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Properties of thermoplastic blends: starch–polycaprolactone

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Abstract

Different compositions of wheat thermoplastic starch (TPS) and polycaprolactone (PCL) are melt blended by extrusion and injected. Different properties are determined: mechanical properties (tensile and impact tests), thermal and thermomechanical properties (DSC and DMTA) and hydrophobicity (contact angle measurement). A large range of blends is analysed with different glycerol (plasticizer):starch contents ratios (0.14:0.54) and various PCL concentrations (up to 40 wt.%). From the behaviour of each polymeric system, it is possible to analyse the relationship properties of each component proportion on the blends. The ageing of the system is studied and shows a structural evolution of the material after injection during several weeks. We have noticed a fairly low compatibility between both polymeric systems. Finally, the addition of PCL to TPS matrix allows to overcome the weakness of pure TPS: low resilience, high moisture sensitivity and high shrinkage, even at low PCL concentration, e.g. 10 wt.%. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Blend; Thermoplastic starch; Polycaprolactone

1. Introduction

An important number of biodegradable polymers (biopolymers) exist that are derived from both synthetic and natural sources [1–3] but most of them are quite costly. Growing environmental concerns have created an urgent need to develop new biodegradable materials that have comparable properties with today's polymeric materials at an equivalent cost. The utilisation of agricultural products in plastic applications is considered as an interesting way to reduce surplus farm products and to develop non-food applications. For years, our laboratory has studied and developed low cost biopolymers such as starch-based materials, obtained from renewable resources. Several authors [4,5] have shown the possibility to transform native starch into thermoplastic resin-like products under destructuring and plasticization conditions. Thermoplastic starch (TPS) is processed like synthetic plastics through extrusion and injection units. Unfortunately, TPS is a very hydrophilic product. Some authors [6] tried to modify the starch structure, e.g. by acetylation, to reduce the hydrophilic character of the chains. This chemical process results in inferior mechanical properties and greater product cost [7]. In addition, some authors [8,9] have described changes in the mechanical properties of TPS in relation with the crystallinity and the contents of plasticizer and water, during ageing.

Moisture sensitivity and critical ageing have lead to the necessity to associate TPS with another biopolymer, to preserve the biodegradability of the final blend. Association between polymers can be blends or multilayer products. Multilayers can be obtained by coating [10] or by coextrusion [11] processes. However, in each case, it is necessary to appraise the compatibility between the different biopolymers through blend analysis. Blending TPS with other polymers has been commonly used [2–5,10,12–25]. Research groups [2–5,12] have developed blends with synthetic polymers such as polyethylene leading to non-fully biodegradable materials. To maintain the biodegradability of the blend, known biopolymer components include [2,3,13–25]: aliphatic polyesters like polycaprolactone [15–21] (PCL), polylactic acid [3] (PLA), polyhydroxybutyrate-co-valerate [15–17,22–24] (PHBV), polyesteramide [25]. Some starch-based blends have been commercialised like Mater-Bi [12,19] (Novamont-Italy) or Bioplast [13] (Biotec-Germany).

PCL has been chosen among the different biopolymers commercially available and widely produced. Previous studies have shown that PCL/TPS blends are readily biodegradable [3,19,20]. According to Bastioli et al. [19],

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Table 1
TPS formulations

TPS formulation	Starch contents (wt.%)	Glycerol contents (wt.%)	Water contents (wt.%)	Glycerol:starch ratio
S74G10W16 *(density: 1.38)*	74	10	16	0.135
S70G18W12 *(density: 1.37)*	70	18	12	0.257
S67G24W9 *(density: 1.35)*	67	24	9	0.280
S65G35W0 *(density: 1.42)*	65	35	0	0.538

blending TPS with PCL increases the apparent biodegradation rate of PCL. The blend is degraded by both α-amylase and lipase [26]. PCL is sufficiently water-resistant and seems to suit our purpose as the hydrophobic component.

Various plasticizers have been used with starch [27,28]. In unpublished previous works, we have shown that under shearing and thermo-pressure conditions, water and glycerol act as a good destructuring–plasticizer agent. Authors [4,28,29] have described glass transition shifts with regard to the ambient temperature, according to the plasticizers contents.

It is possible to modulate the properties of TPS, from a soft material (high plasticizer level) to a brittle material (low plasticizer level) according to moisture and glycerol contents.

The aim of this paper is to report various properties of TPS/PCL blends without specific compatibilizers. Different TPS:PCL ratios are tested but to develop economically viable biodegradable materials, TPS should remain as the major phase in the blend (>50%). Different starch formulations with various glycerol and moisture contents are analysed. Water sensitivity is determined by surface contact angle measurements. Mechanical properties (tensile and impact tests), thermomechanical (DMTA) and thermal (DSC) behaviours are evaluated.

2. Experimental

2.1. Materials

Wheat starch was obtained from Chamtor (France). The amylose and amylopectin contents were, respectively, 25 and 75%. Residual protein content was less than 1%. The glycerol used is a 99.5% purity product. PCL was purchased from Solvay (CAPA 680). The linear polymer is obtained from ε-caprolactone monomer. The number average molecular weight is 69 000 ± 1500 (GPC, THF, 25°C) and the polydispersity is 1.74. The density is 1.11. The Melt Flow Index (MFI) is 7.29 g/10 mn (190°C, 2.16 kg). The grade chosen presents the highest molecular weight and viscosity. Magnesium sterate (99% purity) from Aldrich was used as a demoulding agent in injection moulding; less than 1 wt.% is used for each blend.

Table 2
Mechanical properties of TPS/PCL blends (standard deviations are given between brackets)

Formula	Ageing time: 2 weeks				Ageing time: 6 weeks		
PCL (wt.%)	Modulus (MPa)	Maximum tensile strength (MPa)	Elongation at break (%)	Impact strength (kJ/m^2)	Modulus (MPa)	Maximum tensile strength (MPa)	Elongation at break (%)
PCL CAPA 680 without TPS.							
100	190 (6)	14.2 (1.4)	>550	No break	190 (6)	14.2 (1.4)	>550
Starch 74/glycerol 10/water 16							
0	997 (59)	21.4 (1.0)	3.8 (0.3)	0.63 (0.59)	1144 (42)	21.4 (1.7)	3.4 (0.4)
25	747 (40)	10.5 (0.7)	2.0 (0.1)	1.57 (0.15)	882 (19)	14.2 (0.6)	2.3 (0.2)
40	585 (22)	9.0 (0.3)	2.4 (0.1)	2.99 (0.21)	681 (17)	11.9 (0.3)	3.5 (0.1)
Starch 70/glycerol 18/water 12							
0	52 (9)	3.3 (0.1)	126.0 (2.0)	No break	116 (11)	4.0 (0.1)	104.0 (4.7)
25	93 (15)	5.9 (0.3)	62.6 (6.6)	No break	187 (1)	7.0 (0.2)	41.1 (5.9)
Starch 67/glycerol 24/water 9							
0	26 (4)	2.6 (0.1)	110.0 (11.1)	No break	45 (5)	3.3 (0.1)	98.2 (5.2)
25	80 (4)	5.3 (0.1)	42.2 (1.9)	No break	111 (9)	6.0 (0.1)	38.9 (2.0)
Starch 65/glycerol 35							
0	2 (1)	0.61 (0.24)	90.7 (4.8)	No break	11 (1)	1.37 (0.05)	60.4 (5.2)
10	8 (1)	1.05 (0.02)	61.9 (2.4)	No break	21 (2)	1.88 (0.03)	49.3 (2.5)
25	36 (3)	2.87 (0.06)	43.1 (2.6)	No break	50 (4)	3.54 (0.06)	29.3 (1.5)
40	71 (6)	5.19 (0.04)	50.4 (4.7)	No break	84 (4)	5.78 (0.09)	31.6 (2.8)

2.2. Sample preparation

2.2.1. Blends preparation

Granules of TPS were prepared according to the following procedure. Native starch was weighed and introduced in a turbo-mixer. Glycerol was then added very slowly while starch was slowly agitated. After completion of glycerol addition, the mixture was dispersed at high speed to obtain a homogeneous dispersion. The mixture was then placed in a vented oven at 170°C for 45 min and occasionally stirred, allowing vaporisation of water and diffusion of glycerol into the starch granule. After cooling, the proper amount of water was added to the mixture that was once more dispersed at high speed. The powder was then extruded and granulated.

Various TPS formulations (see Table 1) with different plasticizer:starch ratios were tested to obtain a wide range of TPS behaviour. After equilibration for 8 days in a 65% RH atmosphere, TPS and PCL pellets were mixed together in the adequate proportion. The compositions were then extruded and granulated after cooling and equilibrated at 65% RH for eight days before injection moulding. Various TPS/PCL blends are tested as presented in Table 2.

The blends are denoted as follows; S75G15W10/PCL25 means that the TPS comprises 75 parts of starch (dry basis), 15 parts of glycerol and 10 parts of water; the blend was prepared by mixing 25 wt.% of PCL and 75 wt.% of TPS granules.

2.2.2. Processing conditions

Blends were extruded on a single screw extruder (SCAMIA S 2032, France) equipped with a conical-shaped element (see description and figures in Onteniente et al. [30]). This design is suitable to provide high shearing. The extruder has two heating zones situated around the head and at the die. A die was used to obtain strands that were then pelleted after air-cooling. An injection moulding machine DK Codim NGH 50/100 (France) with a clamping force of 50 tons was used to mould standard dumbbells. The screw regulated in temperature from 100 to 130°C was fed with granules. Injection pressure was 1500 bars. Holding pressure and time were, respectively, 1000 bars and 15 s. Cooling time was set to 15 s. The uniaxial shrinkage is defined by the formula:

$$S = (1 - (L - L_0)) \times 100 \tag{1}$$

where L is the length of the specimen after cooling and L_0 is the length defined by the mould.

Dumbbell specimens produced have an active portion 10 mm wide and 4 mm thick (according to French standard NFT 51-034 1981). The Charpy test samples were cut out from the central part of the dumbbells to get samples without notches whose dimensions were $10 \times 4 \times 60$ mm^3 (according to French standard NFT 51-035 1983).

2.3. Mechanical properties

2.3.1. Tensile test

Tensile strength measurements, Young's modulus and elongation at break were performed on mechanical tensile tester (Instron 4204-G.B.). A crosshead speed of 50 mm/min is used. Ten samples for each blend composition were tested after a two week period conditioning at 23°C and 50% RH. The influence of ageing on the mechanical properties was determined after 6 weeks of conditioning in the same conditions.

2.3.2. Impact test

A mechanical impact tester (JPS-France) with a 4 J pendulum was used for Charpy tests. For each blend composition, ten specimens are tested after 14 days conditioning at 23°C and 50% RH. Impact strength is usually quoted as energy per unit area.

2.4. Contact angle measurements

The contact angle formed between a water droplet placed at the surface of a material and the kinetics of spreading is related to the hydrophobicity of the material. Contact angle measurements were performed with a Kruss G23 (Germany) apparatus. A water droplet was dropped on the surface of a small sample cut from a dumbbell specimen. The evolution of the droplet shape was recorded. A CCD video camera and image analysis software were used to determine the contact angle evolution. Due to variations in the surface smoothness, a large dispersion in the results is obtained in this type of analysis between different kind of materials. Results must be considered only as trends across similar types of material.

2.5. Thermal analysis

The thermal characteristics of the blends were determined using a modulated differential scanning calorimeter (Universal V1.9D TA instrument-USA) cooled with liquid nitrogen circulation. Samples (15–20 mg) were cut from a dumbbell specimen after conditioning and placed in sealed aluminium pans. The pan is hermetic to prevent water evaporation during scanning. A first scan was performed between ambient temperature and 100°C, the sample was then cooled rapidly to −100°C and rescanned until 100°C. Scanning rate was 10°C/min. An empty pan was used as reference. The glass transition temperature was computed as the midpoint of heat capacity increase. The thermal effects were recorded during the second heating run. The first scan allowed us to discard thermal history of the material.

2.6. Thermo-mechanical analysis

Thermo-mechanical properties of the different blends were determined with a dynamic thermo-mechanical analyser (TA instrument DMA 2980-USA). Samples were cut

Table 3
Shrinkage (%) for different TPS/PCL blends

PCL (wt.%)	S74G10W16	S70G18W12	S67G24W9	S65G35
0	7.5	14.4	13.1	9.3
10	–	–	–	1.8
25	2.6	2.2	1.1	0.5
40	1.7	–	–	0.1

from the central part of the dumbbells to get specimens with dimensions $4 \times 10 \times 27.3\ \mathrm{mm}^3$. They were tested by applying a bending constraint using the dual cantilever geometry. The displacement amplitude was set to 14.5 μm. The measurements were performed at a frequency of 1 Hz. The range of temperature was from −100 to 140°C at the scanning rate of 1.5°C/min. Samples are coated with silicone wax to preserve water evaporation during scanning.

3. Results and discussion

3.1. Shrinkage analysis

Shrinkage values are reported in Table 3. The shrinkage obtained for the different starch formulations is very important. Addition of PCL leads to a significant reduction of shrinkage to acceptable values. PCL can be considered as a dimensional stability enhancement modifier.

3.2. Mechanical properties

Complete mechanical properties obtained from tensile and impact strength measurements on injection moulded bars are presented in Table 2. The results obtained after, respectively, 2 and 6 weeks ageing at 50% RH and 23°C are presented. PCL is a ductile polymer with an important elongation at break and a medium Young's modulus. The behaviour of pure TPS is the same as reported by many workers [9]: Young's modulus and tensile strength are seen to decrease while increasing the glycerol content. Depending on the plasticizer content, the elongation at break increases and then decreases for the highest glycerol concentrations. The maximum elongation at break seems to be at a glycerol:starch ratio close to 0.2. These phenomena could be due to a phase separation between starch and glycerol described by some authors [29]. Two kinds of material behaviours can be defined. The S74G10W16 formulation is a stiff and brittle material whereas the other formulations lead to flexible and soft material with very high impact strength (no break of the samples during testing). For PCL-based blends, mechanical properties depend both on plasticization level and PCL content. Two kinds of behaviour are observed. For the S74G10W16 formulation, the addition of PCL results in an improvement of impact properties. The impact strength resistance is improved, as when blending a highly flexible material with a rigid one. On the contrary, Young's modulus and the maximum strength decrease when the PCL content increases. These results are in agreement with the classical rule of mixtures. Mechanical model is based on two bounds. The upper bound is described by the additivity law described by Eq. (2), where E_{upper} is the upper modulus estimation of a blend based on polymeric systems 1 and 2. E_1 and E_2, V_1 and V_2 are, respectively, the modulus and the volume ratio of each polymeric system. The lower bound is given by Eq. (3). Some results are presented in Fig. 1. Most of experimental moduli are close of the estimated upper bound.

$$E_{\mathrm{upper}} = E_1 V_1 + E_2 V_2 \tag{2}$$

$$1/E_{\mathrm{lower}} = V_1/E_1 + V_2/E_2 \tag{3}$$

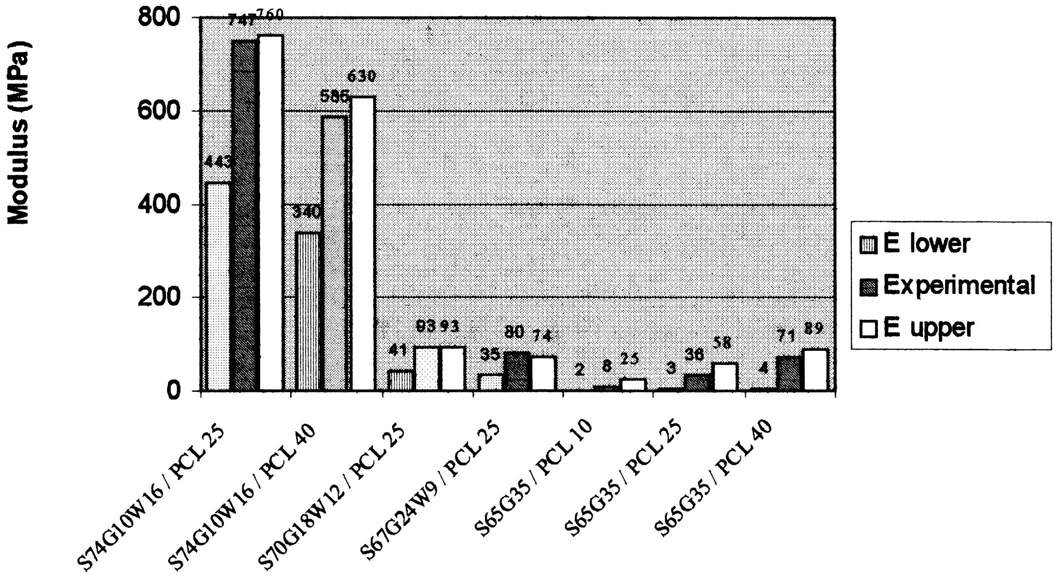

Fig. 1. Modulus estimation on 2 weeks ageing results.

Table 4
Contact angle measurements of TPS/PCL blends

PCL (wt.%)	Initial value (°)	Slope at the origin (°/s)
100	64	−0.1
Starch 74/glycerol 10/water 16		
0	51	−4.2
25	69	−0.4
Starch 70/glycerol 18/water 12		
0	40	−2.0
25	73	−0.1
Starch 67/glycerol 24/water 9		
0	50	−3.2
25	76	−1.1
Starch 65/glycerol 35		
0	32	−3.9
10	56	−0.8
25	68	−0.2
40	69	−0.1

For the S70G18W12, the S67G24W9 and the S65G35 formulations, the addition of PCL increases the mechanical properties. In this case, PCL has a higher modulus than the TPS formulations. Pure PCL has a very high elongation at break. For all the PCL/TPS blends, the elongation at break decreases inversely with PCL content. This is probably due to phase separation between PCL and TPS, because of non-miscibility between TPS and PCL.

Mechanical properties of evolution during ageing are also presented in Table 2. A significant increase of Young's modulus and of the maximum strength is observed. For pure TPS, Young's modulus evolution is from 10 to 550% (for the higher glycerol amount). This is due to post-crystallisation and water evolution inside the material. The evolution is lower for the blends with the highest glycerol content. The most important contribution to modulus comes from PCL, for which properties are quite stable to ageing.

3.3. Contact angle measurements

In Table 4 are presented the results of contact angle measurements. The material behaviours are quantitatively illustrated by measurement of the initial values of contact angle just after deposition of the droplet and by the value of the slope that illustrates the kinetics of absorption. For pure TPS, the water droplet is very rapidly absorbed because of the hydrophilic nature of the material. When PCL is blended with TPS, the evolution of contact angle with time is slower and more constant. In all cases, the presence of PCL leads to a significant improvement of the material's hydrophobicity. The initial contact angle value is higher than one of pure TPS and the kinetics of absorption decreases. These trends are more pronounced for the higher amount of PCL in the blends. The interesting fact of these results is that the introduction of PCL at levels as low as 10 wt.% leads to a significant improvement of water resistance of the materials. During the injection moulding process, a thin skin of PCL rich material is formed at the surface of the sample. This layer is observed after breaking of the samples. PCL acts in this case as a processing aid, like stearate or wax in injection formulation. During the mould-filling phase, we have a preferential migration of PCL toward the cold surface of the mould producing a kind of multilayer structure with a thin PCL skin.

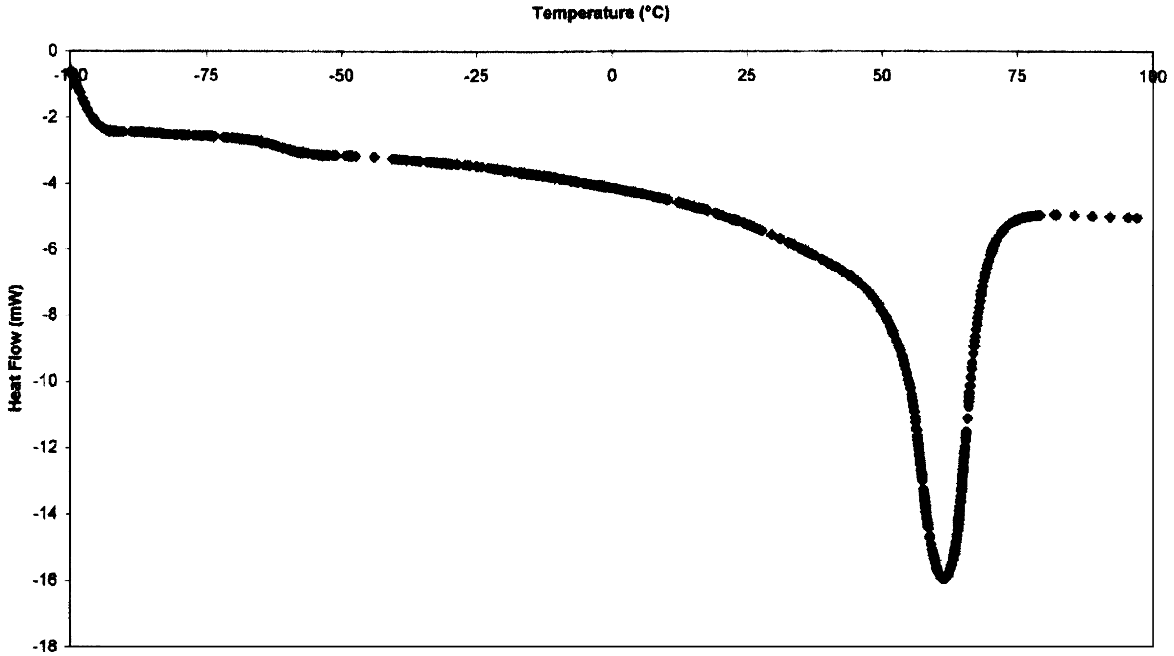

Fig. 2. DSC thermogram for PCL.

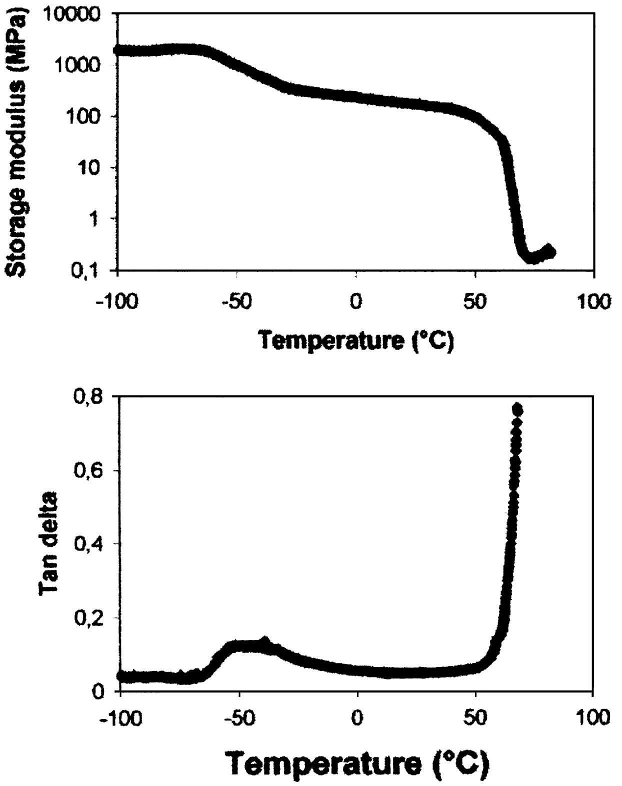

Fig. 3. Storage modulus (upper) and tan δ (lower) curves (DMTA) for PCL.

3.4. Thermal and thermo-mechanical properties

3.4.1. Characteristics of pure PCL

The DSC and DTMA curves obtained with pure PCL are presented in Figs. 2 and 3, respectively. The DSC thermograms recorded during the second scan after heating and quenching of the sample clearly present two different thermal events: an increase of heat capacity at low temperature (−61.5°C) and an endothermic peak at 61°C. These events can be attributed to the glass transition of the polymer for the low temperature event and to the melting of the crystalline domains of the polymers for the other. These attributions are in good agreement with the characteristics observed by DMTA. An important decrease of the storage modulus associated with a tan δ peak (maximum temperature −50°C) is present in Fig. 3 and is consistent with a glass transition, as observed by DSC. A second transition is observed at higher temperatures (maximum of tan δ at 65°C), with a more important order of magnitude as the one described previously and can be associated with the melting of the polymer.

The difference between the temperature corresponding to the transitions observed by DMTA and DSC is attributed to the frequency of the analysis method. This is commonly observed in classical polymeric systems and is very well documented [31]. The thermal characteristics of PCL are reported in Table 5. They are in good agreement with the one reported by other workers [16,17,32].

3.4.2. Characteristics of pure thermoplastic starch

The DSC and DMTA curves obtained with pure TPS are presented in Fig. 4 (DSC) and Figs. 5 and 6 (DMTA). The temperatures associated with the different thermal events are reported in Table 5. The DSC curves present two changes of heat capacity for most of the TPS compositions. The position of the one at higher temperatures is strongly dependent on the amount of glycerol: the higher it is, the lower the temperature of the heat capacity change. This decrease in temperature linked to heat-capacity change can be attributed to a glass transition temperature shift, due to increasing amounts of plasticizer. Moreover, the experimental values are in good agreement with the glass transition temperature reported in the literature [9,28,29]. This glass transition is clearly demonstrated by DMTA where the curves present a loss of modulus and a tan δ peak in the same temperature range.

The second change of heat capacity is invisible by DSC for the less plasticized formulations. But for the others, a change of the heat capacity drop is correlated to the glycerol content. The glycerol DSC curve (Fig. 7) presents a heat capacity drop in the same temperature range as for TPS formulations. We can attribute the observed transition to the plasticizer glass transition. Similar results have been obtained by Lourdin et al. [29]. According to this study, this relaxation is due to the plasticizer. Phase separation for glycerol:starch higher than 0.2 has been shown. This relaxation is also observed by DMTA between −50 and −60°C. The magnitude of the tan δ peak is strongly dependent on the glycerol content, that is also consistent with a relaxation linked to plasticizer glass transition.

Table 5
Thermal (DSC) and thermo-mechanical (DMTA) properties of PCL and TPS ($T_{\beta(\mathrm{DMTA})}$, $T_{\alpha(\mathrm{DMTA})}$, $T_{\phi(\mathrm{DMTA})}$ are determined at the maximum of the tan δ peak. $T_{\mathrm{sec(DSC)}}$, $T_{\mathrm{g(DSC)}}$ are determined at the midpoint of heat capacity increase)

Polymers	Secondary relaxation		Glass transition			Melting		
	$T_{\beta(\mathrm{DMTA})}$	$T_{\mathrm{sec(DSC)}}$ (°C)	$T_{\alpha(\mathrm{DMTA})}$,	$T_{\mathrm{g(DSC)}}$ (°C)	ΔC_p (J/g K)	$T_{\phi(\mathrm{DMTA})}$	$T_{\mathrm{m(DSC)}}$ (°C)	ΔH melt (J/g)
PCL	None		−50.0	−61.5	–	61	65	71.9
S74G10W16	−54.8	Invisible	63.2	43.4	0.36	None		–
S70G18W12	−54.1	−66.7	31.0	8.4	0.42	None		–
S67G24W9	−58.1	−72.2	17.2	−7.3	0.39	None		–
S65G35	−61.6	−77.4	1.4	−20.1	0.23	None		–

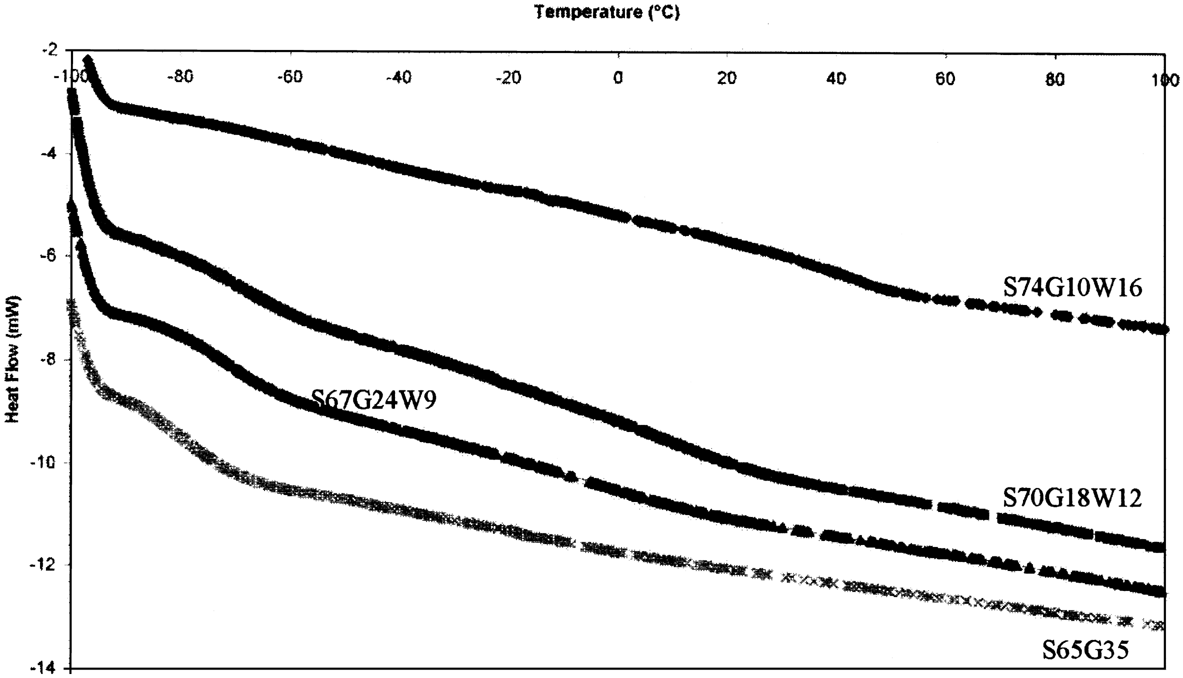

Fig. 4. DSC thermograms for TPS formulations: S74G10W16; S70G18W12; S67G24W9; and S65G35 (from top to bottom).

3.4.3. Characteristics of the blends

The DSC and DMTA curves obtained for blends are presented in Figs. 8–10. Only the most characteristic and interesting curves are presented. Contrary to curves obtained for the pure components, the interpretations of the curves are rather complex for blends. For all the starch formulations, the secondary relaxation is in the same temperature range as the glass transition of the PCL (see Table 5). Moreover, for the less plasticized starch formulation, the glass transition temperature is in the same temperature range as the melting of PCL. As a consequence, it is impossible to separate the contribution of each component on the resulting curves of the blends. However, some characteristics of the curves can be attributed unambiguously. For all the DSC curves, an endothermic peak is observed around 56–60°C. The enthalpy associated with this peak depends on the PCL content and allows us to attribute this to the melting of PCL. It can be noticed that

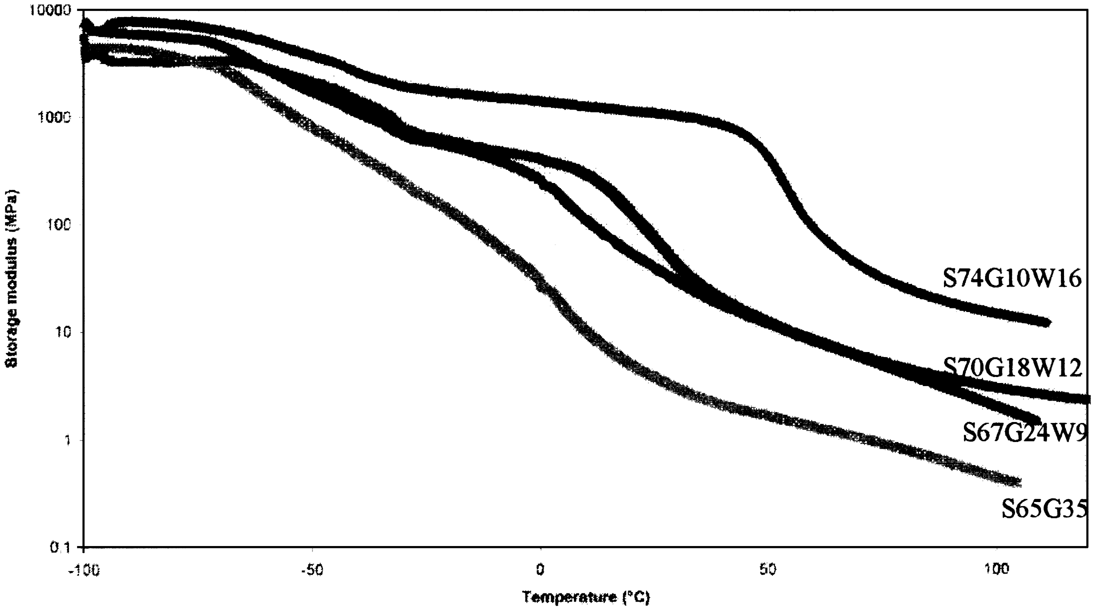

Fig. 5. Storage modulus curves for TPS formulations (DMTA): S74G10W16; S70G18W12; S67G24W9; and S65G35.

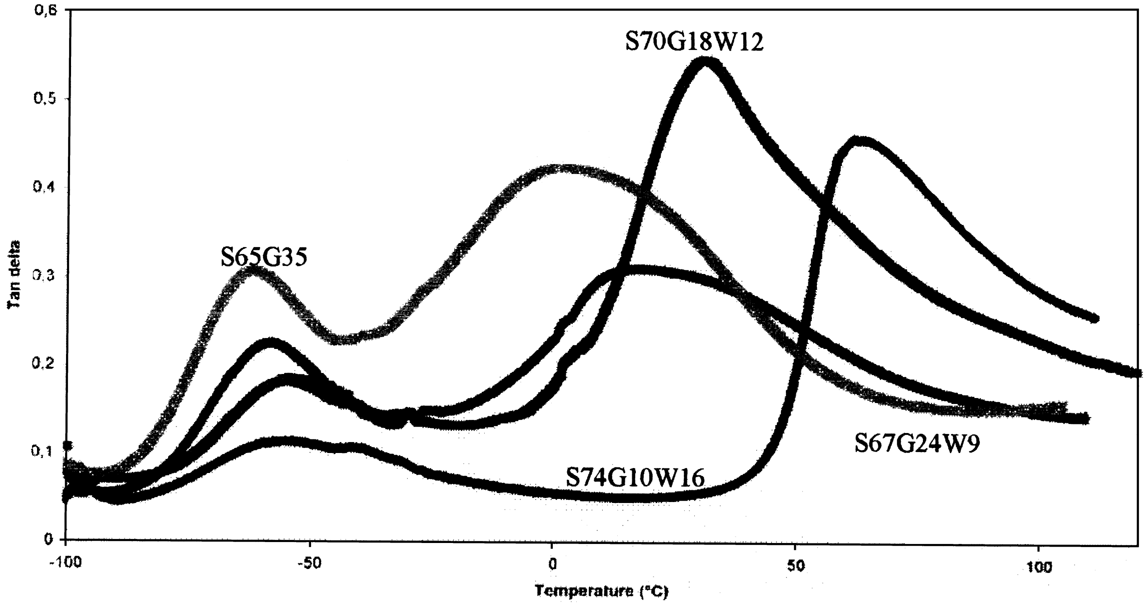

Fig. 6. tan δ curves for TPS formulations (DMTA): S74G10W16; S70G18W12; S67G24W9; and S65G35.

the melting temperature of PCL in the blend is only slightly depressed by the presence of starch. The melting can consequently be attributed to PCL that is pure in the blend probably due to a phase separation of both polymeric systems.

For all the DMTA experiments, a tan δ peak located at low temperature is observed. This peak corresponds to an overlapping of two signals: one attributed to the glass transition of PCL and one arising from secondary relaxation of starch. The temperature corresponding to the maximum of this peak is located between the ones obtained for the pure. Blend temperature is located between PCL-glass transition temperature (−50°C) and β-relaxation temperature for TPS formulations (from −62 to −54°C). For the most plasticized starch formulations, a peak corresponding to the α-relaxation associated with glass transition of starch can be distinctively identified. The temperature of this relaxation is only slightly depressed by the PCL. This slight plasticizing effect is consistent with a phase separation within the blend. If one considers a calculation of the theoretical glass transition temperature with a Couchman–Karasz model [33] for miscible polymers, this value should be given by the

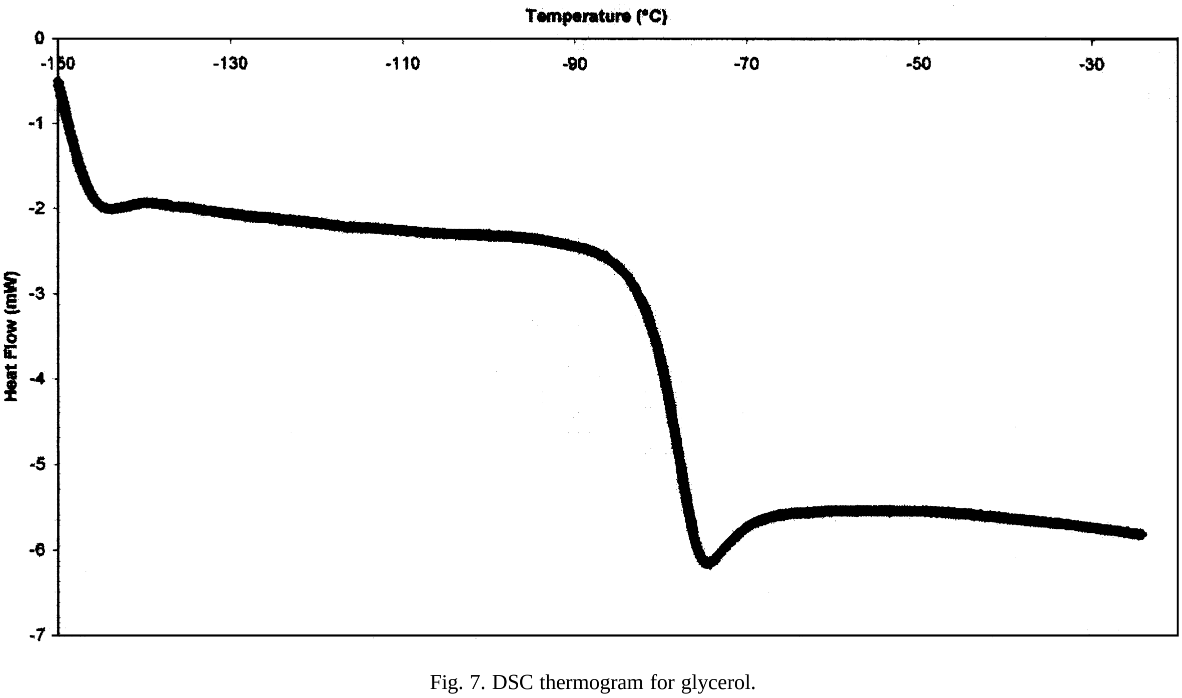

Fig. 7. DSC thermogram for glycerol.

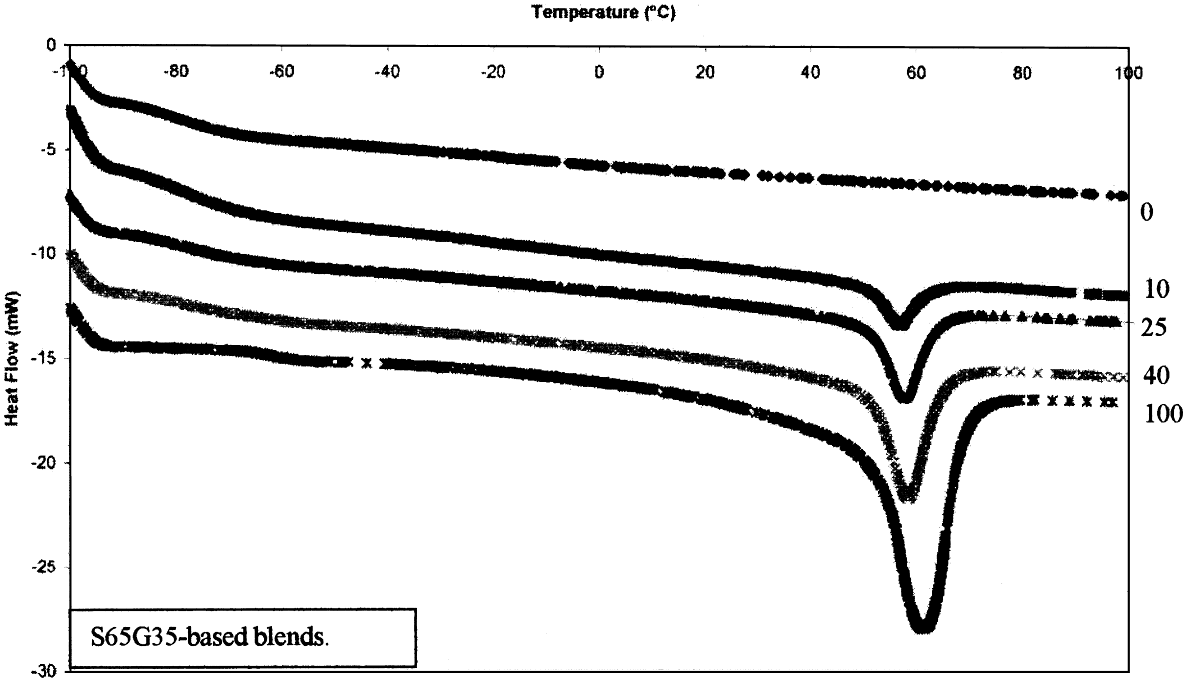

Fig. 8. DSC thermogram for S67G35-based blends (0, 10, 25, 40 and 100 wt.% of PCL from top to bottom).

formula:

$$T_g = \frac{(w_1 \Delta C_{p1} T_{g1} + w_2 \Delta C_{p2} T_{g2})}{(w_1 \Delta C_{p1} + w_2 \Delta C_{p2})} \tag{4}$$

where w_1, w_2, T_{g1} and T_{g2} are, respectively, the mass fraction and the glass transition temperature of each of the polymers. ΔC_{p1} and ΔC_{p2} are the heat capacity change at the glass transition temperature.

The calculated T_g values from the previous formula are reported in Table 6 in comparison with experimental values. Calculations have been made using the glass transition determined by DSC and by DMTA (α-relaxation temperature). As can be seen from the results presented in Table 6, the model for miscible polymers is not valid. The calculated values differ from the experimental ones. The DSC and DMTA curves do not show the transition for certain blends whereas the calculated value indicates that such a determination should be possible if the model is valid. Therefore, these blends should be considered as dispersions of PCL in a TPS matrix, as could be

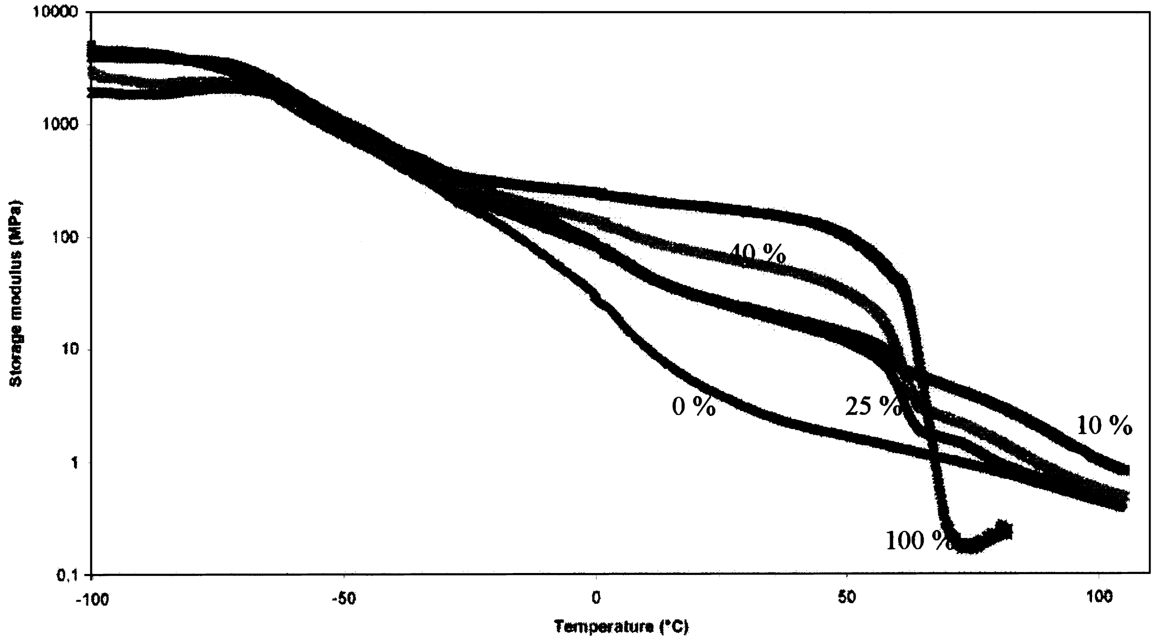

Fig. 9. Storage modulus curves (DMTA) for S65G35-based blends (0, 10, 25, 40, 100 wt.% of PCL).

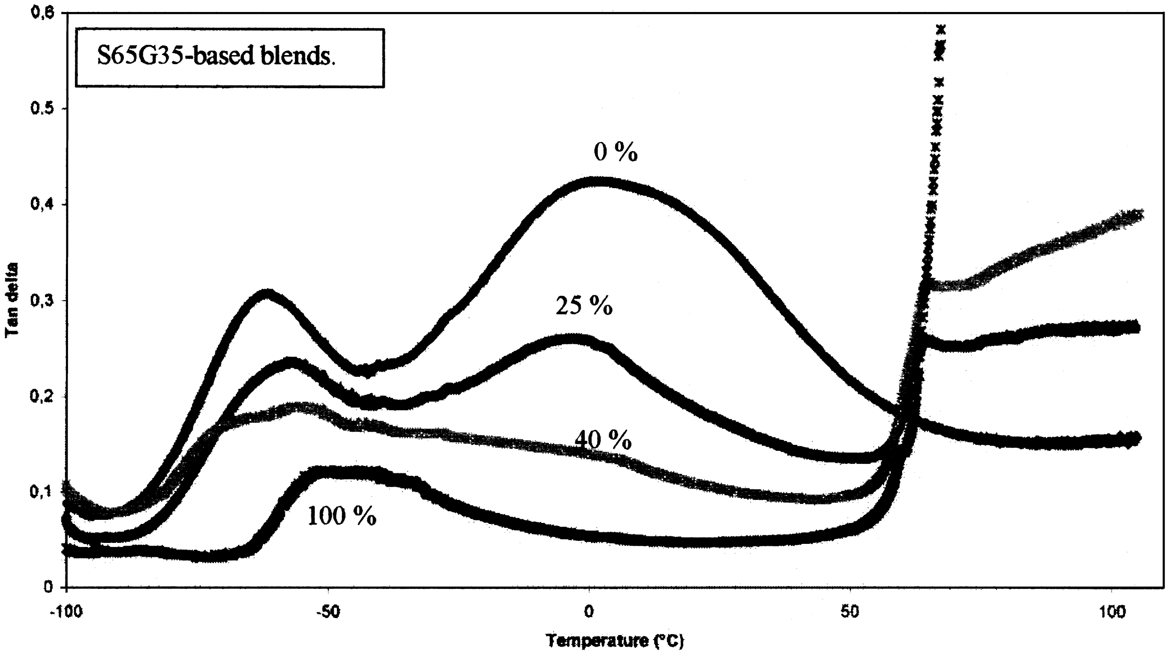

Fig. 10. tan δ curves (DMTA) for S65G35-based blends (0, 25, 40, 100 wt.% of PCL).

concluded from the different experimental results. It can be observed that for the most plasticized starch matrix, the introduction of PCL enables the reduction of the modulus decrease with temperature, as long as the temperature remains below the PCL melting temperature. This is very clearly illustrated in Fig. 9 where the storage modulus curve of the blend is situated over the similar curve for the starch matrix.

4. Conclusion

We have investigated the properties of starch/PCL blends. The blends were prepared by extrusion and injection moulding. The thermal, thermo-mechanical and mechanical characteristics of the blend clearly indicate a phase separation in the blend, as is generally found for non-miscible polymers. We have found the same behaviour from mechanical characteristics. In most of the blends tested, it is possible to find the thermal transition of each component with only a minor shift of the characteristic temperatures. We have observed a significant improvement of the properties of TPS based blend due to the presence of PCL. When the starch matrix has a glassy behaviour, blending with PCL results in a decrease of the material modulus but the impact resistance is improved. On the other hand, when the starch has a rubbery behaviour, PCL increases the modulus of the

Table 6
Comparison between calculated and experimental glass transition temperatures

Blends	T_g (pure PCL) or T_α (°C)	T_g (pure TPS) or T_α (°C)	Calculated Blend T_g (°C)	Experimental T_g (°C)
S74G10W16/PCL 25	−61.5	40.7	29.3	41.0
S74G10W16/PCL 40	−61.5	40.7	20.2	–
S70G18W12/PCL 25	−61.5	8.9	−0.1	–
S67G24W9/PCL 25	−61.5	−1.9	−10.9	–
S65G35/PCL 10	−61.5	−13.1	−16.1	−22.8
S65G35/PCL 25	−61.5	−13.1	−21.1	–
S65G35/PCL 40	−61.5	−13.1	−26.8	–
S74G10W16/PCL 25	−50.0[a]	63.2[a]	50.6	–
S74G10W16/PCL 40	−50.0[a]	63.2[a]	40.5	–
S70G18W12/PCL 25	−50.0[a]	31.0[a]	20.6	31.0
S67G24W9/PCL 25	−50.0[a]	17.2[a]	7.0	12.1
S65G35/PCL 10	−50.0[a]	1.4[a]	−1.7	–
S65G35/PCL 25	−50.0[a]	1.4[a]	−7.1	−3.3
S65G35/PCL 40	−50.0[a]	1.4[a]	−13.1	–

[a] T_α measurements.

materials. The dimensional stability was improved significantly, whatever the starch formulation and with a level of PCL incorporation as low as 10 wt.%. The hydrophobicity of the blends was much more important than the one of starch. Regarding the mechanical properties, two cases have been observed.

Although not totally innovative, the association with PCL is an interesting way to overcome the most important weaknesses of TPSs: poor resilience and moisture sensitivity. This kind of blend is an interesting approach to produce low cost biodegradable material in order, for instance, to increase the use of environmentally friendly material in packaging.

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