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Plasticized starch–cellulose interactions in polysaccharide composites

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Abstract

This paper is focused on the interactions between leafwood cellulose fibres and a plasticized wheat starch matrix. Different plasticized starch (TPS)-based composites have been elaborated. LDPE-based composites are used as reference materials (no fibre–matrix interactions). After extrusion and injection moulding, the properties of the different composites are analysed. Mechanical properties (tensile tests), thermomechanical properties (DMTA) and morphology (SEM) are evaluated. DMTA analysis shows for TPS composites a strong evolution of the main relaxation temperature, which can be linked to the existence of cellulose–starch interactions resulting in a decrease of starch chain mobility. This phenomenon is consistent with the evolution of mechanical behaviour. SEM observations correlate this hypothesis. After cryogenic fracture, TPS composites present fibres, which are embedded in the matrix. On the composites, reinforcing effects have been observed according to the evolution of fibre length and fibre content. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Composite; Thermoplastic starch; Cellulose fibre

1. Introduction

In recent years, great progress was achieved in the development of biodegradable products on the basis of agricultural materials [1,2]. Different approaches have been made to use starch for the production of tailored materials [3]. Native starch is transformed to obtain easy processed starch [4–6]. The so-called 'thermoplastic starch' (TPS) or plasticized starch is obtained after disruption and plastificization of native starch, with water and plasticizer. Unfortunately, properties of such a product do not fulfil all requirements in some applications such as packaging. To improve the properties, research laboratories have developed two strategies: chain modifications (e.g. acetylation) [7], and starch-based multiphased products. Compostable multilayers [8,9] or blends [10–14] have been developed by different associations between TPS and biodegradable polymers which are mainly biodegradable polyesters. These blends present quite good water resistance but mechanical properties are rather poor. TPS–polyester compatibility is more or less weak [12].

To preserve renewability (renewable raw materials), biodegradability and to improve the mechanical resistance of the final products, associations between cellulose fibres and TPS have to be tested. Several studies [15–22] and applications (e.g. automotive market) have demonstrated the interest of using cellulose fibres as reinforcement in thermoplastic matrixes but only few papers are focused on polysaccharide-based composites. Some authors [16–22] have shown that cellulose fibres or microfibrils in a TPS matrix improve the tensile strength. According to Frunke et al. (1998) [22], a significant improvement of water resistance is achieved by adding small amounts of commercial cellulose fibres (till 15%). Also, Dufresne et al. (1998, 2000) [19,20] show an improvement of water resistance by reinforcing plasticized starch films with cellulose microfibrils. This behaviour is related to the hydrophobic character of the cellulose fibres in comparison to starch hydrophilic property. Besides, these authors [19] show an improved thermal stability due to a higher and longer rubbery plateau.

The aim of this work is to test the addition of cellulose fibres in a TPS matrix and to report the subsequent properties. This paper is more particularly focused on the interaction between the fibres and the matrix. Various biodegradable composites have been elaborated with a soft TPS matrix and different fibre lengths and contents. Besides, we have used LDPE-based composites as reference materials, where the fibre–matrix interactions may be considered as poor since no specific compatibilizer are added [15–18]. LDPE grade has been chosen to show at

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Table 1
Mechanical properties of PE and TPS matrix without fibres (Standard deviations given in parentheses)

	Modulus (MPa)	Strength max. (MPa)	Deformation at break (%)	Shrinkage (S in %)
LDPE	111(9)	9.6(0.1)	102(3)	1.4
TPS	87(10)	3.6(0.1)	124(3)	15.4

room temperature, the same stiffness range (≈100 MPa) than the TPS matrix (Table 1). Mechanical properties (tensile, impact tests), thermomechanical (DMTA) and thermal (DSC) behaviours are evaluated. The microstructure is also investigated through SEM analysis.

2. Experimental

2.1. Composites preparation

Natural cellulose fibres from leafwood are obtained from JRS (Arbocel, Germany). Different cellulose fibres with increasing lengths are tested. For a constant average diameter of 20 μm, initial average lengths are, respectively, 60 (SF), 300 (MF) and 900 (LF) microns. Initial shape ratios are, respectively, 3, 15 and 45. Residue on ignition at 850°C during 4 h is less than 0.3%. In a previous paper [18], Amash and Zugenmaier have presented some characteristics of these fibres. According to these authors, the density of the fibres is 1.50 and the cellulose content is greater than 99.5%.

Wheat starch is obtained from Chamtor (France). According to the supplier, amylose and amylopectin contents are, respectively, 26 and 74%, and the residual protein (gluten) content is inferior to 0.2%. Glycerol used has purity close to 99.5%. Magnesium stereate (99% purity-Aldrich) is used as a demoulding agent at low concentration, less than 1 wt%. TPS matrix behaviour varies according to the formulation with corresponding variations of the glass transition [10]. TPS presents a soft and ductile behaviour. Glass transition determined by DSC analysis is 8°C. In a previous paper [10], the authors have presented the evolution of TPS density according to the TPS formulation. For this study, TPS density is 1.37.

Processing stages begin with dry blends preparation. Native wheat starch is weighted and introduced into a turbo-mixer. After addition of glycerol to the starch, the mixture is mixed at high speed (2000 rpm). Then, a vented oven (170°C, 45 min) allows glycerol diffusion into the starch granules as well as water volatilisation from the mixture. To obtain the adequate moisture content (Table 2), a determined quantity of water is added to the dry blend after cooling. After dispersion in the mixer, cellulose fibres are added to the blend. The final mixture is obtained after an ultimate high-speed (2500 rpm) mixing step. The powder is then extruded with a single screw extruder equipped with a conical-shaped element [10]. After a first granulation, pellets are extruded again to improve the fibres dispersion into the TPS matrix. Final pellets are equilibrated at 65%RH (relative humidity) for 8 days. An injection moulding machine DK Codim NGH 50/100 (France) with a clamping force of 50 ton is used to mould standard dumbbells. The screw barrel is regulated in temperature from 100 to 130°C and fed with the pellets. Mould temperature is 16°C. Injection pressure is 1500 bars. Holding pressure and time are, respectively, 1000 bars and 23 s. Cooling time is set to 9 s. After injection, the dumbbell specimens are equilibrated in a temperature and humidity controlled room (23°C, 54%RH), during 6 weeks.

Table 2
Glycerol and water contents before and after processing

	Glycerol content (wt%)	Water content (wt%)	Glycerol/starch (dry basis) ratio
Initial TPS formulation	18.0	12.0	0.26
Final contents (after processing)	17.1	10.7	0.24

Biodegradable composites are denoted as follows. 'TPS–10%MF' means that the composite is prepared by mixing 10 wt% of fibres of medium length (MF) and 90 wt% of TPS. Plasticized starch matrix is elaborated with wheat starch (70 wt%), glycerol (18 wt%) and water (12 wt%). SF, MF and LF fibres have been tested at different contents: 10 and 18 wt%.

Used as reference materials, synthetic composites are based on an untreated LDPE matrix. LDPE grade has been chosen to show at room temperature, the same stiffness range (around 100 MPa) than the TPS (Table 1). Polyethylene (PE) powder is obtained from Atochem, France (Lacqtene 1200MN18C). This is a low density radical PE made by a high-pressure process. MFI is 24 g/10 min (190°C, 2.16 kg) according to ISO standard N°1133. Density is 0.92 (supplier information). Cellulose fibres and PE powder are mixed in a turbo-mixer, then extruded and pelletized. After drying in a vented oven for 4 h at 80°C, pellets are injected to obtain dumbbells specimens in the same processing conditions than the biodegradable composite. Synthetic composites are denoted as follows. 'PE–5%MF' means that the composite is prepared by mixing 5 wt% of fibres of MF and 95 wt% of PE powder. SF and MF fibres have been tested at different contents: 5, 9, 13 and 20 wt%.

2.2. Uniaxial shrinkage

After injection, the uniaxial shrinkage is measured. It is defined by Eq. (1) where L is the length of the dumbbell specimens after cooling and L_0 is the length defined by the mould.

$$S = \left(1 - \left(\frac{L}{L_0}\right)\right) \times 100. \tag{1}$$

2.3. Mechanical properties

Moduli, tensile strengths and elongations at break are performed on a mechanical tensile tester (Instron 4204-GB) according to French standard NFT 51-034, with injected dumbbells specimens (length × thickness: 150×4 mm^2) conditioned at 54%RH and 23°C. Strain–stress curves are obtained with a velocity of 50 mm/min. Each mechanical parameter are determined from ten tested specimens.

2.4. Microscopy observations

Observations and images captures are carried out from cryogenic fractures on the central part of the dumbbell, with a scanning electronic microscope (Philips SEM 515, Netherland) at low accelerating voltage, 2.1 kV, without metal or carbon coating.

2.5. Thermal and thermo-mechanical analysis

The differential scanning calorimeter (Universal M-DSC 2920 TA instrument, USA) is cooled with liquid nitrogen circulation. Samples (10–20 mg) are cut out from a dumbbell specimen after conditioning and then placed in aluminium pans. A scan is performed between ambient temperature and 130°C. Scanning rate is 10°C per minute. An empty pan is used as reference. The glass transition temperature is computed as the midpoint of heat capacity increase. The glass transitions of plasticized starches are sometimes difficult to be determined by DSC analysis because the drop of heat capacity change is quite low at the glass transition. Then, DMTA determination is preferably used to approach this transition which is clearly demonstrated by a broad tan δ peak [11].

The dynamic thermo-mechanical analyser is a TA instrument DMA-2980 (USA). Samples are cut out from the central part of the dumbbells. Specimen dimensions are $4 \times 10 \times 60$ mm^3. They are tested by applying a bending constraint using the dual cantilever geometry. The displacement amplitude are set to 14.5 μm. The measurements are performed at the frequency of 1 Hz. The range of temperature is from −75 to 140°C, at the scanning rate of 1.5°C/min. Samples are coated with silicone wax to preserve water evaporation during scanning.

2.6. Moisture and glycerol contents

TPS moisture content is an important factor because water also acts as a plasticizer. Water content depends on the storage condition (humidity, temperature). Special care is taken to measure water contents because of the trend of TPS to absorb or desorb water. TPS injected specimens are ground under cryogen conditions and then stored at 54%RH and 23°C, during 8 days. The resulting powder is then heated at low temperature (40°C) in a vacuum oven for 3 h. Moisture percent is determined gravimetrically.

Glycerol content is determined using a high performance liquid chromatography (HPLC). After heating, the sample is washed in pure water under vigorous stirring to achieve complete diffusion of the plasticizer in the solution. Glycerol is determined by HPLC on an Acidex Ca$^+$ column (HPX 87C, BIO-RAD, USA) using water elution and differential refractometry detection at 85°C.

3. Results and discussion

For pure TPS, glycerol and water contents are given in Table 2. The evolution of glycerol/starch ratio gives the loss in glycerol. During processing stages, none or little glycerol is lost by volatilisation. In the extruder, to obtain the disruption of the native starch and to decrease the melt viscosity, a certain initial level of water is needed. Final moisture content is adjusted by the storage conditions. In this case, after processing and equilibration at 54%RH and 23°C, moisture content is lower than the initial water content (Table 1). Water contents for MF fibres and MF–TPS composites are given in Table 3. Final water content is inferior in the composites than in the pure TPS. Besides, water content decreases when the fibre content increases. This is partly due to the incorporation of fibres, which present lower water content. From the water contents of TPS and fibres, we can estimate the water content of the composite thanks to the linear Eq. (2), where WC and ww are, respectively, the water content and mass fraction.

$$\mathrm{WC}_{(\mathrm{composite})} = \mathrm{ww}_{(\mathrm{TPS})}\mathrm{WC}_{(\mathrm{TPS})} + \mathrm{ww}_{(\mathrm{Fibres})}\mathrm{WC}_{(\mathrm{Fibres})} \quad (2)$$

The estimations given by Eq. (2), and presented in Table 3, seems to be greater than the values determined on the composite gravimetrically. This difference could be due to interactions between matrix and fibres. Fibres could 'mobilize' sites which were used by water molecules in pure TPS.

Contrary to TPS, LDPE is a semi-crystalline polymer with an important crystallinity phase which determines its mechanical behaviour. The degree of crystallinity of the matrix can be modified by introduction of the fibres into the matrix, as reported by Amash and Zugenmaier (2000) [18]. The fibre surface could generate nucleation sites for the crystallisation and the partial crystalline growth of polyolefine spherulites. To compare the mechanical behaviour of both kind of composites and to estimate the reinforcing effect related to the fibres, we have to determine the crystallinity of the PE composites. The PE matrix crystallinity (X_c) is estimated from DSC experiments thanks to Eq. (3), where $\Delta H_f^0 = 290$ J/g for 100% crystalline LDPE and ww is the

Table 3
Values of water contents measured at 54%RH and 23°C, for fibres and composites and corresponding estimations

	Water contents (%)	Estimated water contents ($\mathrm{WC}_{\mathrm{composite}}$ in %)
MF	7.8	–
TPS–10%MF	9.8	10.4
TPS–18%MF	9.1	10.1

Table 4
DSC results of PE-based composites

Samples	Fibre fraction (ww%)	ΔH_f (J/g)	X_c (%) (crystallinity)
PE	0	104.2	35.9
PE–SF	5	97.9	35.4
	9	86.8	32.9
	13	77.3	30.7
PE–MF	5	97.2	35.2
	9	90.5	34.3
	13	86.1	34.1
	20	77.6	33.4

LDPE mass fraction in the composite, in weight percentage.

$$X_c = (\Delta H_f/\Delta H_f^0)(100/\mathrm{ww}) \tag{3}$$

Table 4 presents DSC results on PE-based composites. LDPE and LDPE composites present a melting temperature close to 110°C (Fig. 1). Data (Table 4) shows a slight reduction of the crystallinity by introducing fibres into an untreated PE matrix. The decrease is much more important for SF than for MF-based composites. This could be due to the greater interfacial surface generated by the shortest fibres. These decreases are not totally in agreement with results presented by Amash and Zugenmaier (2000) [18] on composites based on a treated (maleic anhydride) polypropylene matrix with the same (MF) cellulose fibres. With a compatibilized matrix, these authors show a slight increase of crystallinity with the fibre content. Nevertheless, the change in crystallinity seems to be too small to interfere strongly on the mechanical properties of PE composites. The crystallinity evolution can be considered as negligible and is not taken into account for the comparison of the mechanical behaviour between PE and TPS composites.

To estimate the reinforcing effect of each kind of fibre, composite/matrix ratios are calculated. In Figs. 2–4 are presented the different values of composites/matrix ratios versus the evolution of the fibre volume fraction. Modulus ratio is presented in Fig. 2. PE composites modulus present the usual linear function of the modulus versus the filler volume fraction [21]. This evolution is much more important for TPS composites which do not follow the same trend. On the graph, for a volume fraction of around 9%, we can compare both TPS and PE composites results. Reinforcing effect given by the modulus ratio is more than twice as much for TPS composite. We obtain for SF fibres: 1.77 (PE) and 3.64 (TPS), and for MF fibres: 2.16 (PE) and

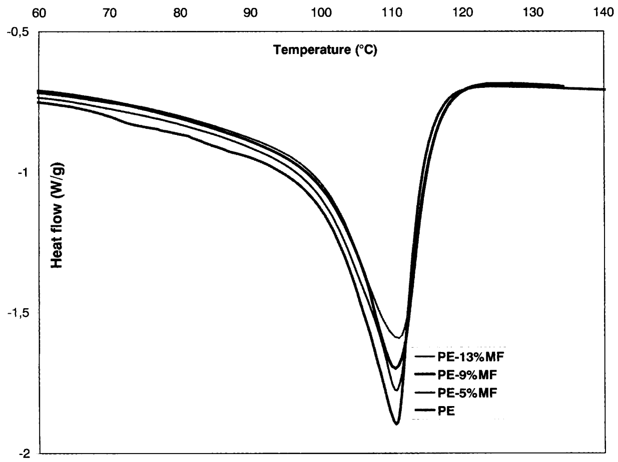

Fig. 1. DSC thermograms. Melting peak of PE-based composites (from bottom to top: PE, PE–5%MF, PE–9%MF and PE–13%MF).

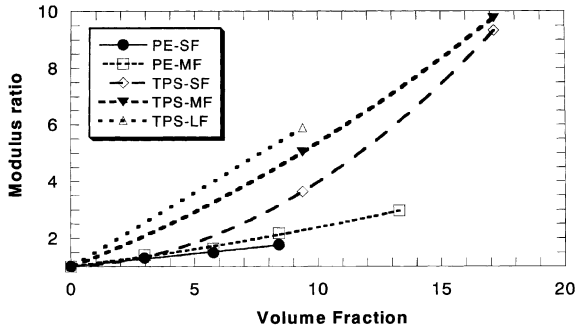

Fig. 2. Modulus ratio versus fibre volume fraction for PE and TPS-based composites.

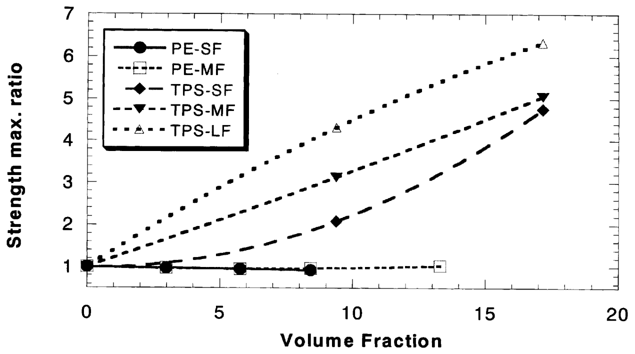

Fig. 3. Maximum strength ratio versus fibre volume fraction for PE and TPS-based composites.

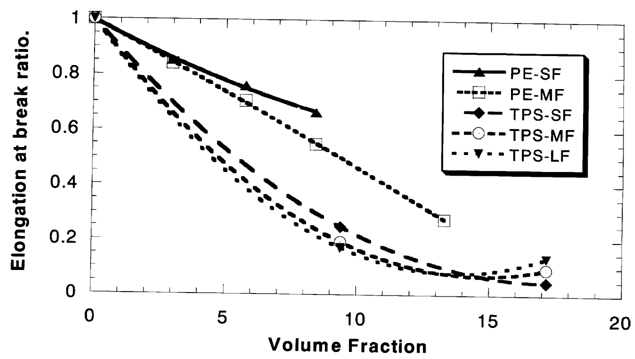

Fig. 4. Elongation at break ratio versus fibre volume fraction for PE and TPS-based composites.

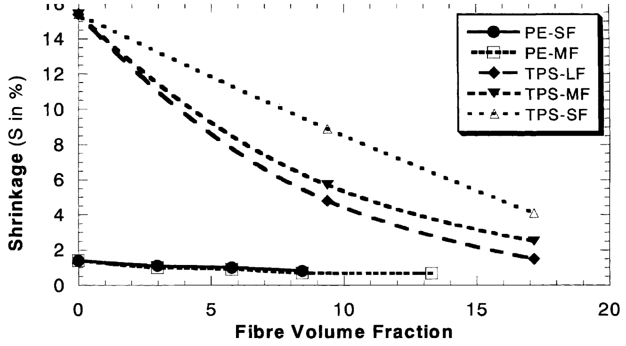

Fig. 5. Shrinkage versus fibre volume fraction for PE and TPS-based composites.

5.03 (TPS). Reinforcement effect increases with the fibre length and with the fibre content. Maximum strength ratios are presented in Fig. 3. For PE-based composites, values are quite constant whatever the fibre length. Besides, we can notice a slight decrease of the ratio with the fibre content. For TPS matrix, the ratio increases drastically with fibre length and fibre content. Fig. 4 presents the elongation at break results. Whatever the matrix and the fibre length, data decrease with fibre content. We can show greater diminution for TPS composites than for PE composites. These different results obtained from tensile tests (modulus, strength maximum and elongation at break) lead to the same conclusion: the reinforcing effect of cellulose fibres is much more efficient in a TPS matrix than in a polyolefin matrix.

For TPS, post injection shrinkage remains quite high (Table 1). It is a drawback, which can limit the material use in some applications. In the Fig. 5 are presented the values on both kind of composites. For PE-based composites the slight shrinkage reduction is mainly due to the 'filler effect'. Fibres present a constant density whatever the temperature and pressure conditions in the injection cycle. For TPS composites, the reductions of shrinkage largely overcome a filler effect. The addition of fibres drastically increases the dimensional stability. According to the fibre length evolution, we can notice that the longest fibres improve much more the shrinkage reduction. Fibre–matrix interactions stabilize the system by forming a kind of 3D organisation and then minimize the shrinkage.

DMTA results are presented in Figs. 6 and 7. Storage modulus (E') and tan δ have been plotted versus temperature. The evolution of tan δ show two relaxations (Fig. 6). The main relaxation (α) associated with a large tan δ peak and an important decrease of the storage modulus can be attributed to the TPS glass relaxation. In a previous publication [11], we have shown that the secondary relaxation (β) could be consistent with the glycerol glass transition. $T_{\beta\ \mathrm{transition}}$ occurs around −50°C. In Fig. 6, the most striking result is the strong evolution of the temperature corresponding to the main relaxation ($T_{\alpha\ \mathrm{transition}}$), by introduction of the fibres to the TPS matrix, which cannot be explained by a slight moisture contents decrease (Table 3). From 0 to 10 wt% fibres, the $T_{\alpha\ \mathrm{transition}}$ shifts from 31 to 59°C. This evolution could be linked to strong fibre–matrix interactions between the two carbohydrate products. The existence of

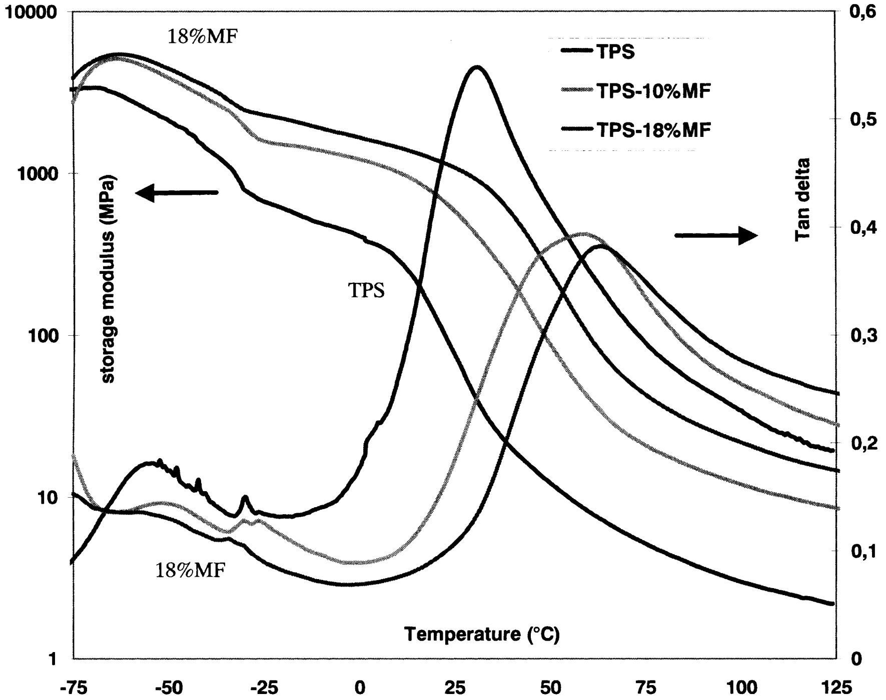

Fig. 6. Storage modulus and tan δ curves (DMTA) for TPS, TPS–10%MF and TPS–18%MF.

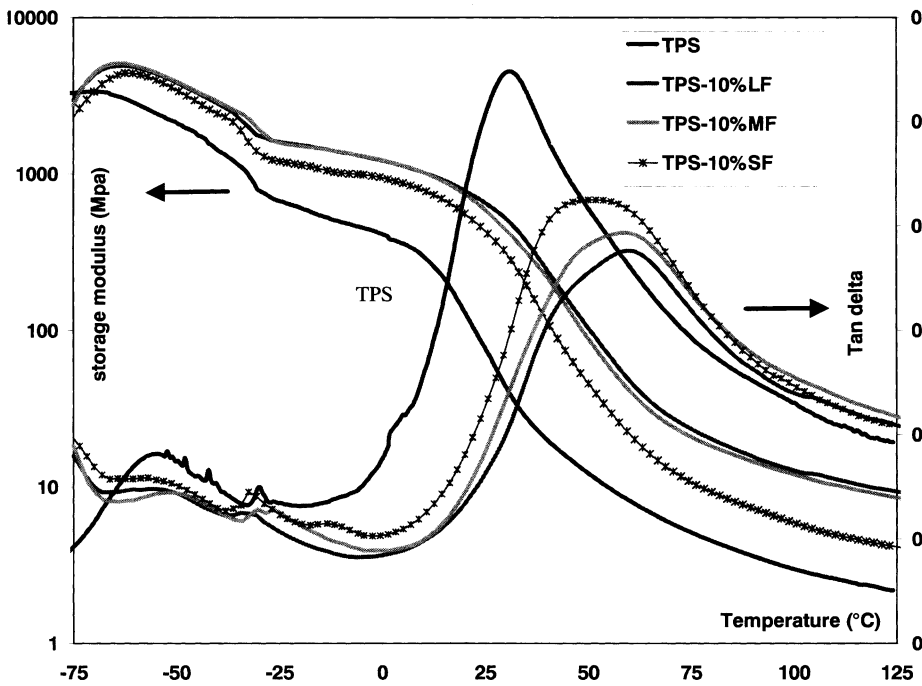

Fig. 7. Storage modulus and tan δ curves (DMTA) for TPS, TPS–10%SF and TPS–10%MF and TPS–10%LF.

such interactions has yet been assumed by Dufresne et al. (1998, 2000) [19,20], on a system composed by plasticized potato starch with microfibrils from potato pulp. Such interactions decrease starch chain mobility and consequently increase the matrix glass transition. In Fig. 6, the $T_{\alpha \text{ transition}}$ presents an increase from 59 to 63°C when fibre content ranges from 10 to 18 wt%. With the introduction of fibres, storage modulus present an increase before and after α transition. By introducing 18 wt% fibres to TPS, the rubber plateau increases of about one decade. In Fig. 7, the $T_{\alpha \text{ transition}}$ are 51, 59 and 60°C for, respectively, SF, MF and LF. $T_{\alpha \text{ transition}}$ increases with fibre length. The addition of fibres involves a reinforcing effect, which can be evaluated by the shift of the storage modulus towards higher values.

Cellulose fibre shape is ribbon-like. On the SEM surface observation obtained from a cryogenic fracture of PE composite (Fig. 8), we can observe the free fibre extremities. The LDPE matrix is inert, we have no fibre–matrix interactions. Fig. 9 is obtained from a cryogenic fracture of TPS composite. On this SEM observation, we can visualize that fibres are embedded in TPS. This is due to

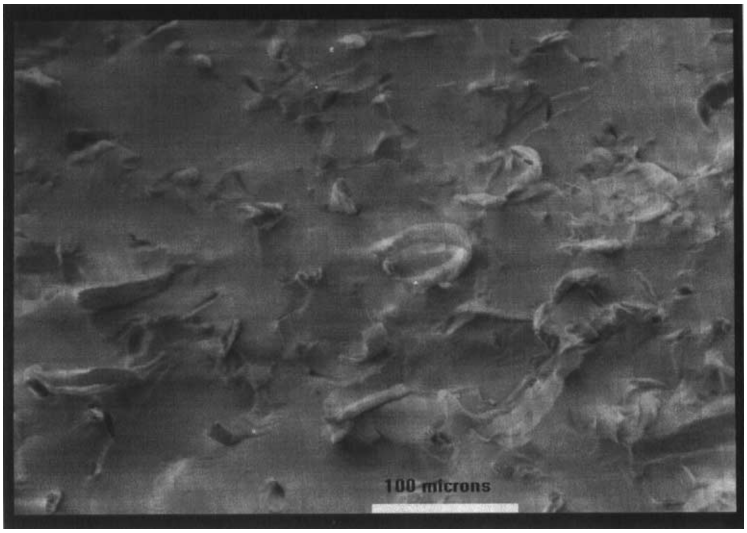

Fig. 8. SEM examination after cryogenic fracture of a PE-based composite: PE–13%MF (white scale = 100 μm).

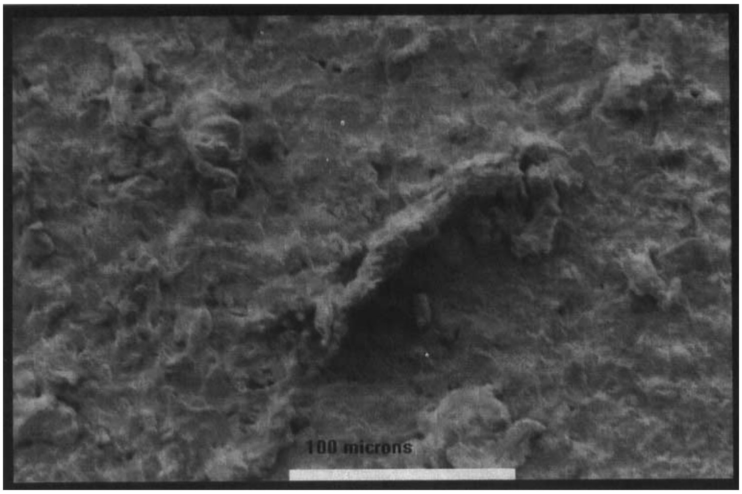

Fig. 9. SEM examination after cryogenic fracture of a TPS-based composite: TPS–10%MF (white scale = 100 μm).

strong interactions between the cellulose fibres and the plasticized starch matrix.

4. Conclusion

Plasticized starch composites are produced by introduction of leafwood cellulose fibres into a matrix obtained from water/glycerol plasticization of wheat starch. Different fibre lengths and contents are used. Properties of such composites are compared to a LDPE composites where fibre–matrix interactions are known to be very poor. We have shown an increase of the main transition temperature (DMTA) of about 30°C by the introduction of fibres. This phenomena could be related to fibre–matrix interactions and a decrease of starch chain mobility. These interactions have influence on the mechanical behaviour. We have shown that the properties of TPS composites are increased. Modulus or maximum strength results show a strong improvement by addition of fibres to the TPS matrix. In comparison, the reported values are much more important than the LDPE composites properties which show a simple reinforcing effect. The interactions between fibres and the inert PE matrix are poor. Although the glass transition temperature of TPS composites cannot be directly determined, we can estimate the temperature shift using DMTA determinations with the change of the temperature of main relaxation. We are in a domain where rubbery to glassy transitions can occur. Then, the strong evolution of mechanical behaviour of TPS composites is due to a common reinforcing effect but also to glass transition shift toward a value close to the ambient temperature. The shrinkage reduction, The difference between the water content determined on TPS composite and the water content calculated from TPS and fibre moisture contents, may be related to the interactions between the carbohydrate matrix and the cellulose fibres, SEM observations have clearly shown this phenomenon. Cryogenic fracture surface shows that fibres are embedded in TPS.

Such biodegradable composites gain enhanced performances properties compared to raw TPS. However, some investigations are currently underway to improve some properties such as the water sensitivity, to fulfil requirements for different applications.

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