



Biodegradable blends of urea plasticized thermoplastic starch (UTPS) and poly(ϵ -caprolactone) (PCL): Morphological, rheological, thermal and mechanical properties

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ABSTRACT

Biodegradable blends of urea plasticized thermoplastic starch (UTPS) and poly(ϵ -caprolactone) (PCL) were prepared in a co-rotating twin screw extruder. The UTPS and PCL content varied in a range of 25 wt%. The materials were characterized by capillary rheometry, scanning electron microscopy (SEM), thermogravimetry (TGA), differential scanning calorimetry (DSC) and tensile tests. Capillary rheometry showed better interaction between UTPS and PCL at 110 °C than at 130 °C. SEM showed immiscibility of all blends and good dispersion of UTPS in PCL matrix up to 50 wt%. However, a co-continuous morphology was found for UTPS/PCL 75/25. Thermal analysis showed that introducing PCL in UTPS, increased T_{onset} due to higher thermal stability of PCL, and blends presented an intermediate behavior of neat polymers. The presence of PCL in blends improved significantly the mechanical properties of neat UTPS. Because they are totally biodegradable, these blends can be vehicles for controlled or slow release of nutrients to the soil while degraded.

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1. Introduction

The growing interest in using eco friendly products has stimulated research and development of new materials such as biodegradable polymers (Cyras, Martucci, Iannace, & Vazquez, 2002). Starch is an abundant and naturally occurring polymer, present in a wide variety of plants, such as corn, wheat, rice, potatoes and others. Native starch is composed mainly of two polysaccharides, amylose and amylopectin, and it is found in granular form, which has no plastic properties (Parker & Ring, 2005). However, when subjected to shear-pressure-temperature and in the presence of plasticizer, it can be melted and processed by conventional processing methods, obtaining the so called thermoplastic starch (TPS). Such plasticizers form hydrogen bonds with the starch, replacing the strong intramolecular interactions of the starch chains, plastifying it (van Soest & Vliegthart, 1997). Many different substances can be used as plasticizers in TPS including water, glycerol, sorbitol, sugar and compounds containing amide

groups, such as urea, formamide and acetamide (Ma & Yu, 2004; van Soest & Vliegthart, 1997). The last three are known to be effective in suppressing TPS retrogradation.

Glycerol has been used as a traditional plasticizer for starch, but in agriculture, glycerol can change root architecture by inhibiting principal root growth and altering lateral root development (Hu, Zhang, Wang, & Zhou, 2014). On the other hand, urea is used in agriculture as nitrogen fertilizer, because it presents 44% of nitrogen in its structure. And the use of urea as a plasticizer for TPS can allow this material to be applied to the soil not causing environmental damage; in addition, it can allow a slow or controlled release of Nitrogen into the soil, in order to gradually nourish it.

Although TPS is a cheap and fully biodegradable material, it presents poor mechanical properties and it is water sensitive. One way to overcome these drawbacks is blending TPS with another biodegradable polymer.

PCL is a semi crystalline, thermoplastic and biodegradable polyester, synthesized by ring opening polymerization of ϵ -caprolactone. It is recognized for its high flexibility, low melting point and good compatibility with many other polymers (Averous, Moro, Dole, & Fringant, 2000; Dubois, Krishnan, & Narayan, 1999), and PCL applications ranges from agricultural to biomedical

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devices (Chandra & Rustgi, 1998; Darwis, Mitomo, Enjoji, Yoshii, & Makuuchi, 1998; Griffith, 2000). However, the large scale use of PLC products is still hampered by its relatively high cost compared to other conventional polymers. Blending PCL with inexpensive materials, such as TPS, could solve this problem (You, Dean, & Li, 2006).

Physical properties such as thermal, mechanical and water absorption of glycerol plasticized TPS when blended with PCL (GTPS-PCL) have been studied by some authors (Averous et al., 2000; Boo-Young, Sang-Li, Shin, Balakrishnan, & Narayan, 2004; Li & Favis, 2010; Shin, Narayan, Lee, & Lee, 2008), including previous works (Carmona, de Campos, Marconcini, & Mattoso, 2014; Carmona, Correa, Marconcini, & Mattoso, 2015). Adding PCL to GTPS resulted in an increase of both hydrophobicity and ductility of the blend as a function of the PCL fraction. Furthermore, it was observed that GTPS and PCL formed an immiscible system, regardless the blend composition.

Shin et al. (2008) studied viscoelastic properties of GTPS-PCL blends and reported that the higher GTPS content, the higher storage and loss modulus, suggesting changes in morphology, from a dispersed phase of GTPS to a co-continuous phase and further, to a dispersed phase of PCL. Ma, Yu, and Ma (2005) studied the effects of urea/formamide on rheological properties of a thermoplastic wheat flour (UFTPF) and they reported that UFTPF exhibited a shear thinning behavior, followed by the power law dependence. In addition, increasing the plasticizer content from 30 to 50 wt% induced the reduction of UFTPF viscosity, did not change the pseudo-plastic index (n) or consistency (K) of the material.

There is a lack of information about properties of urea plasticized thermoplastic starch (UTPS) and its blends. Thus, the aim of this paper is to produce UTPS and UTPS-PCL blends by extrusion and evaluate the effect of UTPS content on the rheological, morphological, thermal and mechanical properties of its blends. This study is important to investigate the processing characteristics of these biodegradable polymer blends.

2. Experimental

2.1. Materials

The corn starch, Amidex 3001[®] (28 wt% amylose), was obtained from Ingredion, Brazil. The urea, used as plasticizer, was purchased from Vetec, Brazil. Stearic acid and citric acid were provided by Synth, Brazil. PCL CAPA[®] 6500 (Perstorp, UK) was used in the blends composition.

2.2. Processing

Urea plasticized thermoplastic starch (UTPS) was prepared from a manual mixture of the following components: 60 wt% native corn starch, 24 wt% urea and 16 wt% water; to this composition, 1 wt% stearic acid and 1 wt% citric acid were added. This mixture was fed into an 18 mm co-rotating twin screw extruder (Coperion ZSK 18), 40 L/D. The screw speed was 300 rpm and the temperature profile was 110, 110, 120, 120, 130, 130 and 110 °C in the seven heating zones. Excess water was removed through two separate vents and through a third port attached to a vacuum pump. The UTPS strands were cooled in air and pelletized. UTPS was then blended with PCL, varying the weight composition of 25 wt% of each polymer.

PCL and UTPS-PCL blends were extruded in the same conditions as UTPS, in order to provide equal thermal and processing history for all samples. The UTPS-PCL blends were named according to their respective composition: UTPS-PCL 75-25; UTPS-PCL 50-50, UTPS-PCL 25-75.

After extruding, all samples, except neat UTPS, were molded in tensile specimens type I – ASTM D-638 in an injection mold-

ing equipment Arburg 270S 400-100. It was applied an injection pressure of 2000 bar, mold temperature of 25 °C, and temperature profile of 70, 110, 120, 120 and 110 °C in the five heating zones.

The neat UTPS specimens, type IV – ASTM D638, were produced by pressing the ribbons obtained from a single screw extruder AX Plastic, with tape profile in the die. The screw rotation speed was 100 rpm and the temperature profile in the three heating zones was kept at 130 °C.

2.3. Rheological properties

The extruded strips were pelletized and tested by Rheograph S2 capillary rheometer (Göttfert). The capillary had a 1 mm radius and L/D was 30. The pellets were placed into the barrel and packed down with a plunger until the extrudate appeared through the capillary exit. The samples remained for 3 min at the test temperature to stabilize, and were then forced through the capillary by the plunger at pre-selected speeds, resulting in shear rates in the range of 100 s⁻¹ up to 10,000 s⁻¹. Shear rates ($\dot{\gamma}$) and viscosities (η) were determined using the Rabinowitsch correction, assisted by WinRheo II software.

2.4. Morphological properties

Morphologies of the cryogenic fracture surfaces of extruded UTPS, PCL and UTPS-PCL blends strips were investigated by Scanning Electron Microscopy (SEM) (JEOL JSM-6510 series) operating at 10 kV. In order to selectively dissolve the UTPS phase in the UTPS-PCL blends, the samples were treated with hydrochloric acid (HCl 1 M) for 3 h. All samples were sputter-coated with gold to avoid charging.

2.5. Thermal analyses

Thermal stability of the blends were evaluated by thermogravimetry using a TGA Q500 (TA Instrument, USA). Analyses were carried out under synthetic air atmosphere (60 mL/min) from room temperature to 600 °C, at a heating rate of 10 °C/min. The onset temperature (T_{onset}) was determined from the TG curve as the intersection of the line extrapolated from the first thermal event with the tangent line to the TG curve, in the range of maximum rate of the decomposition reaction.

DSC measurements of neat PCL, UTPS and polymer blends were performed in a DSC Q-100 equipment (TA Instruments, USA). The tests were carried out with approximately 5 mg of the injected molded samples under nitrogen atmosphere. The temperature setting was adjusted as follows: heating from -50 °C up to 150 °C at a rate of 10 °C/min, followed by cooling to -50 °C at a rate of 10 °C/min. The crystallinity index (C_I) and melting point of PCL and blends of PCL and UTPS were determined by DSC. C_I were determined according to Vertuccio (Vertuccio, Gorrasi, Sorrentino, & Vittoria, 2009), using the Eq. (1):

$$C_I (\%) = \frac{\Delta H_{\text{exp}}}{\Delta H_0 \times f} \times 100 \quad (1)$$

Where ΔH_{exp} is fusion enthalpy (J/g) determined by DSC measurement, ΔH_0 is theoretical enthalpy of the completely crystalline polymer, which is 132 J/g for PCL (Crescenzi, Manzini, Calzolari, & Borri, 1972), and the wt% of PCL in each blend is given by the term f .

2.6. Mechanical properties

Mechanical properties were evaluated in a universal testing machine EMIC DL3000 according to standard ASTM D638. Tests were performed with a speed of 5 mm/min using a loading cell

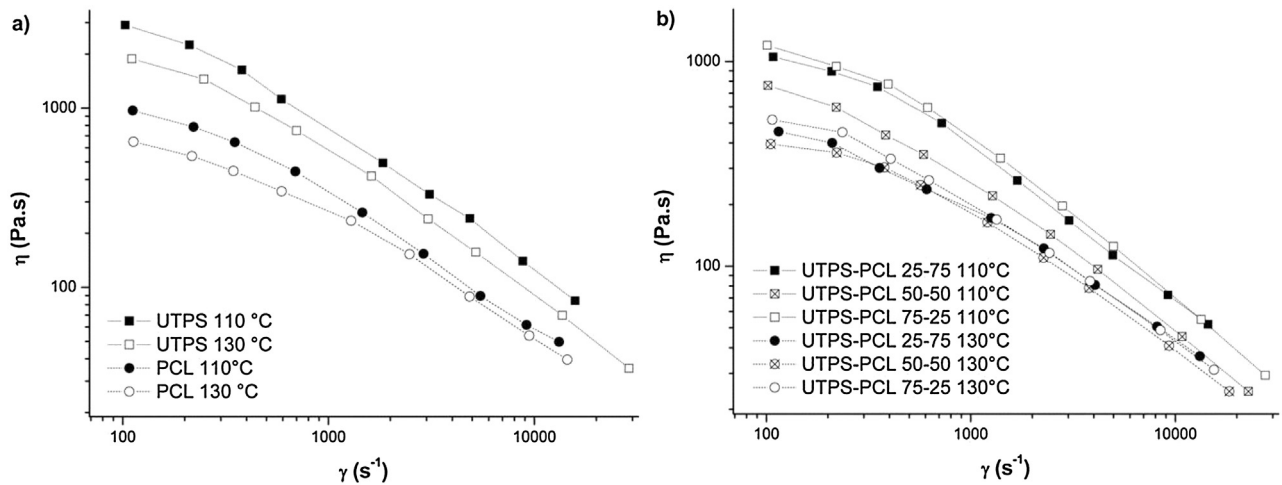


Fig. 1. Viscosities (η) as a function of shear rate (γ) at 110 °C and 130 °C for (a) UTPS and PCL and (b) UTPS-PCL blends.

of 500 kgf after equilibrium in an environment of $52 \pm 3\%$ relative humidity for 15 days. The elastic modulus (E), tensile strength (σ_{\max}) and elongation at break (ε) of these materials were determined and subjected to statistical analysis of variance (ANOVA) using the software Origin Pro 8.

3. Results and discussion

In order to understand the rheological properties during processing of UTPS, PCL and UTPS/PCL blends, rheological experiments were carried at 110 °C and 130 °C, which covered the processing temperature range. The viscosity vs. shear rate curves (η - γ) were plotted using a double logarithmic axis (Fig. 1). Each material exhibited a pseudoplastic behavior, as occurred a reduction of viscosity with the increase of the shear strain. Such flow behavior is also called shear thinning, which is associated to the increase of orientation degree of polymeric molecules and to the impairment in chain entanglement of both UTPS and PCL. It can also be observed that the UTPS presents higher viscosity than PCL at both analyzed temperature (Fig. 1a). However, the addition of PCL in TPS caused a decrease in the viscosity of the blend, resulting in all blends less viscous than neat TPS, regardless of the test temperature. Furthermore, as expected, both blends and neat polymers presented lower viscosities at 130 °C than at 110 °C.

The viscosity ratio in immiscible polymer blends is an important parameter in the morphological development and hence the physical properties (Wu, 1987). In a dispersed phase morphology, the dispersed drops become smaller as the viscosity ratio is closer to unity. With the obtained results from rheological behavior of the polymers, it was possible to observe that UTPS presents higher viscosity than PCL, that is $\eta_{\text{UTPS}} > \eta_{\text{PCL}}$. In this way, Fig. 2 presents the viscosity ratios of neat UTPS and PCL ($\eta_{\text{UTPS}}/\eta_{\text{PCL}}$) as a function of the base-10 logarithm of shear rate (γ) at 110 °C and 130 °C. The values of $\eta_{\text{UTPS}}/\eta_{\text{PCL}}$ at 110 °C are in the range from 2.9 to 1.8 and the values of $\eta_{\text{UTPS}}/\eta_{\text{PCL}}$ at 130 °C are in the range from 3.1 to 1.5. In this way, it can be noted that increasing the shear rate, $\eta_{\text{UTPS}}/\eta_{\text{PCL}}$ are getting closer to 1. It is also observed that at shear rates higher than 400 s^{-1} the values of $\eta_{\text{UTPS}}/\eta_{\text{PCL}}$ at 130 °C became smaller and closer to 1 than those of $\eta_{\text{UTPS}}/\eta_{\text{PCL}}$ at 110 °C.

The double logarithmic η - γ curves of UTPS/PCL blends (Fig. 1) showed rheological behavior similar to neat UTPS and PCL, with viscosity values in the range of those of neat UTPS and PCL. It is well known that the viscosity of a polymer blend can be described

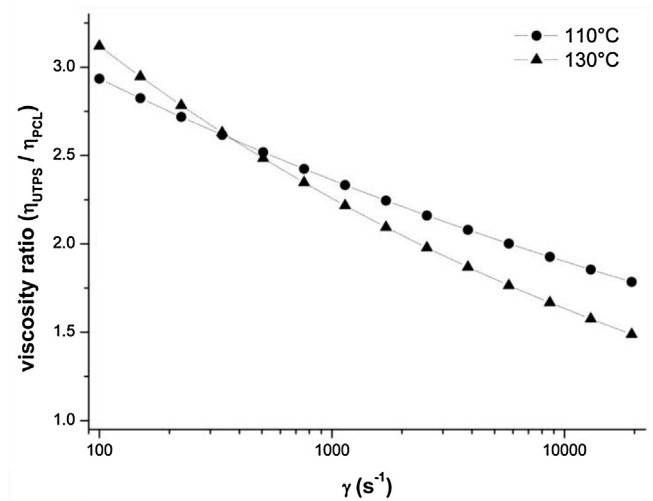


Fig. 2. Viscosity ratio ($\eta_{\text{UTPS}}/\eta_{\text{PCL}}$) vs. shear rate (γ) at 110 °C and 130 °C.

by using the log of the additivity rule (Ferry, 1980; Rohn, 1995), described by Eq. (2):

$$\ln \eta_b = \sum \omega_i \ln \eta_i \quad (2)$$

Where ω_i and η_i are the weight fraction and the viscosity of each component in blend, respectively, and η_b is the viscosity of the blend.

Fig. 3 compares the blend viscosity prediction, based on the log additivity rule (Eq. (2)), with the experimental viscosity at different shear rates, at 110 °C and 130 °C. It can be observed that the experimental viscosity values are lower for all shear rates at both temperatures, except the UTPS/PCL 25/75 at 110 °C. And also, at 110 °C the viscosities of polymer blends are closer to those the theoretical values, suggesting that there might be a better interaction between PCL and UTPS at lower temperatures. This behavior suggests that, at 110 °C and at lower UTPS content, an interdiffusion of the polymer chains across the phase boundaries readily occurs, resulting in an enhancement of the component interactions. As the UTPS content increases, a negative deviation, in relation to the additivity rule, is observed. This behavior has been attributed to a tendency for phase separation in polymer blends (Da Silva, Rocha, Coutinho, Bretas, & Scuracchio, 2000; Schreiber & Olguin, 1983).

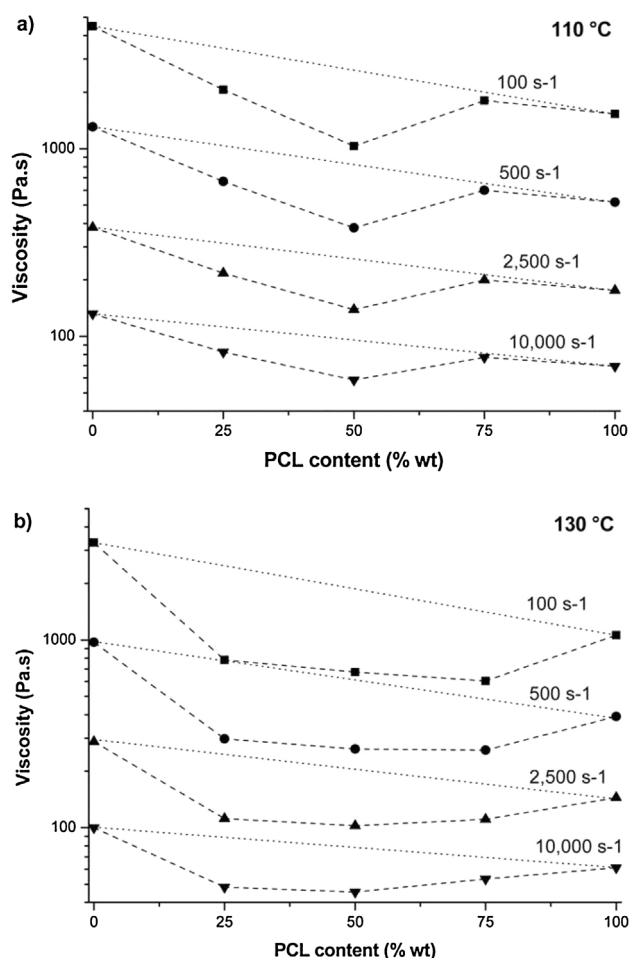


Fig. 3. Comparison between theoretical (dotted lines) and experimental (dashed lines) viscosities of polymer blends as a function of PCL content (wt%) for different shear rates at 110 °C (a) and 130 °C (b).

Table 1

Consistency factor (K) and pseudoplastic index (n) for neat UTPS, PCL and UTSP-PCL blends at 110 °C and 130 °C.

Samples	110 °C		130 °C	
	K (kPa s ^{n})	n	K (kPa s ^{n})	n
UTPS	308.1	0.144	218.6	0.152
PCL	77.8	0.218	43.6	0.272
UTPS/PCL 25/75	76.7	0.236	17.9	0.351
UTPS/PCL 50/50	39.2	0.278	19.2	0.320
UTPS/PCL 75/25	104.2	0.209	21.5	0.328

Pseudoplastic index values, n , and the consistency factor, K , of neat polymers and polymers blend were calculated using the Power Law (Eq. (3)) and they are listed in Table 1.

$$\eta = K\dot{\gamma}^{(n-1)} \quad (3)$$

From the results of n and K of neat UTSP and PCL, their dependence on temperature could be observed: increasing the temperature, there is an increase in the n values and a reduction in the K values. The consistency of the material (K), which is the viscosity of the material when shear rate is equal to 1 s⁻¹, is related to the structure and composition of the material, or to the consistency of the material in the molten state (Wang, Yu, Chang, & Ma, 2008). Note that at a given temperature, $K_{UTPS} > K_{PCL}$ in the same way as $n_{UTPS} < n_{PCL}$.

On the other hand, pseudoplastic index (n) is related to the entanglement degree and/or ability of polymer chains to disentangle under shear, i.e., presenting low n , polymers untangle easier and therefore, they will have a more pronounced non-Newtonian behavior than polymers with higher n (Willet, Millardt, & Jasberg, 1997). Most pseudoplastic polymers present n values from 0.1 up to 0.4, and values higher than 0.4 may indicate that a degradation in polymer chains is taking place (Wang et al., 2008).

Changes in tangle of polymer chains can be represented by changes in pseudoplastic behavior of some materials; the pseudoplastic index n is a measure of the degree of entanglement and/or the ability of polymer chains to untangle under shear. Polymers with low n values easily unravel and therefore have a higher non-Newtonian character, compared to polymers with high n values, such as polybutadiene (Willet et al., 1997).

It is clearly seen that UTSP presented the highest K values, but when blended with PCL (UTSP/PCL blends), K values strongly reduced. An additional reduction in K values of UTSP/PCL blends was observed at 130 °C. At this temperature, neat UTSP and PCL presented n values in the range of 0.15–0.27, respectively. On the other hand, UTSP/PCL blends at 130 °C presented higher n values (0.32–0.35), indicating that neat UTSP and PCL are more pseudoplastic than UTSP/PCL blends. Generally, polymers present n values in the range of 0.1–0.4; and higher n values may indicate degradation of some constituents of the polymeric chains (Wang et al., 2008).

The cryogenic fracture surface of extruded UTSP, PCL and UTSP/PCL blends are shown in Fig. 4a–e. In Fig. 4a it is possible to observe that corn starch was successfully plasticized and UTSP presented a homogeneous morphology. Moreover, it can also be observed some urea domains (indicated by an arrow) possibly due to the excess of urea used in the preparation of UTSP. PCL present a typical cryogenic fracture surface for a low T_g polymer (T_g of PCL is about -65 °C (Labet & Thielemans, 2009)).

Blending UTSP and PCL resulted in immiscible blends, as supported by capillary rheometer analysis, and well dispersed UTSP droplets in a continuous PCL matrix were also observed.

In order to obtain better contrast between UTSP and PCL phases in UTSP-PCL blends, the UTSP phase was removed from the surface using a solution of HCl 1 M. Fig. 4c–e shows the cryogenic fracture surface of these blends. As the UTSP content was increased in UTSP-PCL blends, it can be observed that UTSP droplets change their morphology from spherical (UTSP-PCL 25-75, Fig. 4c) to elliptical (UTSP-PCL 50-50, Fig. 4d), indicating that the coalescence phenomenon took place. Furthermore, it can be observed that the phase-inversion starts when a higher UTSP content is present (UTSP-PCL 75-25, Fig. 4e), resulting in a co-continuous morphology.

The thermal stability was determined by thermogravimetric analysis (TGA). Fig. 5 presents the thermal degradation profile of the neat UTSP and PCL and the blends UTSP/PCL 25/75, 50/50 and 75/25.

It can be seen by the curves TG/DTG (Fig. 5(a) and (b)) that PCL presents greater thermal stability than UTSP. The thermal degradation of PCL starts in the range of 300 °C, while thermal degradation of UTSP occurs at approximately 230 °C. PCL has been suggested to degrade through a two-stage mechanism. The first step is a polymer chain cleavage via *cis*-elimination and the consecutive second step is an unzipping depolymerisation from the hydroxyl end of the polymer chain (Aoyagi, Yamashita, & Doi, 2002). Thermal degradation of UTSP presented four mass loss stages. Up to approximately 130 °C, there is a mass loss due to the presence of water and other volatile compounds. Another weight loss is observed between 130 and 230 °C related to the urea used as a plasticizer of UTSP. Then, the starch chains began to degrade at about 230 °C (mainly due to dehydration of hydroxyl groups and the subsequent formation of unsaturated and aliphatic low molecular weight carbon species

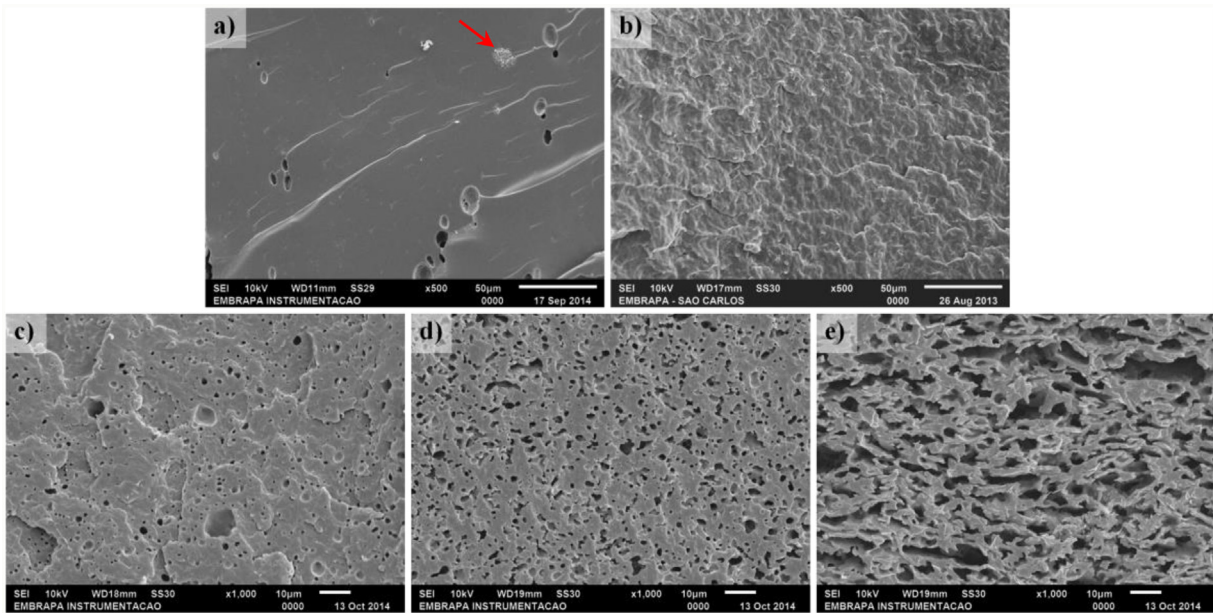


Fig. 4. SEM micrographs of (a) UTPS, (b) PCL, and HCl 1 M treated samples of (c) UTPS/PCL 25/75, (d) UTPS/PCL 50/50 and (e) UTPS/PCL 75/25.

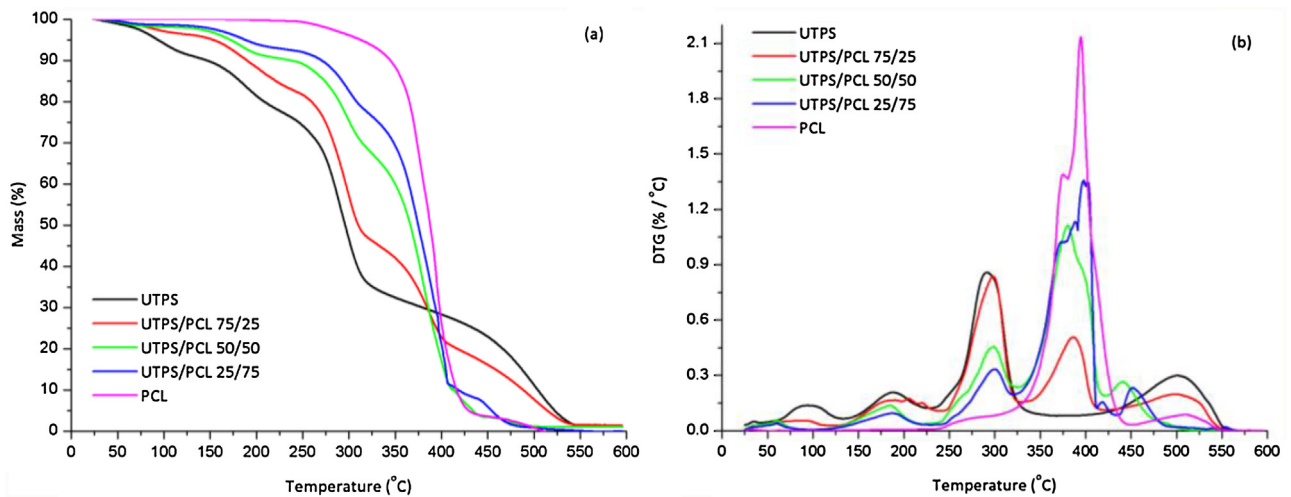


Fig. 5. TG curves (a) and DTG curves (b) of neat PCL and UTPS polymers and their blends, under synthetic air atmosphere at a heating rate of 10 °C/min.

(Sin, Rahman, Rahmat, & Mokhtar, 2011)), and the last stage of thermal degradation is generally carbonization (Shi et al., 2011).

Regarding the blends, the thermal behavior of the UTPS/PCL blend was found to be intermediate to those of neat polymers. However, all the blends presented all the stages of thermal degradation of the UTPS and PCL, but shifted to higher temperatures, due to the increase of PCL content in the blend, because PCL presents higher thermal stability than UTPS. In all the blends, the mass loss up to 120 °C can be attributed to the evaporation of water, and other volatile compounds present in UTPS, followed by the thermodegradation of urea, and thermal degradation of the corn starch occurred between 250 and 330 °C. The fourth stage of thermal degradation of the blends occurred from 350 to 430 °C, due to the degradation of PCL chains; and from 430 °C, the last stage of carbonization.

DTG curves of UTPS/PCL blends (Fig. 5b) show all these stages of thermal degradation of blends and neat UTPS and PCL represented in peaks. The first peak (between 70 and 150 °C) appears only in the UTPS sample, and as already mentioned, it refers to the evaporation of water and some volatiles. This peak is much smaller in the blends or PCL, since the TPS and PCL used in the composition of

the blends were previously dried. The second peak (between 150 and 250 °C) refers to the decomposition of urea, and appears for all blends. The third peak, between 250 and 350 °C, is related to the main decomposition of the starch, and like the second peak, decreases with the increase of PCL content in the blend. On the other hand, the peak between 350 and 450 °C, related to the PCL decomposition, increases its intensity with the PCL increase in the blend, reaching its maximum value for the neat PCL.

The data in Table 2 indicate an increase in the volatile content (water and urea) due to the increase in UTPS content in the material, reaching its maximum on 22.85%, the neat UTPS. Furthermore, the PCL showed little sensitive to moisture absorption. For all the materials containing UTPS, the T_{onset1} is higher than 150 °C. The thermal degradation of urea is an important event because from this, there is the formation of many toxic byproducts, including cyanic acid, biuret and cyanuric acid, among others (Bernhard, Peitz, Elsener, Wokaun, & Kröcher, 2012; Schaber et al., 2004). Thus, its degradation temperature can be a limiting factor, in case of using UTPS in polymer blends where the second polymer has melting temperature greater than 150 °C. However, processing temperatures of

Table 2
Thermal properties of neat polymers UTPS and PCL and their blends.

Sample	% Volatiles (up to 230 °C)	% Organic (up to 600 °C)	% Residues (600 °C)	T _{onset1} ^a (°C)	T _{onset2} ^a (°C)
UTPS	22.8	74.1	3.1	163	271
UTPS/PCL 75/25	16.2	82.3	1.5	156	275
UTPS/PCL 50/50	9.7	89.1	1.1	151	272
UTPS/PCL 25/75	7.3	92.2	0.5	152	274
PCL	0.4	99.5	0.1	–	353

^a T_{onset1} relates to thermodegradation of urea present in UTPS and T_{onset2} relates to thermodegradation of starch chains or PCL (for neat PCL).

Table 3
Crystallization (T_c) and melting (T_m) temperatures, and melting (ΔH_m) and crystallization (ΔH_c) enthalpies for neat PCL and the blends with UTPS, and the crystallinity index (C_i) calculated from ΔH_m (Eq. (1)).

Sample	T _m (°C)	ΔH _m (J/g)	T _c (°C)	ΔH _c (J/g)	C _i (%)
PCL	57.4	67.7	31.0	57.4	51.3
UTPS/PCL 25/75	56.6	53.5	30.7	46.9	54.0
UTPS/PCL 50/50	56.2	51.9	30.2	47.1	78.6
UTPS/PCL 75/25	55.8	13.4	30.3	17.5	40.6

blends UTPS/PCL did not reach temperatures as high as their T_{onset1}, again indicating the importance of PCL in these systems. Regarding the T_{onset2}, it can be seen that the blends with UTPS presented values around 270 °C; while the neat PCL showed values in the order of 350 °C. But in all cases, the T_{onset2} are at least 100 °C above the processing temperature of the materials.

Differential scanning calorimetry (DSC) was used to identify the transition temperatures of the pure PCL and the PCL present in polymer blends as well as their crystallinity (C_i). Fig. 6 shows the DSC curves on 1st heating and cooling of neat PCL and their blends with UTPS.

The DSC curves did not show any thermal transition in neat UTPS, except by the decomposition of urea at around 140 °C, as also observed by TGA. From the DSC curves presented in Fig. 6, there were determined transition temperatures and enthalpies of fusion and crystallization of neat PCL and PCL into the polymer blends, and these values are shown in Table 3.

The incorporation of UTPS into the PCL matrix induced its crystallization until the proportion of 50/50, as shown in Table 3, although a decrease of the melting enthalpy (ΔH_m) was evident. It happened because from Eq. (1): C_i (%) = $\frac{\Delta H_{exp}}{\Delta H_0 \times f} \times 100$, it was possible to obtain the crystallinity index (C_i) for each blend from melting enthalpy. Although there was a decrease in the melting enthalpy of the blends with the increase of the UTPS content, proportionally there was also a decrease in the PCL content (f), responsible for the crystalline portion of the blends. When 75% UTPS is blended to PCL, a phase inversion occurs, and the matrix is now UTPS, and even the blend presenting a co-continuous morphology at this ratio, UTPS makes difficult the formation of PCL crystals in the blend. The new PCL crystals formed in the presence of UTPS were probably less packed, than the crystals formed in the environment containing neat PCL, which required less energy to melt, presenting a decrease in lamellar thickness and an increase in heterogeneity of crystal size (Campos et al., 2013).

From Table 3, it also can be observed that the PCL crystallization temperature (T_c) was constant, even when it was present in the blends, suggesting that the UTPS presented poor interaction with PCL, but did not interfere in the crystallization of PCL. As the PCL crystallizes during cooling, higher T_c values mean greater speed and ease in its crystallization, which did not occur with those blends. It can also be noted that the PCL present in the polymer blends showed higher crystallinity index (C_i) than neat PCL, except the blend UTPS/PCL 75/25. But the melting temperature showed no significant differences when PCL was blended with UTPS.

Table 4
Mechanical properties of neat UTPS and PCL and their blends: maximum tensile strength (σ_{max}), elongation at break (ε) and elastic modulus (E).

Amostra	σ _{max} (MPa)	ε (%)	E (GPa)
UTPS	2.0 ± 0.4 ^a	14 ± 2 ^a	0.14 ± 0.03 ^a
UTPS/PCL 75/25	9.8 ± 0.4 ^b	1.87 ± 0.09 ^b	0.70 ± 0.05 ^b
UTPS/PCL 50/50	10.3 ± 0.5 ^b	2.7 ± 0.6 ^b	0.51 ± 0.09 ^c
UTPS/PCL 25/75	13.4 ± 0.4 ^c	10 ± 2 ^c	0.34 ± 0.04 ^d
PCL	16.2 ± 0.3 ^d	510 ± 52 ^d	0.38 ± 0.03 ^d

Values in a same column sharing a common superscript letter are not significantly different (Tukey's test; P < 0.05; n = 6).

Mechanical properties of the neat polymers and their blends were evaluated by tensile tests. Typical stress–strain curves are shown in Fig. 7, and the values for the tensile strength (reported as maximum tensile strength), elastic modulus and elongation at break are presented in Table 4.

In Fig. 7 the different mechanical behaviors of pure polymers can be observed. PCL is a ductile polymer with great elongation until break, in the range of 500% as described in literature (Labet & Thielemans, 2009; Nampoothiri, Nair, & John, 2010). UTPS presented maximum values of tensile and elastic modulus (around 0.15 MPa and 2 GPa, respectively) lower than the PCL, and elongation at break of around 15%. The use of urea as a plasticizer of the starch resulted in a more rigid and resistant UTPS than a TPS plasticized with the same proportions of glycerol (Campos et al., 2013). And yet, the mechanical properties of UTPS in this study are within the range of values reported in the literature, in which plasticizers containing amide groups were used to obtain TPS, including urea (Zullo & Iannace, 2009).

It can be observed that for the UTPS/PCL blends (Fig. 7) there was a decrease in ductility and tensile strength of the material with the increase of UTPS content, whereas with the increase of PCL content, there was an increase of flexibility of the material.

Table 4 shows the obtained values for the maximum stress (σ_{max}), elastic modulus (E) and elongation at break (ε) of neat UTPS and PCL and their blends.

From results in Table 4, it can be observed that the UTPS and PCL have significant differences in the three tested mechanical properties, as already indicated by the stress–strain curves of the materials (Fig. 7). Regarding the blends UTPS/PCL, there was an increase in the elastic modulus from 0.14 GPa of neat UTPS, to 0.70 GPa with 25 wt% PCL (UTPS/PCL 75/25). Indicating that, depending on the application, it is possible to increase the mechanical properties of UTPS with small amounts of PCL. On the other hand, when 25 wt% of UTPS is added to PCL (UTPS/PCL 25/75) no significant reduction on maximum tensile strength (σ_{max}) and elastic modulus (E) of the blend was observed, if compared to neat PCL, but a substantial loss on the elongation at break (ε) was noted. The blend UTPS/PCL 25/75 presented higher values of maximum tensile strength and elongation at break than blends richer in UTPS. With the increase in UTPS content from 25 wt% (UTPS/PCL 25/75) to 50 wt% (UTPS/PCL 50/50), both maximum tensile strength and elongation at break were reduced. On the other hand, with the increase of UTPS content from 50 (UTPS/PCL 50/50) to 75 wt% (UTPS/PCL 75/25), there

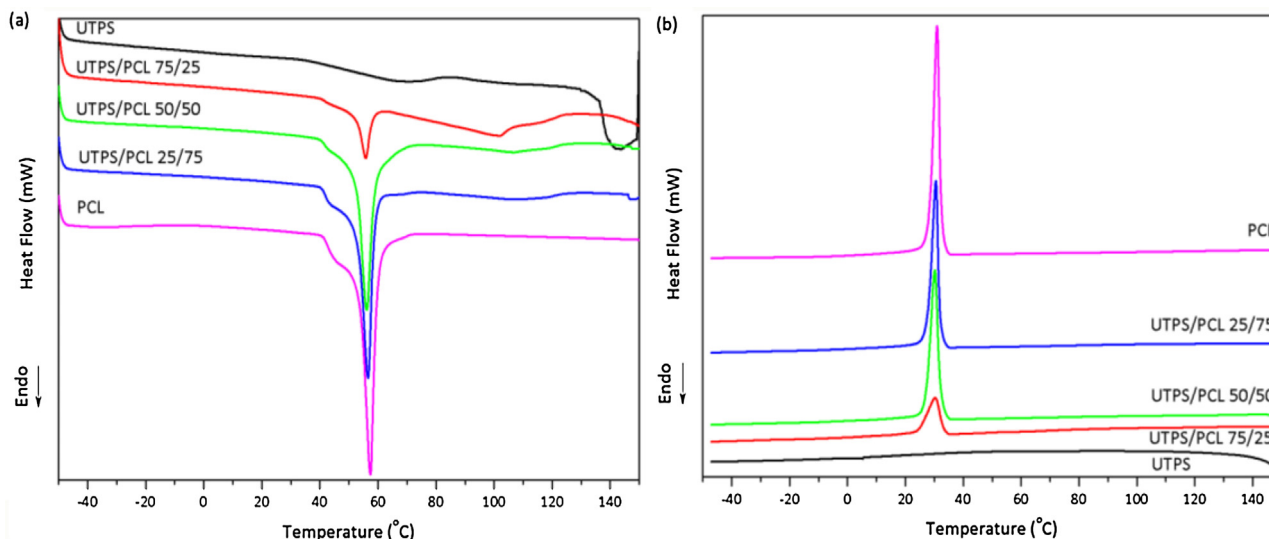


Fig. 6. DSC curves of (a) heating and (b) cooling, for neat PCL and UTPS and UTPS/PCL blends (N_2 atmosphere at $10^\circ C/min$).

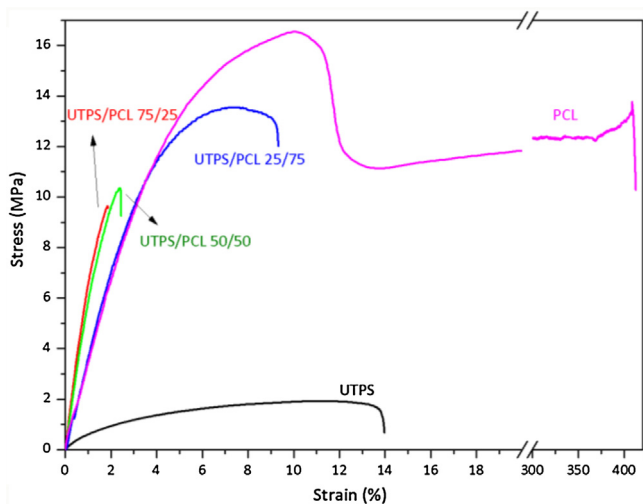


Fig. 7. Stress-strain curves of neat UTPS and PCL and their blends.

were not observed significant changes in these properties, but an increase of around 40% in elastic modulus (E) was observed.

4. Conclusions

UTPS and PCL blends were processed by extrusion and characterized by capillary rheometry, showing that neat UTPS presented higher viscosity values, and the viscosity ratio (η_{UTPS}/η_{PCL}) was in the range of 1.5 up to 3.1, with reduced values at higher shear rates. Each material exhibited a pseudoplastic behavior, as occurred a reduction of viscosity with the increase of the shear strain. UTPS presented higher values of the consistency factor, K , than those from PCL and UTPS-PCL blends, and from determined pseudoplastic indexes, n , both neat UTPS and PCL are more shear thinning than UTPS-PCL blends. SEM images confirmed the UTPS-PCL immiscibility and show the dependence of morphology on the UTPS content. At low UTPS content, it is well dispersed and distributed on a continuous PCL matrix. As the UTPS content increased (up to 50 wt%) the coalescence phenomenon of UTPS droplets took place, resulting in a co-continuous morphology when UTPS content was 75 wt%. Thermogravimetric analysis showed that the addition of PCL in UTPS increased the thermal stability of UTPS, because PCL presents

greater thermal stability than UTPS. Through DSC analysis it was noticed that the UTPS acted as a nucleating agent for the PCL. The poor mechanical properties of UTPS, such as maximum tensile strength and elastic modulus, increased with the increase of PCL in the blends, indicating that, depending on the application, it is possible to increase the mechanical properties of UTPS with small amounts of PCL.

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References

- Aoyagi, Y., Yamashita, K., & Doi, Y. (2002). Thermal degradation of poly[(R)-3-hydroxybutyrate], poly[ϵ -caprolactone], and poly[(S)-lactide]. *Polymer Degradation and Stability*, 76, 53–59.
- Averous, L., Moro, L., Dole, P., & Fringant, C. (2000). Properties of thermoplastic blends: Starch-polycaprolactone. *Polymer*, 41, 4157–4167.
- Bernhard, A. M., Peitz, D., Elsener, M., Wokaun, A., & Kröcher, O. (2012). Hydrolysis and thermolysis of urea and its decomposition byproducts biuret, cyanuric acid and melamine over anatase TiO_2 . *Applied Catalysis B: Environmental*, 115–116, 129–137.
- Boo-Young, S., Sang-Li, L., Shin, Y. S., Balakrishnan, S., & Narayan, R. (2004). Rheological, mechanical and biodegradation studies on blends of thermoplastic starch and polycaprolactone. *Polymer Engineering and Science*, 44, 1429–1438.
- Campos, A., Teodoro, K. B. R., Teixeira, E. M., Correa, A. C., Marconcini, J. M., Wood, D. F., et al. (2013). Properties of thermoplastic starch and TPS/Polycaprolactone blend reinforced with sisal whiskers using extrusion processing. *Polymer Engineering and Science*, 53(4), 800–808.
- Carmona, V. B., de Campos, A., Marconcini, J. M., & Mattoso, L. H. C. (2014). Kinetics of thermal degradation applied to biocomposites with TPS, PCL and sisal fibers by non-isothermal procedures. *Journal of Thermal Analysis and Calorimetry*, 115, 153–160.
- Carmona, V. B., Correa, A. C., Marconcini, J. M., & Mattoso, L. H. C. (2015). Properties of a biodegradable ternary blend of thermoplastic starch (TPS), poly(ϵ -caprolactone) (PCL) and poly(lactic acid) (PLA). *Journal of Polymers and the Environment*, 23, 83–89.
- Chandra, R., & Rustgi, R. (1998). Biodegradable materials. *Progress in Polymer Science*, 23, 1273–1335.
- Crescenzi, V., Manzini, G., Calzolari, G., & Borri, C. (1972). Thermodynamics of fusion of poly- β -propiolactone and poly- ϵ -caprolactone. Comparative analysis of the melting of aliphatic polylactone and polyester chains. *European Polymer Journal*, 8, 449–463.
- Cyras, V. P., Martucci, J. F., Iannace, S., & Vazquez, A. (2002). Influence of the fiber content and the processing conditions on the flexural creep behavior of sisal-PCL-starch composites. *Journal of Thermoplastic Composite Materials*, 15, 253–265.
- Da Silva, A. L. N., Rocha, M. C., Coutinho, F., Bretas, R., & Scuracchio, C. (2000). Rheological, mechanical, thermal and morphological properties of

- polypropylene/ethylene-octene copolymer blends. *Journal of Applied Polymer Science*, 75, 692–704.
- Darwis, D., Mitomo, H., Enjoji, T., Yoshii, F., & Makuuchi, K. (1998). Enzymatic degradation of radiation crosslinked poly (ϵ -caprolactone). *Polymer Degradation and Stability*, 62, 259–265.
- Dubois, P., Krishnan, M., & Narayan, R. (1999). Aliphatic polyester-grafted starch-like polysaccharides by ring-opening polymerization. *Polymer*, 40, 3091–3100.
- Ferry, J. D. (1980). *Viscoelastic properties of polymers*. New York: Wiley.
- Griffith, G. (2000). Polymeric biomaterials. *Acta Materialia*, 48(1), 263–277.
- Hu, J., Zhang, Y., Wang, J., & Zhou, Y. (2014). Glycerol affects root development through regulation of multiple pathways in Arabidopsis. *Public Library of Science*, 9(1), 1–18. <http://dx.doi.org/10.1371/journal.pone.0086269>
- Labet, M., & Thielemans, W. (2009). Synthesis of polycaprolactone: A review. *Chemical Society Reviews*, 38, 3484–3504.
- Li, G., & Favis, B. D. (2010). Morphology development and interfacial interactions in polycaprolactone/thermoplastic-starch blends. *Macromolecular Chemistry and Physics*, 211, 321–333.
- Ma, X., & Yu, J. (2004). The plasticizers containing amide groups for thermoplastic starch. *Carbohydrate Polymers*, 57, 197–203.
- Ma, X. F., Yu, J. G., & Ma, Y. B. (2005). Urea and formamide as a mixed plasticizer for thermoplastic wheat flour. *Carbohydrate Polymers*, 60, 111–116.
- Nampoothiri, K. M., Nair, N. R., & John, R. P. (2010). An overview of the recent developments on polylactide (PLA) research. *Bioresource Technology*, 101, 8493–8501.
- Parker, R., & Ring, S. G. (2005). *Polysaccharides, structural diversity and functional versatility*. New York: Marcel Dekker Inc.
- Rohn, C. L. (1995). *Analytical polymer rheology: Structure-processing-properties relationship*. New York: Hanser.
- Schaber, P. M., Colson, J., Higgins, S., Thielen, D., Anspach, B., & Brauer, J. (2004). Thermal decomposition (pyrolysis) of urea in an open reaction vessel. *Thermochimica Acta*, 424, 131–142.
- Schreiber, H. P., & Olguin, A. (1983). Aspects of dispersion and flow in thermoplastic-elastomer blends. *Polymer Engineering and Science*, 3, 129–134.
- Shi, Q. F., Chen, C., Gao, L., Jiao, L., Xu, H. Y., & Guo, W. H. (2011). Physical and degradation properties of binary or ternary blends composed of poly (lactic acid), thermoplastic starch and GMA grafted POE. *Polymer Degradation and Stability*, 96, 175–182.
- Shin, B. Y., Narayan, R., Lee, S. I., & Lee, T. J. (2008). Morphology and rheological properties of blends of chemically modified thermoplastic starch and polycaprolactone. *Polymer Engineering and Science*, 48, 2126–2133.
- Sin, L. T., Rahman, W. A. W. A., Rahmat, A. R., & Mokhtar, M. (2011). Determination of thermal stability and activation energy of polyvinyl alcohol-cassava starch blends. *Carbohydrate Polymers*, 83, 303–305.
- van Soest, J. J., & Vliegenthart, J. F. (1997). Crystallinity in starch plastics: Consequences for material properties. *Trends in Biotechnology*, 15, 208–213.
- Vertuccio, L., Gorrasi, G., Sorrentino, A., & Vittoria, V. (2009). Nano clay reinforced PCL/starch blends obtained by high energy ball milling. *Carbohydrate Polymers*, 75, 172.
- Wang, N., Yu, J. G., Chang, P. R., & Ma, X. (2008). Influence of formamide and water on the properties of thermoplastic starch/poly(lactic acid) blends. *Carbohydrate Polymers*, 71, 109–118.
- Willet, J. L., Millardt, M. M., & Jasberg, B. K. (1997). Extrusion of waxy maize starch: Melt rheology and molecular weight degradation of amylopectin. *Polymer*, 38, 5983–5989.
- Wu, S. (1987). Formation of dispersed phase in incompatible polymer blends: Interfacial and rheological effects. *Polymer Engineering and Science*, 27, 335–343.
- You, L., Dean, K., & Li, L. (2006). Polymer blends and composites from renewable resources. *Progress in Polymer Science*, 31, 576–602.
- Zullo, R., & Iannace, S. (2009). The effects of different starch sources and plasticizers on film blowing of thermoplastic starch: Correlation among process, elongational properties and macromolecular structure. *Carbohydrate Polymers*, 77, 376–383.