7.7 ± 0.2	25.8 ± 6.2
9	−	−	−	+	−	5.2 ± 0.4	202.7 ± 22.4	6.9 ± 0.3
10	+	−	−	+	+	1.4 ± 0.1	19.7 ± 2.5	32.6 ± 3.5
11	−	+	−	+	+	1.8 ± 0.3	172.5 ± 35.0	1.4 ± 0.8
12	+	+	−	+	−	1.8 ± 0.1	29.1 ± 0.1	33.4 ± 0.7
13	−	−	+	+	+	1.4 ± 0.2	9.0 ± 0.3	1.1 ± 0.6
14	+	−	+	+	−	0.8 ± 0.1	9.3 ± 1.0	20.3 ± 0.5
15	−	+	+	+	−	1.2 ± 0.1	38.6 ± 2.2	5.8 ± 0.9
16	+	+	+	+	+	1.6 ± 0.3	51.9 ± 1.8	6.9 ± 0.8

Results and discussion

Statistical significance of the parameters

As listed in Table 1, it can be observed that the tensile properties of the TPS/PEC blends were in the range of 0.7–5 MPa for σ_T, 1.4–33 % for ε_B, and 8–202 MPa for E. The half-normal probability plots in Fig. 2 provide clear evidence regarding the parameters that had major influences on these properties. Most effects can be fitted to a straight line in plots and thus, they can be considered less important. However, the polymer mass ratio (factor 1) plays a very important role on E, σ_T, and ε_B properties, as the respective points are quite off the line. Thus, starch–PEC interactions dictate the mechanical behavior of TPS/PEC blends. From the technological perspective, this basically means that the mechanical properties of TPS/PEC blends can be more easily adjusted by incorporating different contents of TPS into PEC, when compared to other compositional (DM and glycerol) or processing (shear rate and time) parameters.

There are other important tendencies possible of drawing the half-normal plots. For example, glycerol content (factor 3) strongly affects E, Fig. 2a, and σ_B, Fig. 2b, but it appears less important on ε_B, Fig. 2c. Moreover, there are other key points detected by plots such as the influences of shear rate (factor 4) and mixing time (factor 5) on all the measured properties. Their effects are not very significant when analyzed alone, which suggests a little dependence of the mechanical behavior of TPS/PEC blends on the processing conditions. However, some binary factors

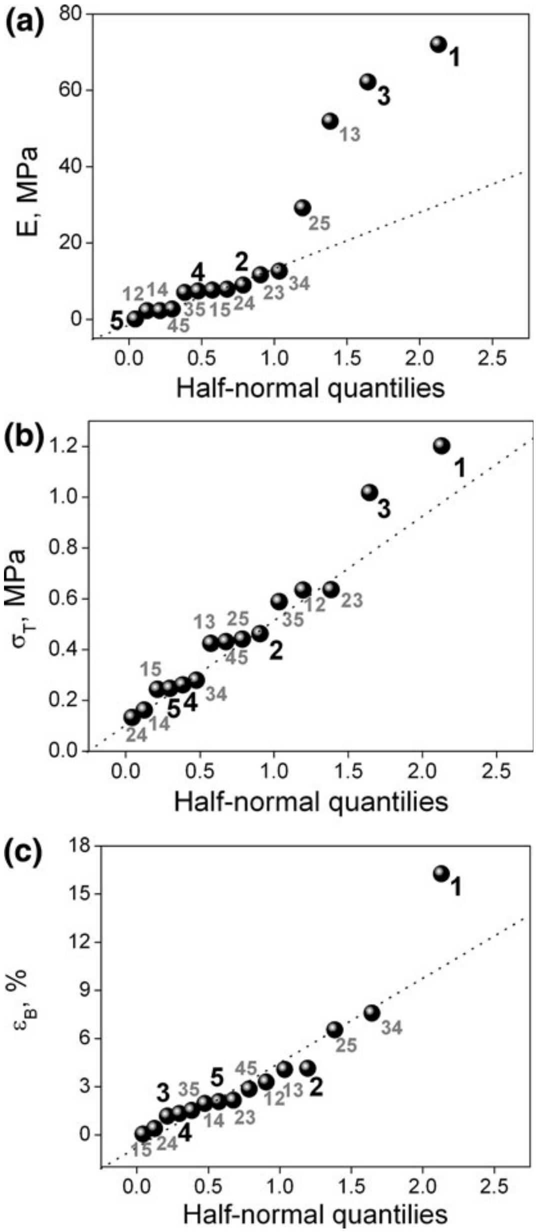


Fig. 2 Half-normal probability plots for **a** elastic modulus *E*, **b** tensile strength σ_T, and **c** elongation at break ε_B, from TPS/PEC blends experiments (*1* starch:PEC mass ratio, *2* DM, *3* glycerol concentration, *4* shear rate, and *5* mixing time)

become more pronounced in plots, such as DM-time (binary factor 25) in Fig. 2a, b, glycerol-time (binary factor 35) in Fig. 2b, and particularly, the shear rate-time (binary factor 45) in Fig. 2b, indicating that some parameters of composition and processing may be influencing each other. Some of these complex dependences are highlighted in the next section.

Relationships among composition, processing, and properties

The single effects of the tensile properties are shown as principal factors plots in Fig. 3a–c, to elucidate the influence of each parameter alone. The most evident observation taken from shifting each parameter level is the strong changes in the mechanical properties of TPS/PEC blends caused by TPS and glycerol. When TPS content was raised from 25 to 75 wt% into blends, *E* and σ_B values decreased strongly to 25 and 1.4 MPa, respectively, whereas ε_B dramatically increased from 6 to 24 %. Hence, it can be assumed that TPS exerts a plasticizing function on PEC-based matrixes, probably due to the increase of amylopectin in blends. Corradini et al. [22] reported that amylopectin is more branched and flexible macromolecule than amylose, and its presence tends to increase the ductility of plasticized starches.

Likewise, when glycerol concentration was raised from 30 to 40 wt%, the values of *E* and σ_T decreased to 30 and 1.5 MPa, respectively, but that also caused a slight

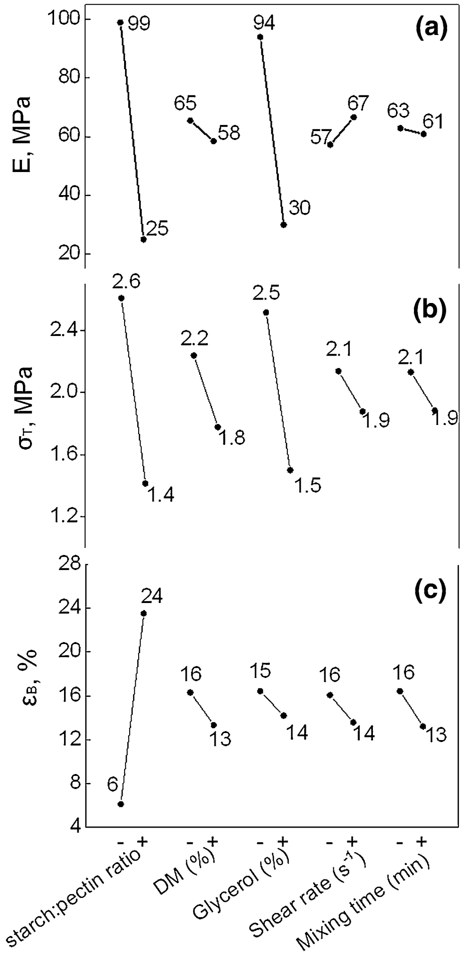


Fig. 3 Principal factor plots for **a** elastic modulus *E*, **b** tensile strength σ_T, and **c** elongation at break ε_B

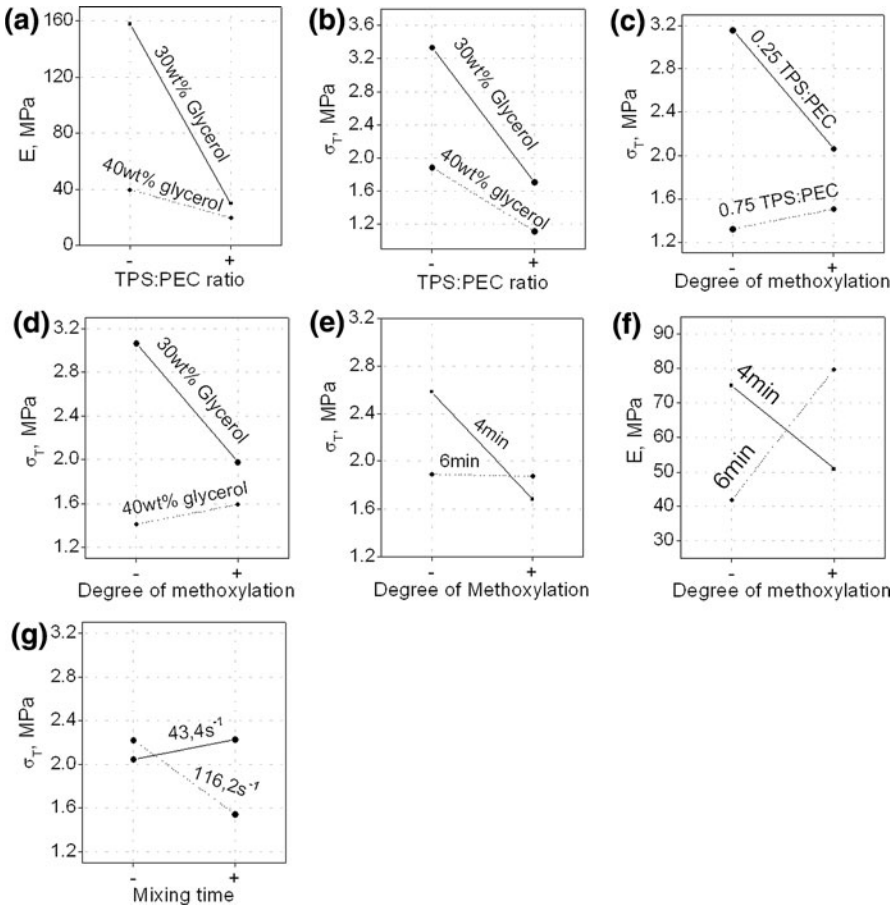


Fig. 4 Interaction binary factor plots. **a** Polymer ratio versus glycerol concentration for *E*, **b** polymer ratio versus glycerol concentration for σ_T, **c** DM versus polymer ratio for σ_T, **d** DM versus glycerol concentration for σ_T, **e** DM versus time for σ_T, **f** DM versus time for *E*, and **g** time versus shear rate for σ_T

decrease in ε_B. It seems obvious that both modulus and tensile strength decrease by increasing glycerol because of its plasticizing function into carbohydrate matrixes. However, in accordance with the behaviors previously observed in plasticized starches, higher elongation values should also occur [23, 24]. Thus, when the glycerol concentration is >30 wt%, the molecular interactions within TPS/PEC blends are impacted without ductile gains, suggesting that a microstructural collapse has occurred because of the excess of plasticizer into materials.

Some composition–composition, composition–processing, and processing–processing interactions can be visualized from binary factor plots in Fig. 4. TPS-rich blends (0.75 polymer ratio) exhibited minor stiffness (lower *E* values) than PEC-rich blends (0.25 polymer ratio) for any glycerol content, but the plasticizing function of TPS was less pronounced under 40 wt% glycerol. So, glycerol can also reduce the PEC–starch interactions, which seems to have large influence on the mechanical properties of blends. This result is shown by the binary factor 13 plot for elastic modulus in Fig. 4a. Identical result is plotted in Fig. 4b which displays the binary factor 13 plot for tensile strength.

From the half-normal plots, the DM of PECs showed to be less significant. However, one can observe a slight decrease in E and σ_T values, while DM value increases, as shown by the principal factor plots in Fig. 3. This may indicate that LM PEC-rich blends are mechanically more resistant than those containing HM PECs. In addition, the DM effect seems to be dependent on the starch and glycerol contents, as suggested by the binary factors 12 and 23 plots shown in Fig. 4c and d, respectively. For PEC-rich blends, σ_T decreased from 3.2 to 2.1 MPa when the DM was raised from 8.4 to 74 %, but for TPS-rich blends this behavior was not observed and σ_T was virtually unchanged, as shown in Fig. 4c. It is very likely that high TPS contents suppress the DM influence on tensile properties because it decreases the PEC–PEC associations into blends, giving rise to TPS–PEC interactions. The same result can be found in the correlation between DM and glycerol illustrated in Fig. 4d.

Figure 4e and f shows the interaction between DM and mixing time for σ_T and E, respectively. The results clearly revealed that after 4 min of processing both properties slightly decreased when the DM increased. As the tensile strength is directly proportional to the molecular weight of polymers, such decreases suggest that HM PECs are more susceptible to the depolymerization under shear and temperature than LM PECs.

Investigations reported by Einhorn-Stoll et al. have established an overall thermal behavior for PECs. In general, the thermal stability of LM PECs is lower than their starting HM PECs because of the lower molecular weight, as well as by the higher number of carboxylate (COO^-) groups which causes degradation reactions induced by hydrogen bonds [25]. However, HM PECs depolymerised by mechanical treatment show lower thermal stability than LM PECs because of their more solid inhomogeneity and other complex factors [26]. Here, the pattern from Fig. 4e suggests that although LM PECs tend to decompose easily because of much inter- and intramolecular hydrogen bonds, the effect of the combined shear and temperature in processing favor in higher extent the degradation reactions of the PECs. Conversely, by melt processing at 6 min, σ_T was similar for both DM values, but it was much lower than what was observed at 4 min, especially for the LM PEC. Thus, at long mixing times both types of PEC might be suffering degradation in similar extent. It is important to note that E strongly increased for high DM at 6 min, which is possibly due to formation of more homogeneous (cleaving of side chains and removal of neutral sugars) and compact structures (more linear PEC chains) from degradation of HM PECs. For these results, the starch–PEC interactions should also be considered and detailed studies will be necessary to elucidate the DM-time dependence.

The shear rate–time relation reflects the pure influence of the processing conditions on the TPS/PEC blends, and an important result can be extracted from their binary factor plot in Fig. 4g. At low shear rates, σ_T of the blends was ~2 MPa, even when starch and PEC were mixed for either 4 or 6 min. Similarly, at low mixing time, the σ_T of blends did not differ from 2 MPa, when the shear rate was increased from 43.5 to 116.2 s^{-1}. Nevertheless, by comparing these observations with processing done with both parameters in their highest levels, σ_T was minor, ~1.5 MPa. This data corresponds to the decrease of 75 % in σ_T of TPS/PEC blends and suggests some breakdown and destruction of the starch and PEC chains under more aggressive processing conditions. Then, our results demonstrate that mild processing conditions (e.g., 116.2 s^{-1} and 4 min) are recommended to avoid the indicated thermodegradation phenomena.

Composition diagrams

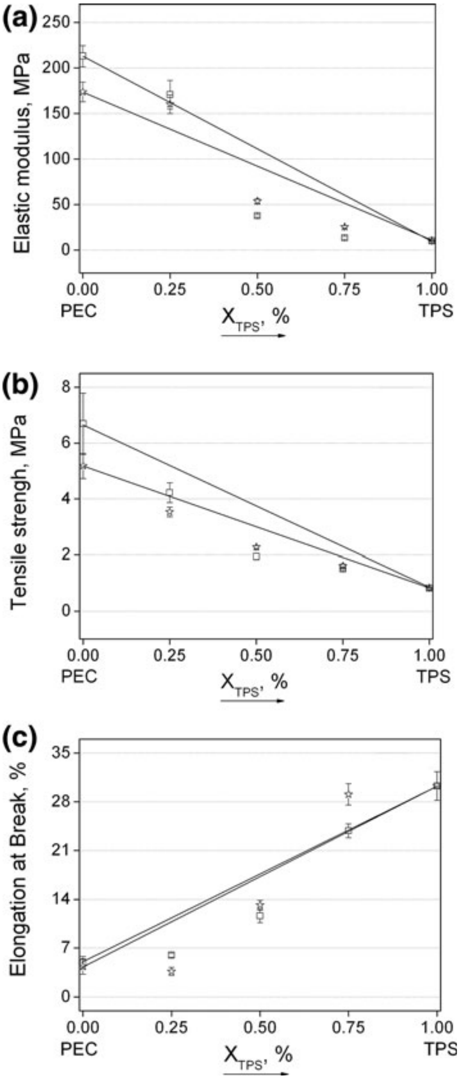
To gain insights into the polymer ratio and DM effects, an additional set of experiments was performed. All formulations, including pure PEC, 0.5 polymer ratio and pure TPS were prepared using 116.2 s^{-1}, 4 min, and 30 wt% glycerol. From these conditions, the composition diagrams were obtained as shown in Fig. 5. Theoretical lines representing the addition law were added to indicate the nature of the interactions within TPS/PEC blends.

As expected from the factorial design results, the diagrams reveal that citrus PEC and corn TPS are mechanically contrasting. PEC's are brittle polymers, represented by higher E and σ_T, but with low ε_B values (≈ 5 %), whereas corn TPS has ductile features, which were represented by higher levels of plastic deformation ($\varepsilon_B = 30.3$ %).

For both LM and HM PECs similar mechanical behaviors can be observed, but it is interesting to note from diagrams that LM PEC showed higher tenacity, because E and σ_T were more pronounced as the DM decreased. LM PECs form weak films because they generally show lower molecular weight [16]. However, the LM PEC used in this study presented higher M_w than HM PEC. So, the results observed here are better explained based on the influence of the DM. Einhorn-Stoll and Hunzek [26] described that the solid state of PECs corresponds to the cohesion of several polymer chains, where both entanglement and conformations are stabilized by hydrogen bonds formed by carboxyl groups (COOH), carboxylate groups (COO^-), and hydroxyl groups (OH). When the COO^- groups are replaced by methyl-esters groups ($COO–CH_3$) of lower polarity, the network interactions are disturbed and, consequently, the resistance of PEC decreases [27]. Espinoza-Herrera et al. [28] have documented that the elastic modulus reflects the molecular interactions which act oppositely to the flow of macromolecules. This hypothesis was confirmed from elastic modulus E in Fig. 5a. The LM PEC showed higher E (~212 MPa), while HM PEC showed minor E (~75 MPa). These values were also distinct at the significance level of 95 % ($p < 0.05$).

The general trend when fixing the processing conditions was to confirm that corn TPS acts as a plasticizer on citrus-PEC matrixes, decreasing both modulus and strength, but providing ductile gains. A counter analysis reveals that PEC reinforces corn-TPS matrixes, decreasing elongation, but increases both modulus and tensile strength. Fishman et al. [16, 29] reported that blends of extruded PEC and high amylose TPS show opposite behaviors due to the stiffness effect caused by linear amylose and its recrystallization property. So, the results presented here are important because they suggest the feasibility of using high amylopectin starches to yield biodegradable TPS/PEC blends with toughness characteristics.

Fig. 5 Diagrams of mechanical properties for TPS/PEC blends: **a** elastic modulus, **b** tensile strength, and **c** elongation at break. All samples were prepared using 116.2 s^{-1}, 4 min, and 30 wt% glycerol. (*squares* LM PEC; *stars* HM PEC)



Two important tendencies were also confirmed from composition diagrams. First, PEC-rich blends (up to 0.25 ratio) containing LM PECs still differ from those prepared with highly methoxylated PECs ($p < 0.05$). For these blends, the presence of TPS (up to 0.25 ratio) only decreased E and σ_T ($p < 0.05$), without expressive increase of ε_B ($p > 0.05$), when compared to pure PEC's. But for TPS contents equal or higher than 50 wt%, both kinds of blends were mechanically similar, and the tensile properties became ruled by the starch–PEC mass ratio. This behavior is precisely the one detected by factorial design in binary factor 12 plot (shown in Fig. 4c), that is, starch–PEC interactions overlap PEC–PEC interactions. Altogether, for 0.50 TPS/PEC ratios the values of E and σ_T were decreased by 70 %, and ε_B was increased by 100 %, compared to pure PEC's ($p < 0.05$). In addition, TPS-rich blends showed E and σ_T 100 % higher than pure TPS ($p < 0.05$), but they showed ε_B values comparable to the thermoplastic ($p > 0.05$).

Second, the addition law provided an indication about the nature of the interaction occurring within blends. Under null hypothesis of no interactions between polymers, the experimental data should follow a theoretical additive profile as function of polymer mass ratio. However, it can be observed that the mechanical properties of TPS/PEC blends showed a deviation to lower values from theoretical lines, evidencing interactions, namely antagonistic, in most part of the spectrum of composition. Indeed, Corradini et al. [15] found that other starch-based blends behave in similar fashion, which were identified as immiscible polymer blends. Then, phase separated morphologies can be expected for the TPS/PEC blends prepared in this study.

Miscibility in starch/PEC blends

With the aim of elucidating their morphologies and mixing state, the TPS/PEC blends were investigated by SEM. Figure 6 shows typical micrographs of the fracture surface of the samples. The surfaces for 25/75, 50/50, and 75/25 TPS/PEC compositions reveal compact microstructures. By comparing the three surfaces, the roughness tends to lower as the TPS content increases. Moreover, TPS and PEC were indistinguishable from SEM micrographs, leading to a conclusion that they are intimately mixed, forming a very homogeneous blend. This fact can really occur because of the chemical similarity between PEC and starch. Both carbohydrates display OH groups on their building blocks, which can form intermacromolecular

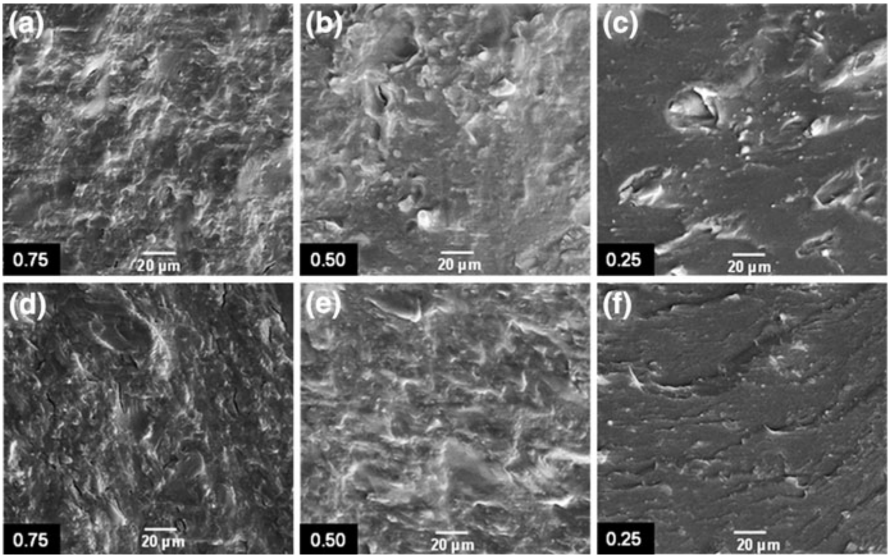


Fig. 6 SEM micrographs for TPS/PEC blends with 0.25, 0.50, and 0.75 polymer ratios. **a**–**c** LM PEC, **d**–**f** HM PEC

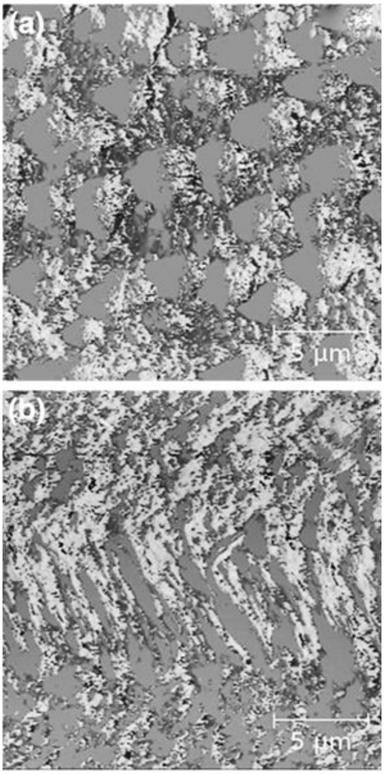


Fig. 7 Phase shift from tapping-AFM images (*gray scale*) of the starch/PEC blend films at polymer ratio **a** 0.25 and **b** 0.75

hydrogen bonds and improve the interfacial compatibility in blends. From SEM results, TPS/PEC blends are taken as miscible polymer systems with a high degree of interfacial adhesion, although it does not corroborate with the results found in the mechanical characterization of the blends.

So, in an effort to confirm the miscibility between PEC and starch, an additional experiment was performed. The 0.25 and 0.75 starch:PEC blends were prepared by casting method and their surfaces were characterized by tapping mode-AFM (described in "Experimental" part). The purpose being to prepare blend films under quasi-ideal mixing conditions and therefore we could eliminate the use of glycerol, which can interfere in the imaging. Phase shift scanning was performed to detect variations in viscoelasticity and elasticity on the film surfaces. These results are shown in Fig. 7.

Both starch- and PEC-rich films have two-phase structures in the microscopic scale as defined by the phase imaging. It was observed because of the strong contrast that exists between PEC (brittle) and starch (ductile). When the tip strikes the film, its oscillation phase is disturbed and it is no longer precisely in step with the phase of the cantilever that is driving the tip. This is a particular consequence of the transfer of small amount of energy to it and depends on the viscoelasticity of the surface. Thus, the highlighted parts of the images can be attributed to the elastic starch domains, while the dark parts in the image can be associated to the one for low elastic PEC. The phase imaging by tapping mode-AFM has been demonstrated as a powerful approach to investigate polymer blends in different ways including the temperature dependence of the surface composition in PMMA/SAN blends [30], phase separation and biphasic morphology of PVC/NBR blends [31], and the immiscibility in chitosan/PCL blend films [32]. However, to the best of our knowledge, a miscibility investigation on fully carbohydrate blends by tapping mode-AFM has not been reported previously.

Therefore, the morphologies depicted in the AFM images evidence the phase separation occurring into starch/PEC blends. Once this phenomenon may also occur in samples prepared via melt processing, the TPS/PEC blends developed here can be better categorized as totally or partially immiscible blends. However, it is important to consider that TPS is made up of rigid amylose and flexible amylopectin and each one may have particular miscibility with PEC, which was not distinguished by the phase shift-AFM characterizations. Further experiments are in progress to confirm this statement, as well as to explore in details the microstructure of these biodegradable materials.

Conclusion

In this study, we reported important relationships among composition, processing, and mechanical properties of biodegradable starch/PEC blends, which were obtained by melt technique. Specifically, TPS content showed strong influence on all tensile properties of the blends due to a plasticizing effect. The processing parameters were found to be insignificant when they were analyzed separately, but they showed to be mutually dependent. It was proposed that as the DM of PEC decreased, the resistance of the blends increased. This effect occurred because of stronger hydrogen bond interactions between LM PEC chains and it was observed on blends with maximum TPS content of 50 wt%. Finally, we concluded this study by presenting the immiscibility between starch and PEC as cast films using AFM and that this phenomenon can explain the mechanical behavior of the thermoplastic blends. The phase characterization using tapping mode-AFM offers a way to investigate the miscibility into fully carbohydrate blends at a level that has been hard to be detected through laborious sample preparation microscopies as TEM and others.

Acknowledgments The authors gratefully acknowledge the Corn Products Brasil Ltd. for supplying the corn starch, EMBRAPA, FINEP/MCT, CAPES, CNPq, and FAPESP for financial supports and scholarships. Adriana Coatrini Thomazi and Paulo Renato Orlandi Lasso from CNPDIA are also acknowledged for the technical assistance at the mechanical and AFM characterizations.

References

1. Sionkowska A (2011) Current research on the blends of natural and synthetic polymers as new biomaterials: review. Prog Polym Sci 36:1254–1276
2. Campos CA, Lía N, Gerschenson LN, Flores SK (2011) Development of edible films and coatings with antimicrobial activity. Food Bioprocess Technol 4:849–875

3. Crouzier T, Boudou T, Picart C (2010) Polysaccharide-based polyelectrolyte multilayers. Curr Opin Colloid Interface Sci 15:417–426
4. Varshney PK, Gupta S (2011) Natural polymer-based electrolytes for electrochemical devices: a review. Ionics 17:479–483
5. Willats WGT, Knoxb JP, Mikkelsen JD (2006) Pectin: new insights into an old polymer are starting to gel. Trends Food Sci Technol 17:97–104
6. Schols HA, Voragen AGJ (2002) The chemical structure of pectins. In: Seymour GB, Knox JP (eds) Pectins and their manipulation. Blackwell Publishing and CRC Press, Oxford, pp 1–29
7. Wong TW, Colombo G, Sonvico F (2011) Pectin matrix as oral drug delivery vehicle for colon cancer treatment. AAPS PharmSciTech. doi:10.1208/s12249-010-9564-z
8. Andrade JR, Raphael E, Pawlicka A (2009) Plasticized pectin-based gel electrolytes. Electrochim Acta 54:6479–6483
9. Bergman M, Djaldetti M, Salman H, Bessler H (2010) Effect of citrus pectin on malignant cell proliferation. Biomed Pharmacother 64:44–47
10. Gohil RM (2011) Synergistic blends of natural polymers, pectin and sodium alginate. J Appl Polym Sci 120:2324–2336
11. Kowalonek J, Kaczmarek H, Dąbrowska A (2010) Air plasma or UV-irradiation applied to surface modification of pectin/poly(vinyl alcohol) blends. Appl Surf Sci 257:325–331
12. Rutiaga MO, Galan LJ, Morales LH, Gordon SH, Imam SH, Orts WJ, Glenn GM, Nino KA (2005) Mechanical property and biodegradability of cast films prepared from blends of oppositely charged biopolymers. J Polym Environ. doi:10.1007/s10924-005-2949-5
13. Coffin DR, Fishman M (1994) Physical and mechanical properties of highly plasticized pectin/starch films. J Appl Polym Sci 54:1311–1320
14. Hoagland PD, Parris N (1996) Chitosan/pectin laminated films. J Agric Food Chem 44:1915–1919
15. Corradini E, Marconcini JM, Agnelli JAM, Mattoso LHC (2011) Thermoplastic blends of corn gluten meal/starch (CGM/starch) and corn gluten meal/polyvinyl alcohol and corn gluten meal/poly(hydroxybutyrate-*co*-hydroxyvalerate) (CGM/PHB-V). Carbohydr Polym 83:959–965
16. Coffin DR, Fishman ML (1993) Viscoelastic properties of pectin/starch blends. J Agric Food Chem 41:1192–1197
17. Fishman ML, Coffin DR, Konstance RP, Onwulata CI (2000) Extrusion of pectin/starch blends plasticized with glycerol. Carbohydr Polym 41:317–325
18. Fishman ML, Coffin DR, Onwulata CI, Konstance RP (2004) Extrusion of pectin and glycerol with various combinations of orange albedo and starch. Carbohydr Polym 57:401–413
19. Wu C-FJ, Hamada M (2000) Experiments: planning, analysis, and parameter design optimization. Wiley series in probability and statistics. Wiley-Interscience, New York
20. Hajjaji N, Renaudin V, Houas A, Pons MN (2010) Factorial design of experiment (DOE) for parametric exergetic investigation of a steam methane reforming process for hydrogen production. Chem Eng Process 49:500–507
21. Moreira FKV (2010) Desenvolvimento de nanocompósitos poliméricos biodegradáveis a partir de pectina, amido e nanofibras de celulose. M.Sc. Thesis, Universidade Federal de São Carlos. Available in: http://www2.ufscar.br/interface_frames/index.php?link=http://www.bco.ufscar.br. Accessed 25 Nov 2011
22. Corradini E, Lotti C, De Medeiros ES, De Carvalho AJF, Curvelo AAS, Mattoso LHC (2005) Estudo comparativo de amidos termoplásticos derivados do milho com diferentes teores de amilose. Polim Cienc Tecnol 15(4):268–273
23. Talja RA, Helén H, Roos HY, Jouppila K (2008) Effect of type and content of binary polyol mixtures on physical and mechanical properties of starch-based edible films. Carbohydr Polym 71:269–276
24. Shi R, Liu Q, Ding T, Han Y, Zhang L, Chen D, Tian W (2007) Ageing of soft thermoplastic starch with high glycerol content. J Appl Polym Sci 103:574–586
25. Einhorn-Stoll U, Kunzeka H, Dongowski G (2007) Thermal analysis of chemically and mechanically modified pectins. Food Hydrocolloid 21:1101–1112
26. Einhorn-Stoll U, Kunzek H (2009) Thermoanalytical characterization of processing-dependent structural changes and state transitions of citrus pectin. Food Hydrocolloid 23:40–52
27. Synytsyaa A, Čopíková J, Matějkab P, Machovič V (2003) Fourier transform Raman and infrared spectroscopy of pectins. Carbohydr Polym 54:97–106
28. Espinoza-Herrera N, Pedroza-Islas R, Martín-Martinez ES, Cruz-Orea A, Tomás SA (2011) Thermal, mechanical and microstructures properties of cellulose derivatives films: a comparative study. Food Biophys 6:106–114

29. Fishman ML, Coffin DR, Onwulata CI, Willett JL (2006) Two stage extrusion of plasticized pectin/poly(vinyl alcohol) blends. Carbohydr Polym 65:421–429
30. You J, Shi T, Liao Y, Li X, Su Z, An L (2008) Temperature dependence of surface composition and morphology in polymer blend film. Polymer 49:4456–4461
31. Gheno SM, Passador FR, Pessan LA (2010) Investigation of the phase morphology of dynamically vulcanized PVC/NBR blends using atomic force microscopy. J Appl Polym Sci 117:3211–3219
32. Cruz DMG, Coutinho DF, Martinez EC, Mano JF, Ribelles JLG, Sánchez MS (2008) Blending polysaccharides with biodegradable polymers. II. Structure and biological response of chitosan/polycaprolactone blends. J Biomed Mater Res B. doi:10.1002/jbm.b.31142