

Biodegradable Blends of Thermoplastic Waxy Starch and Poly(ϵ -caprolactone) Obtained by High Shear Extrusion: Rheological, Mechanical, Morphological and Thermal Properties

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Abstract

The aim of this work was to develop polymer blends of plasticized thermoplastic waxy starch (TPS) and poly(ϵ -caprolactone) (PCL) using the largest amount of TPS possible to obtain a biodegradable material motivated by sustainability issues and to replace petrochemical-based polymers with alternatives based on biopolymers. Addition of TPS to other polymers has been used to obtain cheaper and increasingly biodegradable final products. However, TPS presents limited mechanical properties, and mixing with other polymers such as PCL is necessary to overcome these limitations and improve its processability. TPS was processed by extrusion and thermo-compression using 30 wt% glycerol. The blends were suitably processed by extrusion and further injected. The TPS/PCL blends were studied by varying the amount of PCL in a range of 10 wt% in increasing order of addition. Thermal analysis showed that introducing PCL in TPS increased T_{onset} because of the higher thermal stability of the former, and that the obtained blends presented a behavior intermediate to that of neat polymers.

1. Introduction

In the past decades, in addition to being used in the food industry, starch has been applied to develop thermoplastic starch (TPS) [1]. TPS is obtained when granular starch is subjected to shear–pressure–temperature and, in the presence of plasticizers (e.g., glycerol), is melted and processed using conventional techniques such as extrusion and injection [2]. The incorporation of TPS into biodegradable polymer blends has increased due to environmental requirements for the safe and effective disposal of polymers [3, 4]. TPS presents higher biodegradable potential and bioavailability and lower cost, and has stood out in applications such as packaging, disposable materials, coatings, tubes, and planting vases [2, 5–7]. In contrast, TPS presents poor mechanical properties and hydrophilic characteristics that limit its applications, exhibiting retrogradation behavior at room temperature [8].

To overcome this issue, TPS can be blended with other biodegradable polymers, e.g., poly(lactic acid) (PLA), poly(ϵ -caprolactone) (PCL) and poly(butylene-adipate-co-terephthalate) (PBAT), to improve its properties and obtain final products that are more economically viable [9, 10]. Mixing with PCL is a promising way to improve the thermomechanical and hydrophilic characteristics, biodegradability resistance, and processability properties of TPS [2, 11, 12]. PCL is a semi-crystalline, biodegradable polyester that presents higher flexibility, lower melting point ($T_m \sim 60^\circ\text{C}$), and good compatibility with many other polymers, thus having a wide range of applications [1, 12, 13]. According to the literature, the TPS/PCL blend presents an ideal combination of cost and properties [1].

It is important to note that native starch, which can be obtained from a wide variety of plants such as corn, wheat, rice and potatoes, has a semi-crystalline, granular structure [12]. The micro-scale granules contain crystalline regions of amylopectin branch units and amorphous regions of amylose [14, 15]. Starches can be evaluated according to mass fraction of amylose and amylopectin, which have an influence on TPS final properties. Most regular starches present amylose content in the range of 20–30%, depending on their botanical origin. There are also modified starches, high amylose (> 40%) starches, and

waxy starches that consist almost exclusively of amylopectin [4, 5]. In this context, TPS has been little explored in relation to its main constituents (amylose and amylopectin). In this case, waxy starch presents an advantage, because it exhibits less tendency to retrogradation and plasticizer exudation compared with regular starch [2, 16, 17], with direct amylopectin crystallization effects on TPS properties [18, 19].

Therefore, this study aims to contribute to a better understanding about TPS obtained from waxy starch blended with PCL by high shear extrusion. Considering our previous work on TPS from waxy starch [20], we proposed to use the least amount of PCL to improve TPS processability and obtain an ideal combination of cost and properties.

2. Experimental

2.1 Materials

The following materials were used: waxy corn starch (Amidex 4001® from Ingredion) with approximately 100 wt% amylopectin; glycerol from Nitrogenius; stearic acid ($M_W = 284.48$ g/mol) from Vetec 99.5%; citric acid ($M_W = 192.13$ g/mol) from Chemco 99.5%, and poly(ϵ -caprolactone) (PCL) CAPA 6500® (Perstorp, UK).

2.2 Preparation of the TPS/PCL blend

Waxy starch was mixed with 30 wt% glycerol, followed by addition of citric acid (1 wt%) and stearic acid (1 wt%) as processing agents. This blend was plasticized on a higher shear rate co-rotating twin-screw extruder at 200 rpm (Coperion 18 mm and $L/D = 40$). The temperature profile of the feed channel to the matrix was 90, 95, 100, 105, 110, 115 and 120°C. TPS/PCL pellets were blended on a double-screw extruder at 300 rpm with the following temperature profile from the feeding zone to the dosing zone: 90, 95, 100, 105, 110, 120 and 130°C. A scan of the blends was performed varying the amount of PCL in a range of 10 wt%.

After extruding, the TPS/PCL blends were molded in type I -- ASTM D-638 tensile specimens on an injection molding equipment (Arburg Allrounder 270S). Injection pressure of 2000 bar, mold temperature of 25°C, and temperature profile of 70, 110, 120, 120 and 110°C were applied in the five heating zones.

Due to the high viscosity of neat TPS and the TPS/PCL 90/10 blend, it was necessary to produce the specimens by pressing the ribbons obtained from a single screw extruder (AX Plastic) (rotation speed was 100 rpm and the heating zones were kept at 130°C). In this case, the specimens were obtained from type IV - ASTM D638 model with pressing of 5.0 tons and a final pressing of 10.0 tons at 130°C.

2.3 Rheological properties

Neat TPS, neat PCL, and the TPS/PCL blends were pelletized and tested on a Rheograph 2S capillary rheometer (Göttfert). The capillary had a 1 mm radius and L/D was 30. The pellets were placed into the

barrel and packed using a plunger until the extrudate appeared through the capillary exit. The analyses were carried out at temperatures close to the processing temperatures (90–120°C) by extrusion and injection of the materials. 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. The shear rates ($\dot{\gamma}$) and viscosity values (η) were determined using the Rabinowitsch correction, assisted by the WinRheo II software.

2.4 Mechanical properties

Uniaxial tensile tests of the specimens were performed in a universal testing machine (EMIC®) according to ASTM D 638 at a speed of 5 mm/min with a 500 kgf load cell at 25°C (± 2°C) and relative humidity (RH) of 52% (± 3%) [21]. Young's modulus (E), tensile strength (σ_{max}), and strain at break (ϵ) were evaluated. The analysis of variance (ANOVA) and Tukey's test at 5% significance using OriginPro (version 9.0) were performed.

2.5 Morphological Analysis

The cross-section of the specimens obtained by cryogenic fracturing was analyzed by scanning electron microscopy (SEM) (JEOL®, model JMS 6510) using an accelerating voltage of 10 kV. The samples were mounted on copper pin stubs and then coated with gold. In order to selectively dissolve the TPS phase in the TPS/PCL blends, the samples were treated with hydrochloric acid (HCl 3 N) for 2 h.

2.6 Thermal Analysis

Thermal stability of the blends was evaluated using a TGA Q500 thermogravimetric analyzer (TA Instrument, USA). The analyses were carried out under synthetic air (60 mL/min) and inert gas (40 mL/min) atmospheres from room temperature to 600°C at a heating rate of 10°C/min. The onset temperature (T_{onset}) was determined from the TGA curve as the intersection between the line extrapolated from the first thermal event and the tangent to the curve at the temperature of the on maximum decomposition rate of the material.

Differential scanning calorimetry (DSC) measurements of the neat PCL and polymer blends were performed on a DSC Q-100 (TA Instruments, USA). The tests were carried out under nitrogen atmosphere from -75 to 150°C at a heating rate of 10°C/min, followed by cooling to -75°C at a rate of 10°C/min. Changes of phase or state and the corresponding melting enthalpies were then determined from the melting peaks of DSC thermograms. The crystallinity index (C_c) was determined using the following equation [11, 22].

$$CI(\%) = \frac{\Delta H_f}{\Delta H_f^0 \times W} \times 100 \text{ Eq. 1}$$

where: ΔH_f is the fusion enthalpy determined by the DSC measurement, ΔH_f^0 is the theoretical enthalpy of the completely crystalline polymer, which is 136 J/g for PCL [23], and w corresponds to the amount of PCL in the blend.

3. Results And Discussion

3.1 Rheological properties

The rheological behavior of the neat polymers and polymer blends was analyzed by capillary rheometry. Figure 1 shows the viscosity (η) vs. shear rate ($\dot{\gamma}$) curves of all blends.

It can be observed that the neat polymers and the TPS/PCL blends showed pseudoplastic behavior, with a reduction in viscosity and an increase in shear rate. It was not possible to measure viscosity for the neat TPS at shear rates $> 2,000 \text{ s}^{-1}$ due to equipment overload caused by the high TPS viscosity. This behavior indicates that TPS injection is not possible, which was also verified in processing, and justifies the need to manufacture blends that allow TPS fluidity.

Addition of PCL to TPS caused a decrease in the viscosity of the blends, resulting in blends less viscous than the neat TPS and with a behavior intermediate to that of neat polymers. This fact provides an improvement in TPS processability, facilitating its fluidity.

Corradini et al. [19] studied the rheological behavior of TPS obtained from regular starch and waxy starch in an internal mixer and found that the torque for regular starch remained constant at 12 Nm after 2 min of processing, while the torque for waxy starch remained constant at 5 Nm after that period. The native starch, with lower amylopectin content, presented higher viscosity during processing, which was attributed to linear amylose chains. Similar behavior has also been observed in starch pastes solubilized in water, where waxy starch showed a smaller viscosity value than that of regular starch, and resisted mechanical agitation 56% less than regular corn starch gel [24].

Although waxy starch has a higher molar mass, its viscosity is lower than that of regular starch, since amylopectin, its major constituent, is a highly branched macromolecule formed by short chains that reduces its ability to form tangles [19]. In addition, the amylose content present in regular starches results in higher viscosity and greater elastic flow behavior in the melted state [25].

Understanding the differences in the structure of the types of starches and their influence on the rheological behavior of TPS is important to ensure better fluidity of starch in the TPS extrusion and injection processes. The use of waxy starch results in better performance of the TPS blends.

3.2 Mechanical properties

Mechanical properties of the neat polymers and their blends were evaluated by tensile tests. Typical stress–strain curves are shown in **Fig. 2**.

The values for maximum tensile strength (σ_{max}), fracture strain (ϵ), Young's modulus (E) are presented in Table 1.

Table 1

Mechanical properties of neat TPS and PCL and their polymer blends in ascending order of PCL content: tensile strength (σ_{max}), fracture strain (ϵ) and Young's modulus (E)

Samples	σ_{max} (MPa)	ϵ (%)	E (MPa)
TPS	(1.3 ± 0.1) ^a	(11.9 ± 1.8) ^a	(81 ± 1) ^a
TPS/PCL 90/10	(1.2 ± 0.2) ^a	(7.6 ± 1.9) ^a	(81 ± 3) ^a
TPS/PCL 80/20	(2.0 ± 0.1) ^a	(22.7 ± 4.0) ^a	(90 ± 2) ^a
TPS/PCL 70/30	(3.6 ± 0.2) ^{a,b}	(13.3 ± 1.6) ^a	(146 ± 1) ^b
TPS/PCL 60/40	(5.3 ± 0.2) ^{b,c}	(9.5 ± 0.9) ^a	(175 ± 8) ^c
TPS/PCL 50/50	(6.4 ± 0.2) ^c	(9.0 ± 0.7) ^a	(207 ± 9) ^d
TPS/PCL 40/60	(7.5 ± 0.1) ^{c,d}	(57.6 ± 16.7) ^b	(241 ± 13) ^e
TPS/PCL 30/70	(8.8 ± 0.1) ^d	(113.5 ± 15.6) ^c	(311 ± 22) ^f
TPS/PCL 20/80	(14.5 ± 1.4) ^e	(517.3 ± 17.5) ^d	(309 ± 19) ^f
TPS/PCL 10/90	(17.5 ± 1.3) ^f	> 550	(384 ± 12) ^g
PCL	(19.7 ± 1.3) ^g	> 550	(374 ± 12) ^g
Difference letter on the same column means the difference of mean values is statistically significant by Tukey's test ($p < 0.05$).			

Neat PCL exhibited a tensile strength of approximately 20 MPa and a very ductile behavior with great fracture strain ($\epsilon = > 500\%$), as described in the literature [11, 26]. In contrast, neat TPS presented poor mechanical properties, reaching 1.3 MPa. When TPS and PCL were blended, there was a pronounced increase in mechanical properties compared with those of neat TPS. In general, the gain on mechanical properties of the blends over neat TPS was attributed to neat PCL. In this case, TPS acted simply as a filler that does not possess desirable mechanical properties in itself [3].

A study that compared native and waxy starches showed that the TPS from waxy starch exhibited fracture strain 3 times greater than that of native starch, while E and σ_{max} were higher for the native starch [19], justifying the results obtained for TPS in this study. Furthermore, all the blends analyzed here presented strength resistance comparable to that of low-density polyethylene [3, 27], which suggests that these TPS/PCL blends can be applied to packaging.

For the TPS/PCL blends, there was an increase in E with increasing PCL content, and a behavior similar to maximum strength was found, in which the samples presented Young's modulus values intermediate to that of neat polymers. In this case, E values of TPS and PCL were 80 and 370 MPa, respectively. This

fact indicates that it is possible to increase the mechanical properties of TPS with addition of small amounts of PCL. These results for E were superior to those reported in a previous study that obtained TPS from regular starch [3]. Therefore, TPS/PCL blends obtained from waxy starch tend to present a higher E value than those of blends obtained from regular starch.

Neat TPS showed $\epsilon = 12\%$, while neat PCL and the TPS/PCL 90/10 blend endured rupture strain above the equipment limit of 650%. As expected, due to the very ductile behavior of PCL, the specimens endured higher deformation rates with increasing PCL concentration. A contrary behavior was observed for the TPS/PCL blends obtained from regular starch plasticized with 35% glycerol, where the fracture strain decreased inversely with increasing the PCL content. This was attributed to phase separation between PCL and TPS, resulting from the non-miscibility between the polymers [13].

Figure 3 presents the E , ϵ , and σ_{max} values by tensile tests as a function of TPS content in the TPS/PCL blends.

Variation in the values of E showed a linear trend according to TPS mass fraction variation (Fig. 3a). In this case, a synergistic behavior was observed only for the TPS/PCL 10/90 blend, whereas the blends containing 20 and 30% TPS presented additivity behavior and the other blends showed incompatibility behavior [28, 29]. According to the photomicrographs for the sample containing 10% TPS, in which synergism occurs, the starch phases are distributed more evenly and are well dispersed throughout the PCL matrix. For the other samples from 30% TPS, the starch phases are no longer homogeneous with each other and do not present a regular dispersion throughout the PCL matrix.

For all blends, there was an incompatibility behavior, since the fracture strain (Fig. 3b) and maximum resistance (Fig. 3c) values were lower than those of neat PCL [28, 29]. According to the photomicrographs, blends with up to 20% TPS presented the most homogeneous and dispersed starch phases compared with those of samples starting at 30% TPS, resulting in a drop in fracture strain and maximum strength between samples with 20 and 30% TPS. The highest crystallinity index for the PCL phase in the TPS/PCL 30/70 blend may have prevented a further drop in mechanical properties.

3.3 Morphological analysis

Considering that TPS and PCL were melt blended in a higher shear twin-screw extruder varying the amount of PCL in a range of 10 wt% in increasing order of addition, **Fig. 4** shows the SEM photomicrographs of the cryogenic fracture surfaces of starch granules, neat polymers, and TPS/PCL blends in ascending order of PCL addition.

The starch granules presented polyhedral form and dimensions $< 10 \mu\text{m}$ (Fig. 4a). Neat TPS showed a continuous matrix of plasticized starch (Fig. 4b). The plasticization process involves the loss of the crystalline character as a result of the disruption of starch granular structure [1]. It is possible to observe the presence of some pores and lumps, which can be attributed to the presence of water and air bubbles or starch granules that did not have the original granule structures completely ruptured. Normally, in plasticization of starch in an extruder using glycerol, the plasticizer breaks the hydrogen bonds and

disrupts the granular crystalline organization [3]. Neat PCL (Fig. 4l) showed a continuous morphology characteristic of typical cryogenic fracture for a low glass temperature (T_g) polymer [11].

The photomicrographs evidence a homogeneous PCL/TPS distribution in the blends, which resulted in an immiscible blend leading to phase separation [8]. In the blend containing 90% TPS, it was not possible to perform the acid chemical treatment to remove the TPS phase (Fig. 4c). The high concentration of TPS and the thin thickness of the sample made the treatment unfeasible, causing most of the sample to solubilize. Note that the morphology obtained was in the form of drops, showing the PCL phase dispersed in the TPS matrix.

In blends with 80 to 60% TPS, co-continuous morphology was formed (Fig. 4d-f). The coalescence between its particles occurred more intensely as the TPS concentration was increased. The high degree of co-continuity in these blends may be explained by the lower viscosity of the PCL phase compared with that of the TPS phase. Therefore, even if PCL is a minor component, it tends to form a continuous phase [25]. For these blends, there was also a tendency for the TPS phase be concentrated in the middle of the specimens because of the probably higher viscosity of TPS. This TPS encapsulation can make the blend more resistant to any type of degradation [1].

With the decrease in TPS content, there was a phase change that allowed the formation of droplet-shape morphology, showing a decrease in the particle size of the TPS dispersed in the continuous PCL matrix (Fig. 4g-k). Regarding PCL concentration, it is important to note that with increasing its concentration, the blends showed a very dispersed morphology with the PCL matrix and finer TPS domains guaranteed by the higher shear extrusion [25].

The viscosity ratio between the polymers in immiscible blends is an important parameter in the morphological formation and, consequently, in their physical properties [11]. The TPS/PCL viscosity ratio at 1000 s^{-1} calculated when PCL was in the rich phase in the blend was 4.94, whereas the PCL/TPS viscosity ratio calculated at same shear rate when TPS was in the rich phase of the blend was 0.20. These values indicate that only the PCL droplets break in the TPS matrix, but the opposite does not occur, which means that the TPS droplets do not break in the PCL matrix, as observed in the SEM photomicrographs.

3.4 Thermal Analysis

Thermal stability was determined by TGA. Figure 5 presents the thermal degradation profile and derivative thermogravimetric (DTG) curves of the neat polymers and their respective TPS/PCL blends.

The T_{onset} values measured from the TGA curves are summarized in Table 2.

Table 2
 T_{onset} of neat TPS and PCL
 polymers and TPS/PCL blends

Samples	T_{onset} (°C)
Neat TPS	281
TPS/PCL 90/10	272
TPS/PCL 80/20	274
TPS/PCL 70/30	268
TPS/PCL 60/40	281
TPS/PCL 50/50	280
TPS/PCL 40/60	291
TPS/PCL 30/70	276
TPS/PCL 20/80	276
TPS/PCL 10/90	322
Neat PCL	350

The degradation temperatures for neat TPS and neat PCL were 280 and 350°C, respectively. Therefore, PCL has greater thermal stability than TPS, as illustrated in Fig. 5a. The TPS weight loss up to 140°C is due to water and other volatile compounds. The shoulder between 200 and 250°C on the DTG curve of neat TPS refers to the evaporation of glycerol. The thermal degradation of TPS and glycerol started at around 250–350°C, mainly due to dehydration of the hydroxyl groups and the subsequent formation of unsaturated and aliphatic low molecular weight carbon species [2, 11, 30]. The peaks above 400°C on the DTG curve for all samples are due to the carbonization in oxidative atmosphere (Fig. 5b) [31].

Most of the blends showed intermediate thermal stability behaviors compared with those of the neat polymers. With increasing the TPS amount, the blends presented a behavior similar to that of neat TPS because of its lower thermal stability. On the DTG curves, the peak that refers to TPS decomposition decreases with increasing the PCL content in the blend. Consequently, the peak that refers to PCL decomposition increases its intensity with increasing the PCL amount in blend, approaching the behavior of neat PCL. An increase of 10°C in the thermal stability of the TPS/PCL 40/60 blend was observed in relation to the other blends. This behavior can be explained by the coalescence exhibited by this blend in the SEM photomicrographs.

Differential scanning calorimetry was used to identify the main transition temperatures correlated to the mechanical properties of the blends. The glass (T_g), melting (T_m) and crystallization (T_c) temperatures, enthalpies of fusion (ΔH_m), and crystallinity indexes (C_i) related to PCL were measured for each blend

Fig. 6 shows the DSC curves for the first heating and cooling flows of the neat TPS and PCL polymers and the TPS/PCL blends.

Table 3 presents the data for transition temperatures and C_i calculated from ΔH_m .

Table 3
Glass transition temperature (T_g), melting temperature (T_m), enthalpy of fusion (ΔH_m), crystallinity index (C_i), and crystallization temperature (T_c) values for the neat TPS and PCL polymers and their blends

Samples	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_m (J/g)	C_i (%)
TPS/PCL 90/10	-60.2	31.6	59.6	7.0	52
TPS/PCL 80/20	-60.2	28.8	61.8	15.1	56
TPS/PCL 70/30	-59.5	29.7	61.4	20.8	51
TPS/PCL 60/40	-60.8	28.5	62.1	30.3	56
TPS/PCL 50/50	-62.6	31.1	62.9	39.4	58
TPS/PCL 40/60	-61.9	30.1	63.5	46.9	58
TPS/PCL 30/70	-60.1	30.0	63.0	60.1	63
TPS/PCL 20/80	-60.0	29.3	64.7	64.1	59
TPS/PCL 10/90	-59.8	30.0	61.0	71.0	58
Neat PCL	-59.4	31.0	58.4	72.6	53

The neat TPS curve did not show any thermal event because TPS is an amorphous material due to the plasticization process that destroys the starch grains and disrupts the crystalline orders [15]. In contrast, neat PCL presented higher crystallinity index (53%), showing the T_m around 58°C, corresponding to crystals fusion (Fig. 6a) [3, 8, 11, 26].

Blending of TPS with PCL caused a slight increase of up to 5°C on the T_m of the TPS/PCL 40/60 blend, as observed in the dotted lines of the DSC diagrams. These results are in accordance with the coalescence TPS phases in the PCL matrix observed in the SEM photomicrographs, suggesting that there is higher molecular interaction in this blend that affects the thermal stability and T_m of the blend. The peak corresponding to T_m is attenuated with increasing the TPS content in the blend as a result of the increased concentration of amorphous material, being the peak area also in accordance with PCL content [1].

It should be noted that the T_g values of these materials were not evident. This fact is possibly related to the domain of the crystalline phase over the amorphous phase [8]. The T_g of the neat PCL was obtained with a subtle inflection of the curve around 60°C, providing PCL-based materials with high flexibility at

room temperature [1, 26]. Wide variations in T_g did not occur with addition of TPS to the TPS/PCL blends. In this way, TPS and PCL can be blended without affecting this parameter.

The T_c related to PCL crystallization is observed at around 30°C, as reported in the literature (Fig. 6b) [11]. The blends presented T_c close to that of the neat PCL and did not interfere with PCL crystallization when a controlled cooling rate was applied. The crystallization peak was also attenuated by increasing the TPS fraction in blends.

The C_f related to PCL was calculated according to the Eq. 1 presented in the DSC assay methodology. The C_f of PCL represents the crystalline fraction of the material related to the thermal processing history. Neat PCL presented 53% crystallinity, as reported in the literature [11, 26]. PCL is a semi-crystalline polymer, and the presence of other substances and processing can induce or restrict their crystallinity [2]. When PCL was blended with TPS, it became slightly more crystalline in most of the blends. Incorporation of TPS into the PCL matrix induced its crystallization, reaching the maximum of 63% for the TPS/PCL 30/70 blend, suggesting that TPS acted as a nucleating agent. At the other concentrations, the PCL crystallinity remained similar to that of the neat PCL. Higher ΔH_m values have been correlated with the crystalline fraction of polymers. Although there was a decrease in the ΔH_m of the blends with the increase in TPS content, proportionally, there was also a decrease in the PCL content, which was responsible for the crystalline portion of the blends [11].

4. Conclusions

Waxy starch was plasticized using 30 wt% glycerol as plasticizer in a twin-screw extruder. TPS/PCL were processed by higher shear rate extrusion. Low concentrations of PCL were sufficient to improve the processability and guarantee the viability of the TPS injection process. Blends with concentrations from 20% PCL were well processed by higher shear rate extrusion and able to be injected, producing homogeneous materials. Capillary rheometry showed that neat TPS had higher viscosity values than neat PCL, affecting the processability of blends with higher TPS content. The mechanical properties of the blends were improved with PCL addition, indicating that it is possible to enhance the mechanical properties of TPS with addition of small amounts of PCL. SEM images confirmed the TPS/PCL immiscibility and show the dependence of morphology on TPS content. Thermogravimetric analysis showed that the addition of PCL to TPS increased the thermal stability of the blends because of the greater thermal stability of PCL. Lastly, the DSC analyses showed that TPS acted as a nucleating agent for PCL, increasing the crystallinity index, and may affect the mechanical properties of the blends.

Declarations

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Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Data availability

The datasets generated during the current study are available from the corresponding author on reasonable request.

Conflict of interest

The authors declare that they have no competing interests.

References

1. Ninago MD, López OV, Lencina MMS et al (2015) Enhancement of thermoplastic starch final properties by blending with poly(ϵ -caprolactone). *Carbohydr Polym* 134:205–212. <https://doi.org/10.1016/j.carbpol.2015.08.007>
2. Carmona VB, Corrêa AC, Marconcini JM, Mattoso LHC (2015) Properties of a Biodegradable Ternary Blend of Thermoplastic Starch (TPS), Poly(ϵ -Caprolactone) (PCL) and Poly(Lactic Acid) (PLA). *J Polym Environ* 23:83–89. <https://doi.org/10.1007/s10924-014-0666-7>
3. Shin BY, Lee S, Il, Shin YS et al (2004) Rheological, mechanical and biodegradation studies on blends of thermoplastic starch and polycaprolactone. *Polym Eng Sci* 44:1429–1438. <https://doi.org/10.1002/pen.20139>
4. Van Soest JJG, Vliegthart JFG (1997) Crystallinity in starch plastics: Consequences for material properties. *Trends Biotechnol* 15:208–213. [https://doi.org/10.1016/S0167-7799\(97\)01021-4](https://doi.org/10.1016/S0167-7799(97)01021-4)
5. Avérous L PJH (2009) Review: Biocomposites based on plasticized starch. *Biofuels Bioprod Biorefining* 3:329–343. <https://doi.org/10.1002/bbb>
6. de Campos A, Tonoli GHD, Marconcini JM et al (2013) TPS/PCL Composite Reinforced with Treated Sisal Fibers: Property, Biodegradation and Water-Absorption. *J Polym Environ* 21:1–7. <https://doi.org/10.1007/s10924-012-0512-8>
7. Rudnik E (2007) Properties and applications. In: *Compostable Polymer Materials*. Elsevier Science, Amsterdam, pp 38–69

8. Gutiérrez TJ, Alvarez VA (2017) Films Made by Blending Poly(ϵ -Caprolactone) with Starch and Flour from Sagu Rhizome Grown at the Venezuelan Amazons. *J Polym Environ* 25:701–716. <https://doi.org/10.1007/s10924-016-0861-9>
9. Khan B, Bilal Khan Niazi M, Samin G, Jahan Z (2017) Thermoplastic Starch: A Possible Biodegradable Food Packaging Material—A Review. *J Food Process Eng* 40:. <https://doi.org/10.1111/jfpe.12447>
10. Mathew AP, Dufresne A (2002) Plasticized waxy maize starch: Effect of polyols and relative humidity on material properties. *Biomacromol* 3:1101–1108. <https://doi.org/10.1021/bm020065p>
11. Correa AC, Carmona VB, Simão JA et al (2017) Biodegradable blends of urea plasticized thermoplastic starch (UTPS) and poly(ϵ -caprolactone) (PCL): Morphological, rheological, thermal and mechanical properties. *Carbohydr Polym* 167:177–184. <https://doi.org/10.1016/j.carbpol.2017.03.051>
12. Carmona VB, De Campos A, Marconcini JMJM, Mattoso LHC (2014) Kinetics of thermal degradation applied to biocomposites with TPS, PCL and sisal fibers by non-isothermal procedures. *J Therm Anal Calorim* 115:153–160. <https://doi.org/10.1007/s10973-013-3259-0>
13. Averous L, Moro L, Dole P, Fringant C (2000) Properties of thermoplastic blends: Starch-polycaprolactone. *Polymer* 41:4157–4167. [https://doi.org/10.1016/S0032-3861\(99\)00636-9](https://doi.org/10.1016/S0032-3861(99)00636-9)
14. Shanks RA, Gunaratne LMWK (2011) Gelatinization and retrogradation of thermoplastic starch characterized using modulated temperature differential scanning calorimetry. *J Therm Anal Calorim* 106:93–99. <https://doi.org/10.1007/s10973-011-1620-8>
15. Mohammadi Nafchi A, Moradpour M, Saeidi M et al (2013) Thermoplastic starches: Properties, challenges, and prospects. *Starch/Staerke* 65:61–72. <https://doi.org/10.1002/star.201200201>
16. Wang S, Li C, Copeland L et al (2015) Starch Retrogradation: A Comprehensive Review. *Compr Rev Food Sci Food Saf* 14:568–585. <https://doi.org/10.1111/1541-4337.12143>
17. Li JH, Vasanthan T, Hoover R, Rossnagel BG (2004) Starch from hull-less barley: IV. Morphological and structural changes in waxy, normal and high-amylose starch granules during heating. *Food Res Int* 37:417–428. <https://doi.org/10.1016/j.foodres.2003.09.016>
18. Šárka E, Dvořáček V (2017) Waxy starch as a perspective raw material (a review). *Food Hydrocoll* 69:402–409. <https://doi.org/10.1016/j.foodhyd.2017.03.001>
19. Corradini E, Lotti C, Medeiros ES, De et al (2005) Estudo comparativo de amidos termoplásticos derivados do milho com diferentes teores de amilose. *Polímeros* 15:268–273. <https://doi.org/10.1590/S0104-14282005000400011>
20. Manoel AF, Claro PIC, Mattoso LHC et al (2017) Thermoplastic Waxy Starch Films Processed by Extrusion and Pressing: Effect of Glycerol and Water Concentration. *Mater Res* 2–6. <https://doi.org/10.1590/1980-5373-mr-2016-0881>
21. ASTM D (2014) ASTM D-638. Standard Test Method for Tensile Properties of Plastics. *ASTM Int*
22. Vertuccio L, Gorrasi G, Sorrentino A, Vittoria V (2009) Nano clay reinforced PCL/starch blends obtained by high energy ball milling. *Carbohydr Polym* 75:172–179.

<https://doi.org/10.1016/j.carbpol.2008.07.020>

23. De Kesel C, Lefèvre C, Nagy JB, David C (1999) Blends of polycaprolactone with polyvinylalcohol: A DSC, optical microscopy and solid state NMR study. *Polymer* 40:1969–1978.
[https://doi.org/10.1016/S0032-3861\(98\)00253-5](https://doi.org/10.1016/S0032-3861(98)00253-5)
24. Weber FH, Queiroz FPC, Chang YK (2009) Caracterização físico-química, reológica, morfológica e térmica dos amidos de milho normal, ceroso e com alto teor de amilose. *Ciência e Tecnol Aliment* 29:748–753. <https://doi.org/10.1590/S0101-20612009000400008>
25. Nevoralová M, Ujčić A, Kodakkadan YNV, Starý Z (2019) Rheological characterization of starch-based biodegradable polymer blends. *AIP Conf Proc* 2107:. <https://doi.org/10.1063/1.5109511>
26. Amass W, Amass a, Tighe B (1998) A review of biodegradable polymers: Uses, current developments in the synthesis and characterization of biodegradable polyesters, blends of biodegradable polymers and recent advances in biodegradation studies. *Polym Int* 47:89–144.
[https://doi.org/10.1002/\(SICI\)1097-0126\(1998100\)47:2<89::AID-PI86>3.0.CO;2-F](https://doi.org/10.1002/(SICI)1097-0126(1998100)47:2<89::AID-PI86>3.0.CO;2-F)
27. Walker AM, Tao Y, Torkelson JM (2007) Polyethylene/starch blends with enhanced oxygen barrier and mechanical properties: Effect of granule morphology damage by solid-state shear pulverization. *Polymer* 48:1066–1074. <https://doi.org/10.1016/j.polymer.2006.12.038>
28. Sarath CC, Shanks RA, Thomas S (2014) Polymer Blends. In: *Nanostructured Polymer Blends*. Elsevier, Waltham, pp 1–14
29. Utracki LA (1989) *Polymer Alloys and Blends: Thermodynamics and Rheology*. Hanser Publishers, New York
30. Prachayawarakorn J, Sangnitidej P, Boonpasith P (2010) Properties of thermoplastic rice starch composites reinforced by cotton fiber or low-density polyethylene. *Carbohydr Polym* 81:425–433.
<https://doi.org/10.1016/j.carbpol.2010.02.041>
31. Rosa MF, Medeiros ES, Malmonge JA et al (2010) Cellulose nanowhiskers from coconut husk fibers: Effect of preparation conditions on their thermal and morphological behavior. *Carbohydr Polym* 81:83–92. <https://doi.org/10.1016/j.carbpol.2010.01.059>

Figures

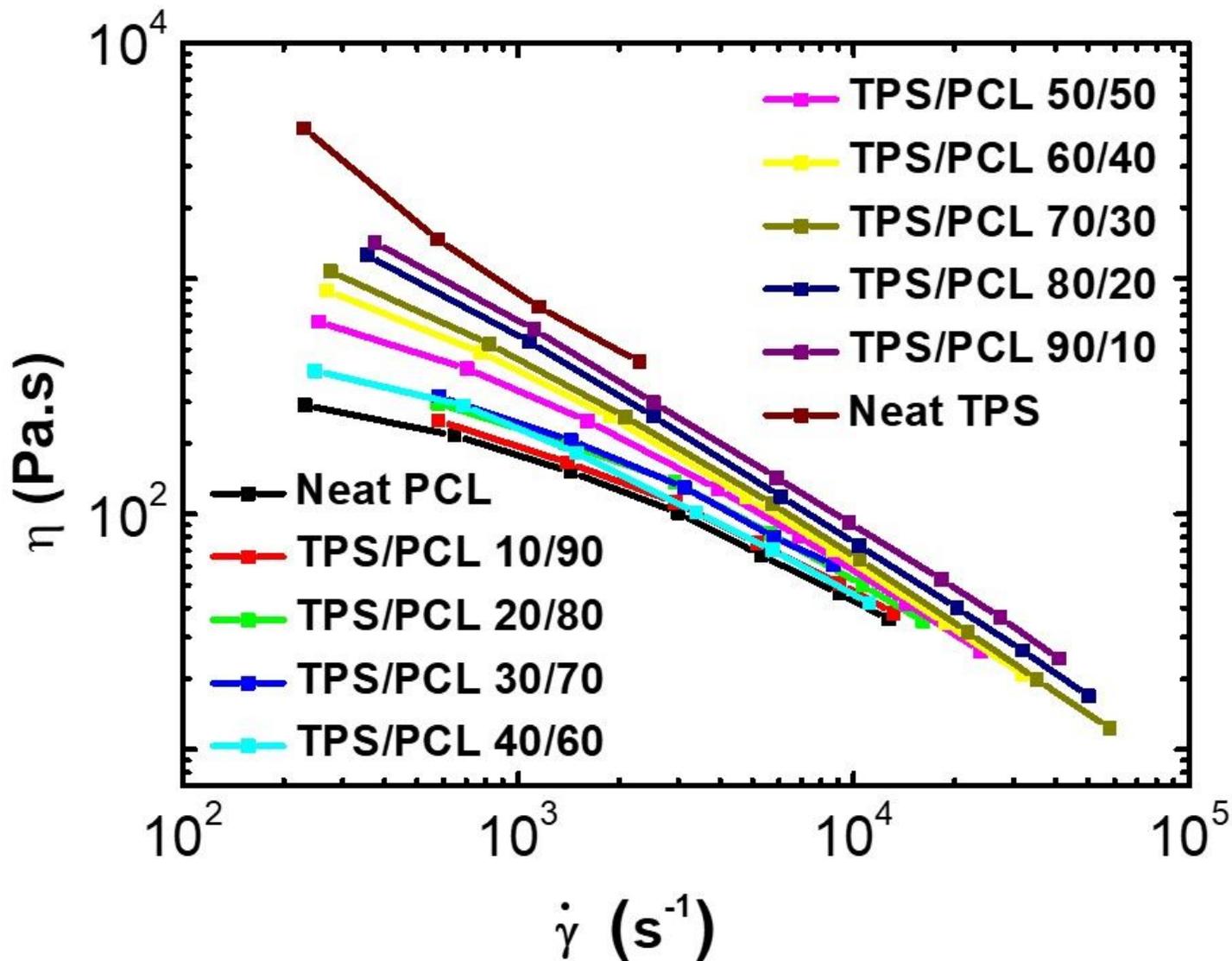


Figure 1

Viscosity vs. shear rate curves of TPS, PCL, and TPS/PCL blends.

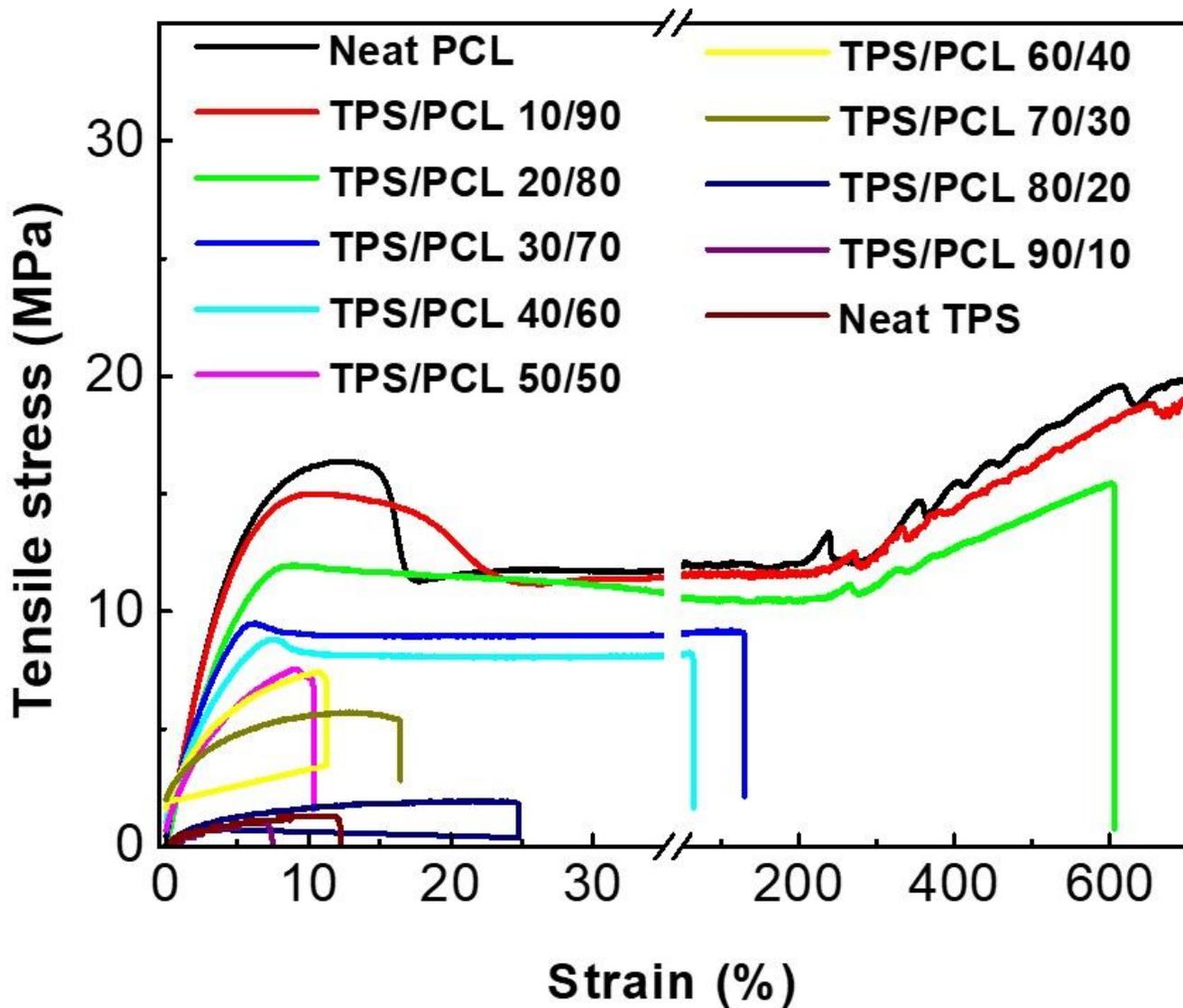


Figure 2

Stress-strain curves of neat TPS and PCL and TPS/PCL blends.

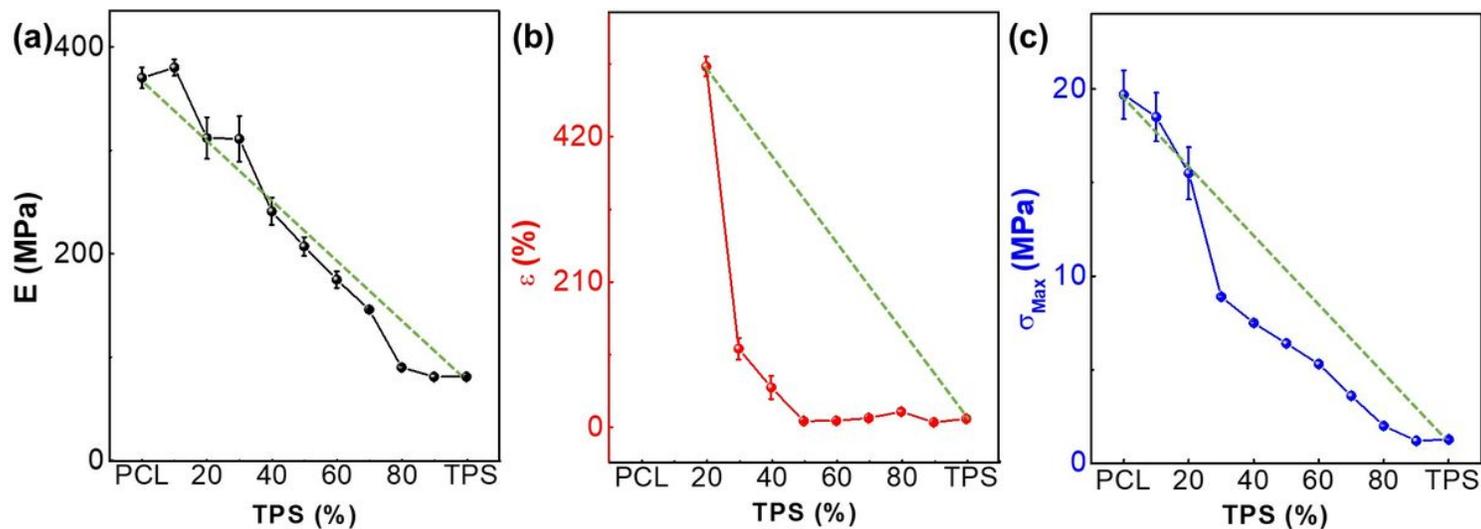


Figure 3

(a) Young's modulus (E), (b) fracture strain (ϵ), and (c) maximum strength (σ_{max}) as a function of the mass fraction of TPS present in the polymeric blends.

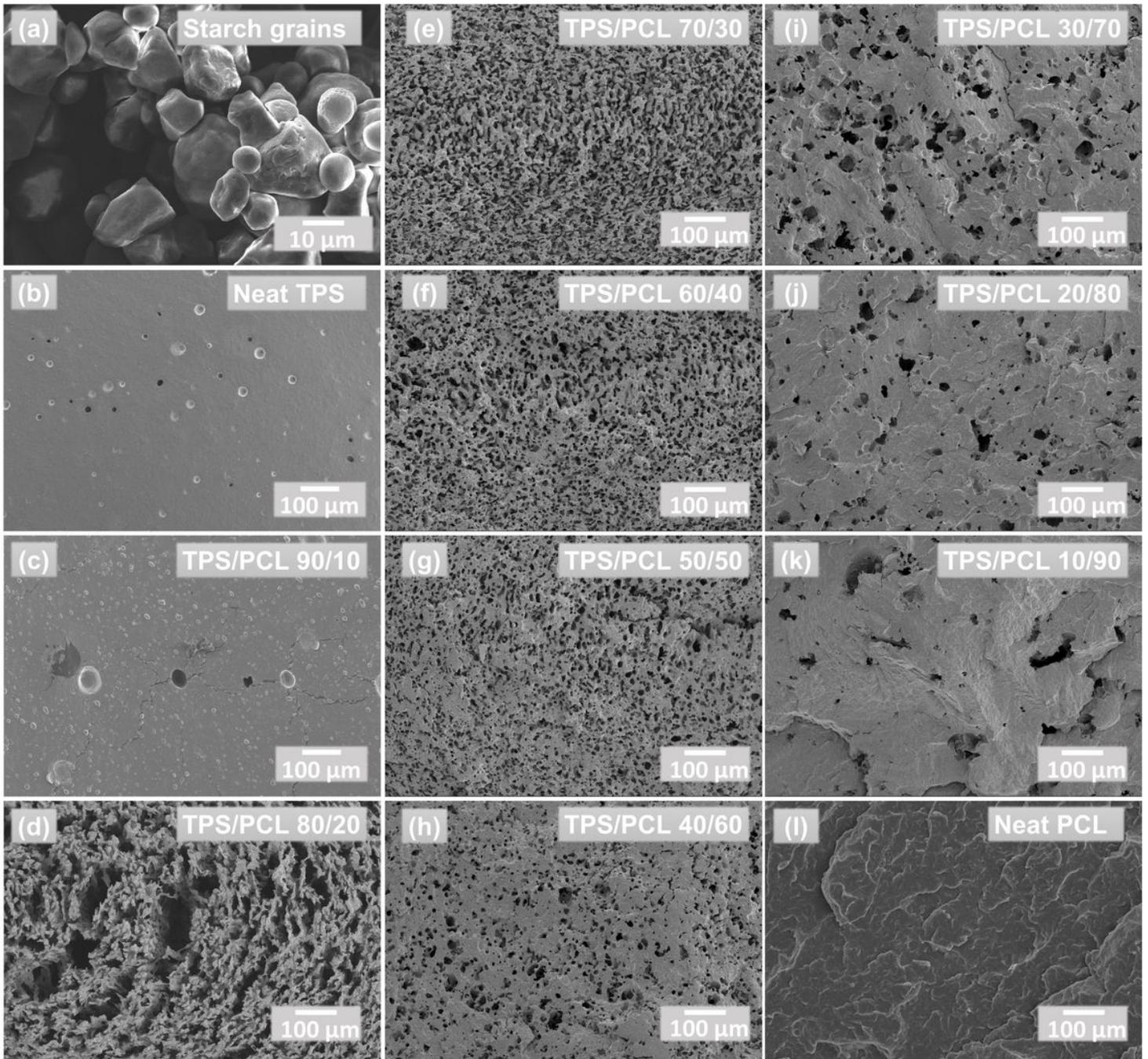


Figure 4

SEM photomicrographs of the starch granules (a), neat TPS (b), TPS/PCL blends (c-k) with their respective blends in increasing order of PCL addition, and neat PCL (l).

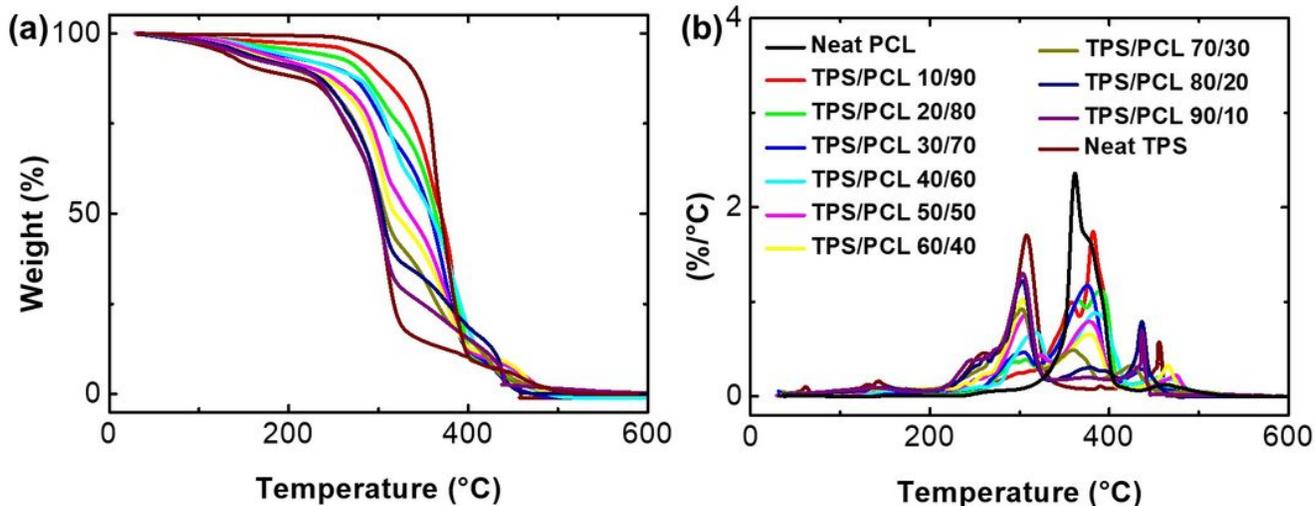


Figure 5

Thermogravimetry and DTG curves of neat TPS and PCL polymers and TPS/PCL blends.

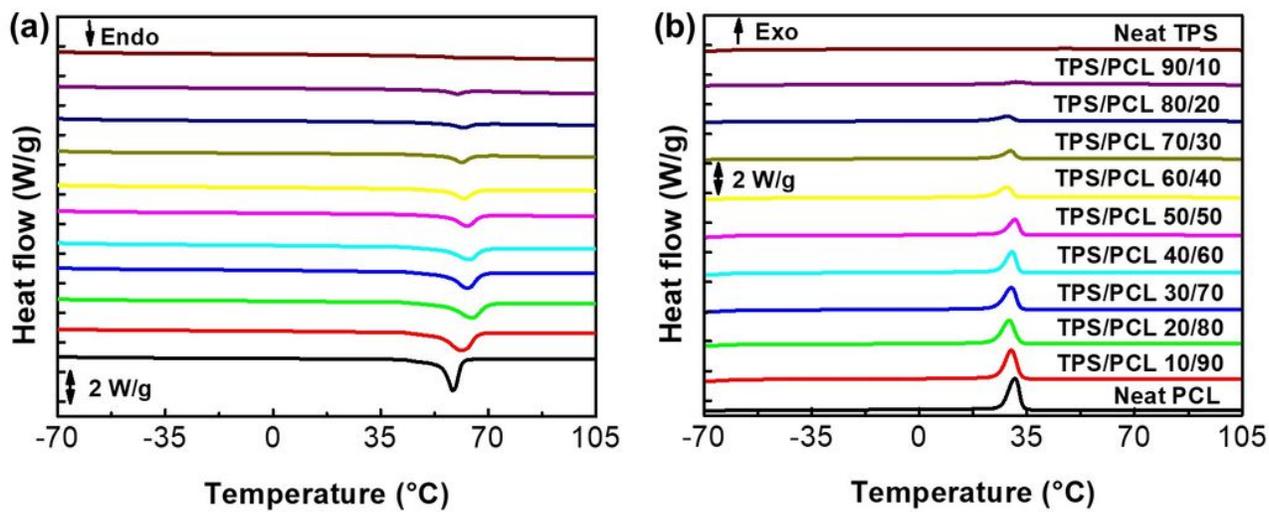


Figure 6

DSC curves for heating (a) and cooling (b) the neat TPS and PCL polymers and the TPS/PCL blends.

Supplementary Files

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