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Biocomposites based on plasticized starch: thermal and mechanical behaviours

L. Averous[a,*], N. Boquillon[b]

[a]LIPHT, ECPM (ULP), 25 rue Becquerel, 67087 Strasbourg Cedex 2, France
[b]Agro industry Research and Development, ARD, Route de Bazancourt, 51110 Pomacle, France

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Abstract

The paper is focusses on the study of the thermal and mechanical behaviour of reinforced agro-materials. Various formulations based on plasticized starch matrix have been carried out, varying matrix formulation, filler content, fibres length and nature. Cellulose and lignocellulose fibres, which show unequal surface tensions, have been tested. After extrusion and injection moulding, the properties of these wheat starch-based biocomposites are analysed. Mechanical properties (tensile tests), thermo-mechanical properties (DMTA) and thermal degradation (TGA) are analysed. DMTA analysis shows important variations of main relaxation temperature, which can be linked both, to interactions resulting in a decrease of starch chain mobility and to a regular reinforcing effect. These results are consistent with the static mechanical behaviour, which vary according to the filler content (up to 30 wt%), fibre nature (cellulose vs. lignocellulose) and fibre length (from 60 μm to 1 mm). Besides, we have shown that the addition of cellulose fillers improves the thermal resistance of these biocomposites. Finally, we have tested the impact of the addition of biodegradable polyesters into these composites without significant effect on the post-processing stability.

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Keywords: Composite; Plasticized starch; Cellulose fibres; Mechanical properties

1. Introduction

Ecological concerns have resulted in a renewed interest in natural and compostable materials, and therefore issues such as biodegradability and environmental safety are becoming important. Tailoring new products within a perspective of sustainable development or eco-design, is a philosophy that is applied to more and more materials. It is the reason why material components such as natural fibres, biodegradable polymers can be considered as 'interesting'—environmentally safe—alternatives for the development of new biodegradable composites.

Biocomposites (biodegradable composites) consist of biodegradable polymers as the matrix material and biodegradable fillers, usually biofibres (e.g. lignocellulose fibres). Since both components are biodegradable, the composite as the integral part is also expected to be biodegradable (Mohanty, Misra, & Hinrichsen, 2000c). Fig. 1 shows a classification of biodegradable polymers in four families. Except the fourth family, which is of fossil origin, most polymers (family 1–3) are obtained from renewable resources (biomass). The first family are agro-polymers (e.g. polysaccharides) obtained from biomass by fractionation. The second and third families are polyesters, obtained, respectively by fermentation from biomass or from genetically modified plants (e.g. polyhydroxyalkanoate: PHA) and by synthesis from monomers obtained from biomass (e.g. polylactic acid: PLA). The fourth family are polyesters, totally synthesised by the petrochemical process (e.g. polycaprolactone: PCL, polyesteramide: PEA, aliphatic or aromatic copolyesters). A large number of these biodegradable polymers (biopolymers) are commercially available. They show a large range of properties and they can compete with non-biodegradable polymers in different industrial fields (e.g. packaging).

Cellulose-based fibres are the most widely used, as biodegradable filler. Intrinsically, these fibres have a number of interesting mechanical and physical properties

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[*] Corresponding author. Tel.: +33-3902-42707; fax: +33-3902-42716.
E-mail address: averousl@ecpm.u-strasbg.fr (L. Averous).

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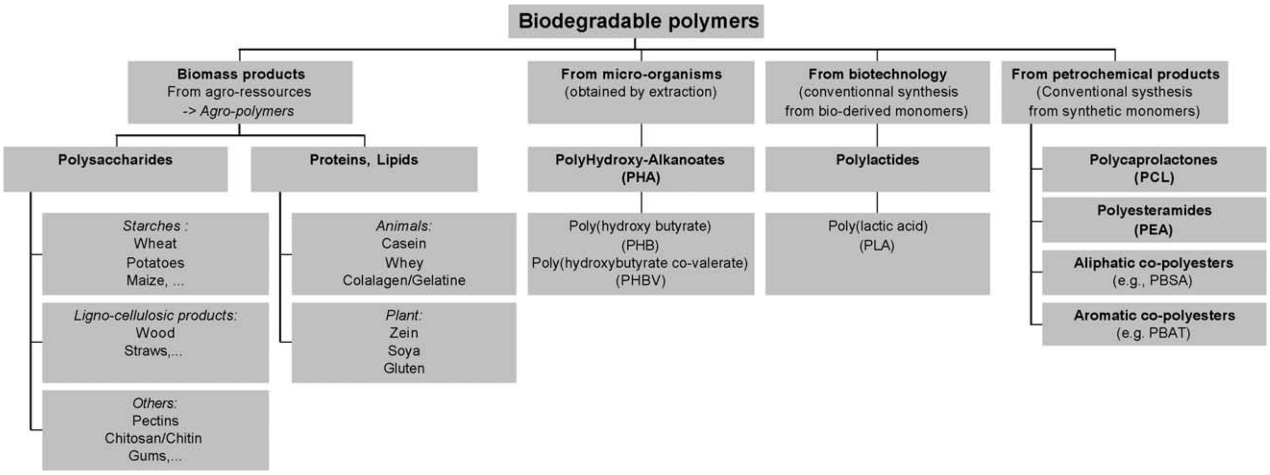

Fig. 1. Classification of biodegradable polymers.

(Bledzki & Gassan, 1999; Mohanty et al, 2000c). With their environmentally friendly character and some techno-economical advantages, these fibres are of interest in an increasing number of industrial sectors (e.g. automotive) to replace glass fibres.

Although some authors (Wollerdorfer & Bader, 1998) have tested complex associations such as cellulose fibres with both, biopolyester and plasticized starch; most of studies are merely based on the biopolyester matrix (Mohanty et al, 2000c; Netravali & Chabba, 2003). PHA has been combined with cellulose fibres (Bourban et al., 1997; Wollerdorfer & Bader, 1998), cellulose whiskers (Dufresne, 2000), jute fibres (Wollerdorfer & Bader, 1998; Mohanty, Khan, & Hinrichsen, 2000a), abaca fibres (Shibata, Takachiyo, Ozawa, Yosomiya, & Takeishi, 2002), pineapple fibres (Luo & Netravali, 1999), flax fibres (Van de Velde & Kiekens, 2002), wheat straw fibres (Avella et al., 2000) or lignocellulosic flour (Dufresne, Dupeyre, & Paillet, 2003). PLA has been associated to paper waste fibres, wood flour (Levit, Farrel, Gross, & McCarthy, 1996), kenaf (Nishino, Hirao, Kotera, Nakamae, & Inagaki 2003), jute (Plackett, Logstrup Andersen, Batsberg Pedersen, & Nielsen, 2003) or flax fibres (Oksman, Skrifvars, & Selin, 2003; Van de Velde & Kiekens, 2002). Some authors have tested flax (Van de Velde & Kiekens, 2002) or sisal (Ruseckaite & Jimenez, 2003) with PCL. Mohanty, Khan, & Hinrichsen (2000b) have reinforced PEA with jute fibres. Aliphatic copolyesters have been used with cellulose fibres (Wollerdorfer & Bader, 1998), bamboo fibres (Kitagawa, Watanabe, Mizoguchi, & Hamada, 2002) or flax, oil palm, jute or ramie fibres (Wollerdorfer & Bader, 1998). Aromatic copolyesters (e.g. polybutylene adipate-co-terephthalate: PBAT) have been associated with wheat straw fillers (Le Digabel, Boquillon, Dole, Monties, & Averous, 2003).

Another important biocomposites category is based on agro-polymers matrixes, mainly focussed on starchy materials. Plasticized starch, the so-called ‘thermoplastic starch’ (TPS) is obtained after disruption and plasticization of native starch, with water and plasticizer (e.g. polyol) by applying thermomechanical energy in a continuous extrusion process. Unfortunately, TPS shows some drawbacks such as a strong hydrophilic character (water sensitive), rather poor mechanical properties compared to conventional polymers and an important post-processing variation of the properties. TPS properties reach equilibrium only after several weeks. To improve these material weaknesses, TPS is usually associated with others compounds. Biocomposites (TPS/cellulose-based fillers) have been studied by different authors. Various types of fibres, microfibrils or whiskers have been tested such as microfibrils from potato pulp (Dufresne & Vignon, 1998; Dufresne, Dupeyre, & Vignon, 2000), bleached leafwood fibres (Funke, Bergthaller, & Lindhauer, 1998; Avérous, Fringant, & Moro, 2001), fibres from bleached eucalyptus pulp (Curvelo, De Carvalho, & Agnelli, 2001), flax and ramie fibres (Wollerdorfer & Bader, 1998), wood pulp (De Carvalho, Curvelo, & Agnelli, 2002) and tunicin whiskers (Angles & Dufresne, 2000, 2001; Mathew & Dufresne, 2002). Most of these authors have shown that between both polysaccharides, a high compatibility occurs. They have found high improvements of the performances (e.g. tensile and impact tests results), which are in part linked to an usual matrix reinforcement (Bledzki & Gassan, 1999). Another part of the mechanical properties increase is brought by the inter-relations fibre-matrix. The main attributes are higher moduli (Dufresne & Vignon, 1998; Dufresne et al., 2000; Funke et al., 1998; Avérous et al., 2001; Curvelo et al., 2001), reduced water sensitivity due to fibre–matrix interactions and to the higher hydrophobic character of the cellulose, which is linked to its high cristallinity (Funke et al., 1998; Avérous et al., 2001; Curvelo et al., 2001). Fibres addition induces variation of properties, due to the formation of a 3D network between the different carbohydrates, through hydrogen bonds.

This paper complements and expands a previous publication (Avérous et al., 2001), which was based on the analysis of some starchy composites, reinforced with bleached cellulose fibres. The aim of this paper is focussed on the thermal and mechanical properties of biocomposites based on different plasticized starch matrixes and various cellulose-based fibres. We have analysed the influence of fibres lengths and the impact of fibres nature (low cost paper pulp and bleached cellulose fibres), associated with different filler contents. To obtain a better water resistance, biodegradable polyesters are usually associated with TPS. Biodegradable polyesters have also been tested as potential post-processing stabilizers of the reinforced starchy phase. For this purpose and following previous papers (Avérous, Fauconnier, Moro, & Fringant, 2000a; Avérous & Fringant, 2001; Avérous, Moro, Dole, & Fringant, 2000b; Martin, Schwach, Avérous, & Couturier, 2001), we have tested two different biodegradable polyesters (PEA and PCL), which show variable affinities with TPS (PEA-TPS > PCL-TPS). On these different biocomposites, we have studied mechanical properties (tensile tests). Besides, Thermo-mechanical behaviours (DMTA) are reported. And finally, thermo-gravimetric analysis (TGA) have been used to test the thermal resistance in relation to the incorporation of fibres into the starchy matrix.

2. Experimental

2.1. Materials

2.1.1. Fillers

Natural cellulose fibres from leafwood are supplied by Omya Rettenmier (JRS-Arbocel, Germany). Different semi-crystalline cellulose microfibres with increasing lengths are tested. The fibres are like ribbons, with an average diameter close to 20 μg, determined by image analysis (Fig. 2a, and below). Initial average lengths are respectively 60 (SF), 300 (MF) and 900 (LF) microns. Initial shape ratios (length/diameter) are respectively 3, 15 and 45. Cellulose content is greater than 99.5%. Residue on ignition at 850 °C during 4 h is less than 0.3%. In a previous paper, Amash and Zugenmaier (2000) have presented some characteristics of these fibres. According to these authors, fibres density is 1.50 g/ml. To withdraw fibres aggregates, which lead to non-homogeneous fibres distribution into the composites, the fibres are sieved on a 1 mm grid.

Paper pulpfibers (PPF) supplied by La Rochette (France) are prepared before incorporation. PPF is obtained from broad-leaved species through a semi-chemical pulping treatment involving a chemical fractionation at 175 °C using ammonium sulfite followed by a mechanical treatment in a refiner. Paper pulp is taken on a production line before mixing with recycled fibres and sheet forming. Moisture content is then 65 wt%. To prepare the filler (PPF), the pulp sample is rinsed with distilled water and then pressed until 30% residual water content. These fibres are oven dried 12 h. Residual water content decreases below 3 wt%. PPF are finally grinded using a hammer mill fitted with a 1 mm grid. Fibres density is close to 1.5. Fibres size is determined by image analysis (see Fig. 2b, and below). Compared to LF, PPF fibres are less homogeneous in terms of length and diameter, but a majority of fibres seems to exhibit a shape ratio close to 45, like LF fibres.

2.1.2. Matrix materials

For this study, wheat starch from Chamtor (France) has been used. According to this supplier, amylose and amylopectin contents are respectively 26 and 74%, and the residual protein (gluten) content is less than 0.2%. Glycerol (99.5% purity -Chamtor) is the plasticizer. Magnesium stereate (99% purity -Aldrich) is used as a demoulding agent at low concentration, less than 1 wt%. Different plasticized starch matrixes have been tested and named, TPS_1 (rather brittle at room temperature) or TPS_2 (higher plasticizer content, soft at room temperature). TPS_1 is prepared with dried wheat starch (70 wt%), glycerol (18 wt%) and water (12 wt%) and, TPS_2 with dried wheat starch (65 wt%) and glycerol (35 wt%). After equilibration in a temperature and humidity controlled room (23 °C, 54%RH) for 2 weeks (No significant variation between 2 and 6 weeks), moisture contents are 10.7 and 12.6 wt% for

(a) (b)

Fig. 2. Images from LF (a) and PPF fibres, obtained by optic microscopy. Scale = 100 μg.

Table 1
Main materials characteristics

	PCL Solway (CAPA 680)	PEA Bayer (BAK 1095)	TPS_1	TPS_2
Density (g/ml)	1.11	1.07	1.37	1.34
Melting point, in °C (DSC)	65	112	None	None
Glass transition, in °C (DSC)	−61	−29	8	−20
Cristallinity, in %	67	33	None	None
Modulus[a], in MPa	190 (6)	262 (12)	87 (10)	12 (1)
Elongation at break[a], in %	>500	420 (59)	124 (3)	60 (5)
Max. tensile stress[a], in MPa	14.2 (1.4)	17.2 (5.2)	3.6 (0.1)	1.4 (0.3)
Biodegradation[b] (Mineralization in %)	100	100	100	100
Surface tension[c] ($\sigma = \sigma^d + \sigma^p$), in mJ m^{-2}	52	59	42	32
Dispersive component (σ^d), in mJ m^{-2}	41	37	23	20
Polar component (σ^p), in mJ m^{-2}	11	22	19	12

[a] According to NF 51-035 1983. Standard deviations given in bracket. TPS materials are tested 4 weeks after injection.

[b] At 60 days in controlled composting according to ASTM 5336 (Bastioli, 1998).

[c] Determinations from contact angles measurements of probes liquids.

TPS_1 and TPS_2, respectively. But, these values decrease after addition of cellulose-based fibres (Avérous et al., 2001). The variation of TPS density according to the formulation is shown on Table 1 along with others properties such as glass transition temperatures.

2.1.3. Biodegradable polyesters

Two different biodegradable polyesters have been used, polycaprolactone and polyesteramide. They have been provided by Solvay (CAPA 6800) and Bayer (BAK 1095), respectively. Fig. 3 and Table 1 give the chemical structures and the properties of these polyesters. Poly ε-caprolactone (PCL), which is synthesised by ROP (Ring Opening Polymerisation) of ε-caprolactone, shows a very low Tg (−61 °C) and a low melting point (65 °C). Polyesteramide (PEA) is industrially obtained from the statistical copolycondensation of polyamide monomers and adipic acid (Grigat, Koch, & Timmermann, 1998). Bayer had developed different commercial grades under BAK® trademark but their productions stopped in 2001. PEA exhibits high polar component (Table 1) and then, good compatibility with other polar products, such as starchy compounds (Avérous et al., 2000a).

2.1.4. Biocomposites preparation and formulations

Processing began with dry blend preparation. Native wheat starch is weighed 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. After cooling, water is added to the dry blend according to the formulation (Avérous and Fringant, 2001). 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 (Avérous et al., 2000b) with or without polyester granules. After a first granulation, pellets are again extruded to improve dispersion. Final pellets are equilibrated at 50%RH (Relative Humidity) for 8 days. An injection-moulding machine (DK Codim NGH 50/100-France) with a clamping force of 50 tons 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 20-25 °C. Injection pressure is 1500 bars. Holding pressure and time are 1000 bars and 20 s, respectively. Cooling time is set to 10 s. After injection, the dumbbell specimens are equilibrated in a temperature and humidity controlled room (23 °C, 54%RH), during 2, 4 or 6 weeks.

Table 2 compiles the different associations we have carried out. Biodegradable composites are denoted as follows. 'TPS_2/15 wt%MF + 10 wt% Polyester' means that the composite is prepared by mixing 15 wt% of medium length fibres (MF) with 85 wt% of TPS_2. To this formulation, we have added 10 wt% of polyester.

2.2. Characterizations

2.2.1. Fibre size

Fibre size is determined on a Zeiss Axioskop 2 Plus microscope fitted with ×10 magnification lens Images (e.g. Fig. 2) are recorded through Axiovision software. Fibres are put in suspension, at a concentration of 4 g/l using a pulp disintegrator at a constant speed of 2975 ± 25 rpm.

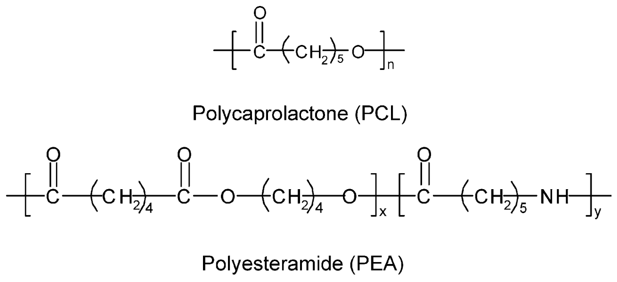

Fig. 3. Chemical structures of both biodegradable polyesters.

Table 2
Composites: (a) TPS_1-based formulations (b) TPS_2-based formulations

TPS_1-based composites					
Filler (wt%)	0, 15 or 30				
Polyester (wt%)	+0, 10 or 25				
Post-injection periods: 2 and 6 weeks (equilibration 23 °C, 54%RH)					
TPS_2-based composites		SF	MF	LF	PPF
Filler (wt%)	0	4, 8, 12 or 16	4, 8, 12 or 16	10 or 20	10 or 20
Post-injection period: 4 weeks (equilibration 23 °C, 54%RH)					

A drop of suspension is settled on a glass slide. The slide is then oven dried until complete water evaporation.

2.2.2. Mechanical properties

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

2.2.3. Thermo-mechanical analysis

For convenience, two kinds of thermo-mechanical determinations have been performed. Samples were tested in bending mode using dual cantilever geometry on TA Instruments DMA-2980 (GB) dynamic thermo mechanical analyser. Samples are cut out from the central part of the dumbbells. Specimen dimensions are $4 \times 10 \times 60\ mm^3$. The displacement amplitude is set to 10 μm. The measurements are performed at a frequency of 1 Hz. Over a temperature range from − 100 to 120 °C, at a scanning rate of 1.5 °C/min. Samples are coated with silicone wax to avoid water evaporation during scanning.

Measurements were also made on a TA Instruments AR1000 rheometer fitted with torsion solid clamps. Sample size are $4 \times 10 \times 40\ mm^3$, cut from central part of the dumbbells. The shear measurements are performed at the frequency of 1 Hz and 0.01% strain. The range of temperature is from − 50 to 120, at a scanning rate of 3.0 °C/min. This analyser has been used to test all TPS_2/LF and PPF composites (see Table 2b).

2.2.4. Thermo-gravimetric analysis

TGA are carried out with a Setaram TGDTA92 (France) apparatus, at a rate of 10 °C/min from ambient to 650 °C. Analysis are performed under a nitrogen atmosphere with a 20 ml/min flow rate. Degradation temperatures are determined from the DTG scans, as the peak maximum.

3. Results and discussions

3.1. TPS behaviour

The glass transition of plasticized starch is sometimes difficult to be determine by DSC analysis, because the heat capacity change is quite low at the glass transition Then, DMTA determination is preferably used to obtain this transition, which is clearly demonstrated by a broad tangent δ peak. Fig. 4 illustrates the variation of tangent δ, loss and storage modulus for TPS_2 matrix. The perturbations close to − 20 °C are due to the DMTA apparatus, linked to

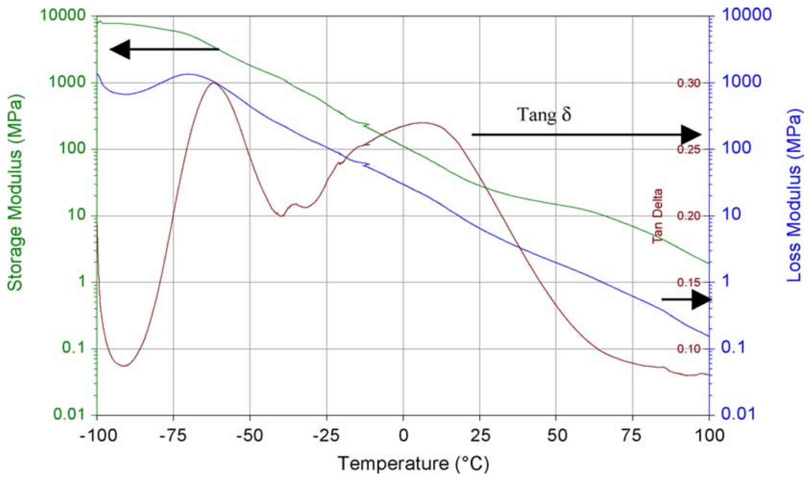

Fig. 4. Rheological TPS_2 behaviours: storage and loss modulus, tangent delta vs. temperature.

Table 3
DMTA results

	wt%	α Transition		β Transition	
		T_α (°C)	Height at T_α	T_β (°C)	Height at T_β
	0	3 (1)	0.27 (0.01)	− 66 (1)	0.30 (0.01)
SF	8	6(1)	0.26 (0.01)	− 64 (1)	0.28 (0.01)
	12	9 (1)	0.27 (0.01)	− 63 (1)	0.27(0.01)
MF	8	7 (1)	0.24 (0.01)	− 64 (1)	0.28 (0.01)
	12	12 (1)	0.22 (0.01)	− 62 (1)	0.26 (0.01)
LF	10	7 (1)	0.23 (0.01)	nd	nd
	20	15 (1)	0.23 (0.01)	nd	nd
PPF	10	12 (1)	0.21 (0.01)	nd	nd
	20	18 (1)	0.22 (0.01)	nd	nd

nd = not determined.

an internal change of the cooling system. Tangent δ drawing shows two relaxations (α and β). The main relaxation (named α), associated with a large tangent δ peak and an important decrease of the storage modulus, can be attributed to the TPS glass relaxation. From TPS_1 to TPS_2, we can follow the T_α decrease linked to the plasticizer level ($T_\alpha TPS_1 = 31$ °C, $T_\alpha TPS_2 = 3$ °C). With the formulations we have used out, we are always in the situation where the glycerol content is above the anti-plasticization critical concentration, described by Lourdin et al. (1997a). Besides, we are in a range where glycerol demixing can occur. In a previous publication, Avérous et al. (2000a,b), as other authors (Lourdin, Bizot, & Colonna, 1997a), have shown the second relaxation (named β) could be consistent with the glycerol glass transition. T_β transition, temperature of the second maximum of tangent δ, occurs around − 50 to − 70 °C. β relaxation is linked with high values of the loss modulus. Maximum of loss modulus corresponds to the initial transition region, the so-called 'onset' temperature (Turi, 1997). Several authors (Avérous et al., 2000b; Lourdin, Bizot, & Colonna, 1997b) have shown that the secondary transition is dependent on the glycerol concentration and more particularly on the 'free' glycerol, due to phase separation. T_β decreases with the glycerol content ($T_\beta TPS_1 = -54$°C, $T_\beta TPS_2 = -66$ °C). Glycerol mobility is higher because we are in the case of heterogeneous systems with glycerol rich domains, which increase with glycerol content. Then, higher plasticized materials can show poorer mechanical properties. Table 1 compares the mechanical properties obtained from tensile tests on TPS_1 and TPS_2 materials. TPS_1, which is less plasticized, shows the highest values. Compared to TPS_2, a higher elongation at break is observed for TPS_1. Besides, if we compare the surface tension of both matrixes, TPS_1 shows higher values.

3.2. Influence of the filler content and fibre length

We have mainly compared the behaviours of two different fibre lengths: SF and MF Table 3 shows the values of T_α and T_β for 'TPS_2-cellulose fibres' biocomposites. The values of the heights of tangent delta at T_β and T_α seem to decrease as the fibre length increases. This decrease means a decrease of the mobile units at T_α. Such a behaviour has been shown on reinforced thermoplastics. Besides, the impact of the filler content on the tangent δ heights seems not to be very significant. In agreement with results obtained on TPS_1 matrix, described elsewhere (Avérous et al., 2001), we can show that both transitions temperatures increase with the addition of cellulose-based fibres. These temperature increases depend on the fibre length (SF vs. MF) and fibre content and must be due both to interfacial effects, strong H-bond interactions between polar components (e.g. carbohydrates), and to mechanical reinforcing effects. If we compare T_α variation for TPS_2 and TPS_1 composites, we can see that temperature shifts are much more important for TPS_1-based composites (e.g. ΔT_α(TPS_1/0 and 10%SF) = 20 °C). It seems that we get a coupling between the variations of T_α and T_β.

Fig. 5 shows the variations of storage and loss modulus for different SF-based composites. For each composite, we can observe an important decrease of both moduli

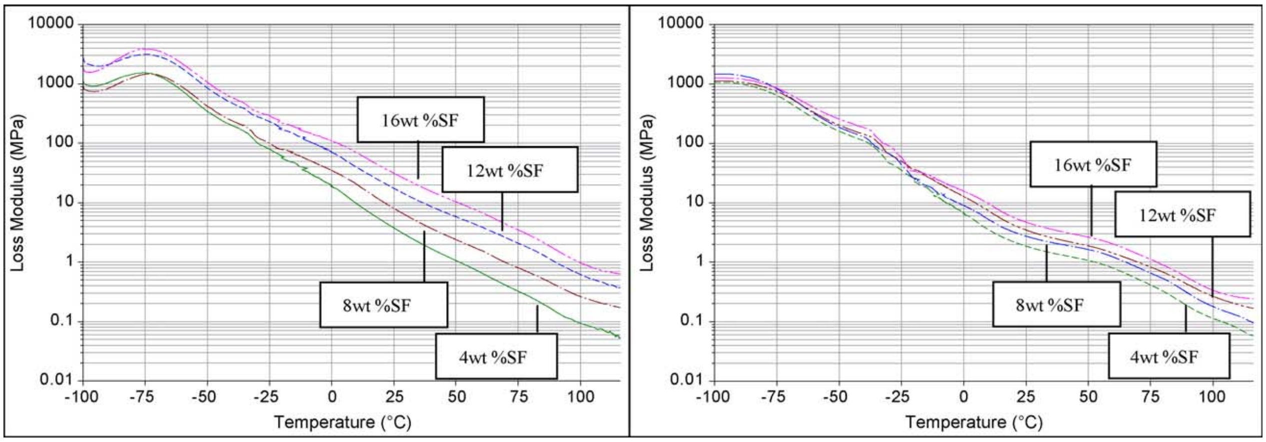

Fig. 5. TPS_2/SF composites with different filler contents. Variations of loss and storage modulus vs. temperature.

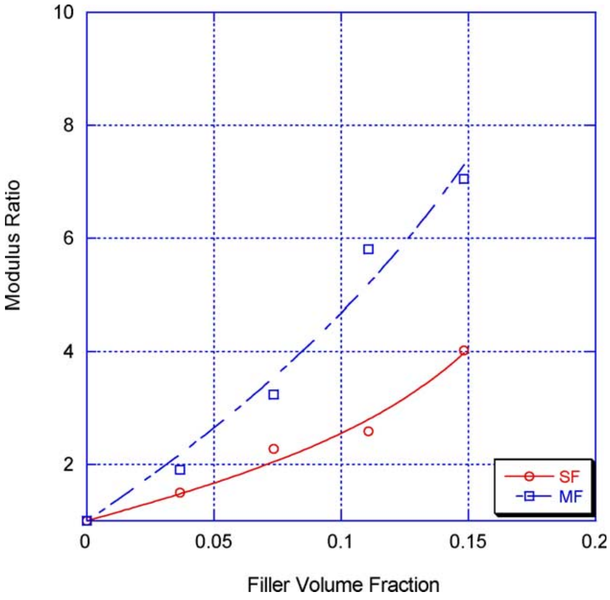

Fig. 6. TPS$_2$/SF and MF composites. Variation of modulus ratios (composite/matrix) vs. filler volume fraction.

according to the temperature. From −100 to +100 °C, more than 3 and 4 decades are lost for storage and loss modulus. A modulus increase is shown with the fibre content raise. Storage modulus shows a plateau above ambient temperature. After the plateau, curves evolution is typical of an amorphous material with a gradual decrease in the storage modulus.

To estimate the reinforcing effect of each kind of fibre, composite/matrix ratios are calculated from tensile test results. On Figs. 6–8 are shown the different variation of composites/matrix ratios versus the fibre volume fraction, for composites based on TPS$_2$ matrix and, SF or MF fibres.

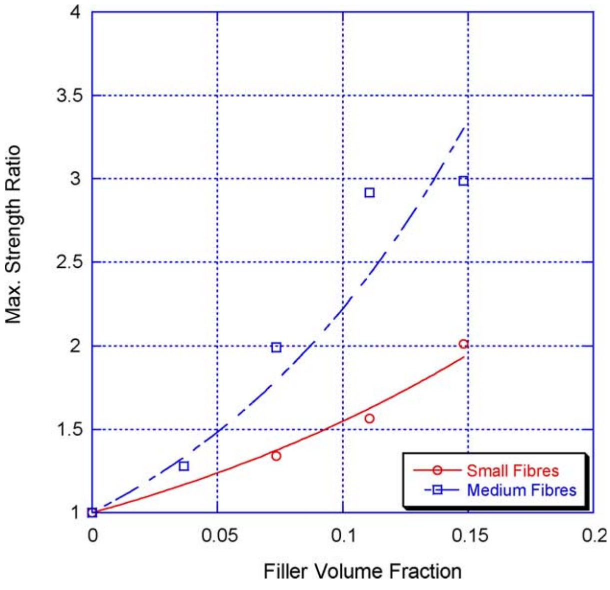

Fig. 7. TPS$_2$/SF and MF composites. Variation of maximum strength ratios (composite/matrix) vs. filler volume fraction.

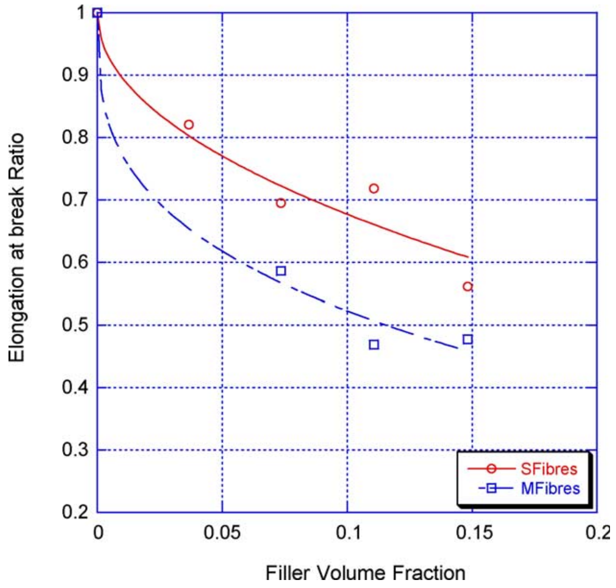

Fig. 8. TPS$_2$/SF and MF composites. Variation of elongation at break ratios (composite/matrix) vs. filler volume fraction.

Volume fractions (v) are determined from the fractions in weight (ww) according to Eq. (1), using the density of each component (d).

$$v_i = \frac{ww_i/d_i}{\sum_i ww_i/d_i} \tag{1}$$

According to previous 2D/3D simulations (Favier, Dendievel,- Canova, Cavaille, & Gilormini, 1997), in our case i.e., with the added fillers contents and with the fillers shape ratios (3 and 15), it seems that we are below or at the limit of the percolation threshold for TPS$_2$ composites. Modulus ratio is shown on Fig. 6. TPS$_2$ composites modulus displays a regular behaviour; reinforcement effect increases with the fibre length and, with the fibre content. The trends, we have drawn (solid and dashed lines) on Fig. 6 are based on a Nielsen model-like fitting (Nielsen & Landel, 1994). TPS$_1$ composites values have been given in a previous publication (Avérous et al., 2001), we obtain rather the same trends for both TPS matrixes.

Maximum strength ratios are shown on Fig. 7. In agreement with previous results with TPS$_1$ composites (Avérous et al., 2001), the ratio increases drastically with the fibre length and the fibre content. This behaviour is typical of a good fibre-matrix adhesion (Nielsen & Landel, 1994). Eq. (2) has been fitted (solid and dashed lines) on the variation of the maximum strength vs. the filler volume fraction (v_f). The interaction parameter (B) is given by Eq. (3) (Voros & Pukanszky, 1995) with the interphase thickness (l), the specific area of the fibres (A_f) and K_1 K_2, which are constants. After adjustment, we obtain $B = 7.7$ and 11.3 for SF and MF-based composites, respectively. If we assume that at low content, the fibres are rods not in contact, A_{MF} is inferior to A_{SF}. That means, the interphase thickness (l) is more important for MF compared to SF composites. This result is on agreement with the α relaxation decrease, related to the diminution of tangent δ height, according to the fibres length.

$$\frac{\sigma_{\mathrm{composite}}}{\sigma_{\mathrm{matrix}}} = \frac{1 - v_{\mathrm{f}}}{1 + 2.5v_{f}} \times \exp(B \times v_{\mathrm{f}}) \tag{2}$$

$$B = l \times A_{\mathrm{f}} \times K_1 + K_2 \tag{3}$$

Fig. 8 shows the values of elongation at break. Elongation decreases with fibres content and length. Eq. (4) has been fitted (solid and dashed lines) on elongation data, with filler volume fraction (v_{f}) and an index (m). By adjustment, we have found $m = 0.49$ and 0.32 for SF and MF-based composites, respectively. The prediction by the Nielsen model (Nielsen & Landel, 1994) for elongation with perfect adhesion is $m = 1/3$, is very close to the result obtained with MF composites.

$$\frac{\varepsilon_{\mathrm{composite}}}{\varepsilon_{\mathrm{matrix}}} = (1 - v_{\mathrm{f}}^{m}) \tag{4}$$

Table 4 shows the comparison between both matrixes, TPS_1 and TPS_2, for a same volume filler fraction e.g. $v_{\mathrm{f}} = 10\%$. Modulus and maximum strength ratios are greater and elongation ratios are lower for TPS_1, compared to TPS_2. These results are in agreement with the T_{α} shifts, previously described for TPS composites. These results could be also linked with the difference of surface tension between both matrixes (see Table 1). For all the studied TPS composites, the compatibility at the interface is quite good. It seems that interface filler-matrix of TPS_1 is much more stronger than TPS_2 one. The hypothesis would be that TPS_1 composite is based more on starch–cellulose interactions compared to TPS_2, where glycerol content is higher and then, hydroxyl carbohydrate sites are saturated with glycerol molecules. In this latter case, the transfer at the interface is weaker during mechanical solicitations (static or dynamic).

3.3. Influence of the type of filler

We have compared two types of fibres: semi-crystalline cellulose fillers (LF) and lignocellulose fillers (PPF). Both fillers have roughly the same lengths (around 1 mm), determined by image analysis. Table 4 shows main mechanical results. Although PPF composites show the highest modulus ratios, LF composites get higher mechanical properties. For the latter, we obtain both, higher maximum strength and higher elongation at break, whatever filler content (10 or 20 wt%). If we compare (Table 4) the behaviour of LF and PPF composites from 10 to 20 wt%, the increase of the maximum strength ratio is lower for PPF-based composites. Besides, the decrease of the elongation at break ratio is higher for PPF-based composites. The quality of the interfaces fillers-matrix could not be equal; LF seems to bring higher adhesion with the matrix. Elsewhere (Le Digabel et al., 2003), we have shown that surface properties vary according to the fibre nature. Cellulose fibres show polar components and surface tensions greater than lignocellulose fibres. Dispersive and polar components are determined using contact angle measurements, with water and diiodomethane (Wu, 1982). These components are shown in Tables 1 and 5, for TPS matrixes and fibres, respectively. From these results and using the Wu equation (Eq. (5)), the interfacial tension has been estimated. Works of adhesion are obtained through Eq. (6) (Wu, 1982). Works of adhesion are 84 and 76 mJ m^{-2} for TPS_2-cellulose fibres and TPS_2-lignocellulose fibres, respectively. These latter results are on agreement with mechanical determinations, the matrix-filler interface and adhesion is greater with cellulose fibres. At the surface of lignocellulose fibres, the presence of lignins, which are less polar than cellulose (Pouteau, Dole, Cathala, Avérous, & Boquillon, 2003), decreases the adhesion and the load transfer at the interface during mechanical solicitations and then, the global mechanical properties such as the maximum strengths or the elongations at break. Besides, this interface phenomenon could be associated with a difference of filler dispersion, between both fillers. The filler dispersion during processing is also linked with the fibre surface properties.

Table 4
Mechanical results (Tensile tests)

Type of fibres	Modulus ratio		Elongation at break ratio		Maximum strength ratio	
	SF	MF	SF	MF	SF	F
TPS_1/10 vol% fibres	5.4	6.0	0.22	0.17	2.2	3.0
TPS_2/10 vol% fibres	2.6	5.0	0.68	0.52	1.6	2.4
Type of fibres	LF	PPF	LF	PPF	LF	PPF
TPS_2/10 wt% fibres	3.4	4.0	0.48	0.42	2.6	2.0
TPS_2/20 wt% fibres	9.9	10.8	0.34	0.25	5.4	3.6

Post-processing time = 4 weeks.

$$\sigma_{\mathrm{Fibre-TPS}} = \sigma_{\mathrm{Fibre}} + \sigma_{\mathrm{TPS}} - \frac{4\sigma^{d}_{\mathrm{Fibre}} \cdot \sigma^{d}_{\mathrm{TPS}}}{\sigma^{d}_{\mathrm{Fibre}} + \sigma^{d}_{\mathrm{TPS}}} - \frac{4\sigma^{p}_{\mathrm{Fibre}}\sigma^{p}_{\mathrm{TPS}}}{\sigma^{p}_{\mathrm{Fibre}} + \sigma^{p}_{\mathrm{TPS}}} \tag{5}$$

$$W_{\mathrm{Fibre-TPS}} = \sigma_{\mathrm{Fibre}} + \sigma_{\mathrm{TPS}} - \sigma_{\mathrm{Fibre-TPS}} \tag{6}$$

Table 5
Surface tension results

	Lignocellulose	Cellulose
Dispersive component (mJ m^{-2}) σ^{d}	33 (2)	39 (2)
Polar component (mJ m^{-2}) σ^{p}	15 (2)	22 (2)
Surface tension (mJ m^{-2}) $\sigma = \sigma^{d} + \sigma^{p}$	48 (2)	61 (2)

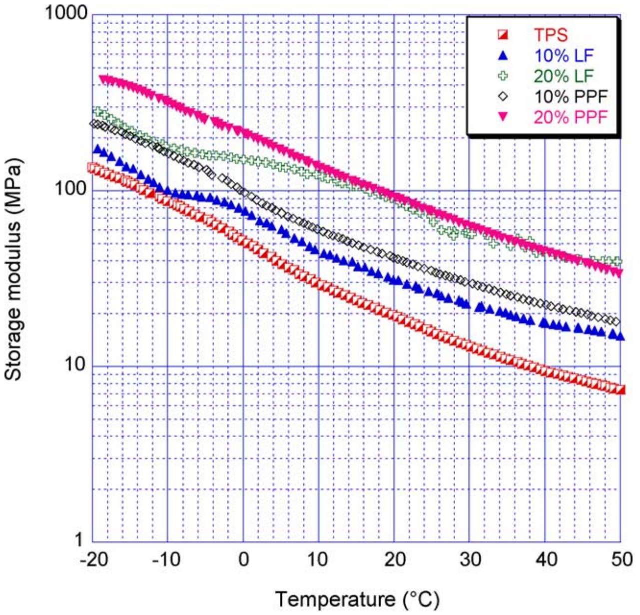

Fig. 9. TPS_2 and TPS_2/LF or PPF composites. Variation of storage modulus vs. temperature.

Fig. 9 shows the variation of storage modulus vs. temperature, for PPF and LF composites. Behaviour of both composites is different. Compared to PPF composites, LF composites show a small plateau from −10 to 0, or 10 °C. In this temperature range, PPF composites modulus decreases continuously as do TPS materials. In the temperature range illustrated by Fig. 9, PPF composites show a higher modulus, compared to LF composites. This is in agreement with results obtained by tensile tests (Table 4).

Table 3 shows the data concerning the α relaxation. Compared to LF composites, PPF composites show higher shifts of relaxation temperatures. Theses shifts are accompanied with a depression of the tangent δ heights. These results are in agreement with the variation of storage modulus (Fig. 9) or tensile modulus (Table 4). These variations of tangent δ should be associated with a higher reinforcing effect of PPF, compared to LF.

TGA have been carried out to test the thermal behaviour of both composites. Fig. 10 and Table 6 show main results. Temperature onset is close to 300 °C. At this temperature, mass losses are determined and given on Table 6. The loss variations are because at equilibrium, cellulose-based composite have lower water content, compared to unfilled TPS (Avérous et al., 2001). Cellulose cristallinity decreases its polar character. Then, cellulose addition into a starchy matrix decreases the global water content. Besides, the diverse interactions brought by the fillers take original water sites of TPS. Then, the loss of weight decrease, with an increase of the filler content. Table 6 shows that the degradation temperatures increase with the filler content. These temperature variations are rather low, but more important for PPF compared to LF composites. This result is on agreement with the temperatures degradation of neat fillers. We have shown that lignocellulose fibres show a higher degradation temperature compared to cellulose fibres. This latter result is on agreement with Ruseckaite and Jiménez (2003) works. It seems that degradation temperatures of these composites are between the values of each component (fibres and matrix), with an additional additive effect.

3.4. *Influence of biodegradable polyester addition*

Ageing is an important issue for TPS-based materials after processing (Avérous et al., 2000a). We have therefore,

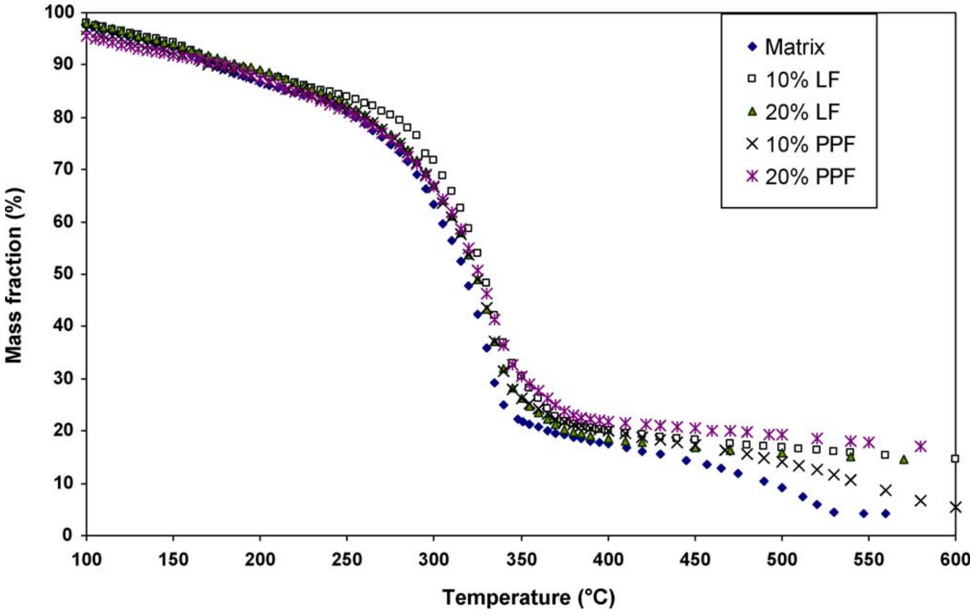

Fig. 10. Thermograms: Mass fraction (%) vs. temperature. TG of neat TPS_2, or LF and PPF- TPS_2 composites.

Table 6
TGA results

	Degradation temperature (Max DTG peak)	Loss of weight, at 300 °C (onset) in %
TPS_2	332 (1)	36.3
TPS_2/10 wt% LF	335 (1)	28.3
TPS_2/20 wt% LF	336 (1)	33.0
TPS_2/10 wt% PPF	335 (1)	33.5
TPS_2/20 wt% PPF	339 (1)	33.2
LF Fibres	362 (2)	3.5
PPF Fibres	370 (2)	7.1

followed the variation of mechanical properties during several weeks, after injection moulding and the modulus has been used to estimate the ageing. To determine the post-processing variation of different formulations, the ratio of modulus at 6 weeks divided by the modulus at 2 weeks is calculated. TPS_1 is the starchy matrix for this analysis. Table 7 demonstrates that TPS shows significant variations of the modulus after processing. Table 7 shows that the addition of fibres decreases drastically the ageing variation, beyond a dilution effect. This is due to the fibre-matrix interactions, which create a kind of stabilising 3D network based on low intermolecular bonds. Besides, it seems that this effect is linked with the fibre length. An increase in the fibre length improves post-processing stabilization. For the different blends, the addition of biopolyester to TPS phase does not improve significantly the TPS stabilization. We obtain the same trend for the tested polyesters. The difference of 'TPS-polyester' compatibility, which depends on polyester nature, is not visible on these results. If we combine both systems (blend and composite), we obtain a complex 'TPS-biopolyester-fibres' system. This latter shows intermediate values between both basic systems: blend and composite. Table 7 shows that the addition of a biopolyester to a composite decreases the initial effect of stabilization. Some fibres, which are embedded into the polyester phase, do not participate to 'TPS-filler' stabilizing interactions. Although the polyesters bring higher water resistance, they do not act as ageing stabilizers but as diluents (dilution effect) and soft fillers.

Table 7
Post-processing ageing results. Ratios: Modulus at 6 weeks/Modulus at 2 weeks

Systems studied	Without polyester	PEA	PCL
TPS_1	2.15	–	–
TPS_1/15 wt% SF	1.19	–	–
TPS_1/15 wt% MF	1.08	–	–
TPS_1/15 wt% LF	1.07	–	–
TPS_1/30 wt% LF	1.07	–	–
TPS_1 + 25 wt% polyester	–	2.21	2.01
TPS_1/15% MF + 10 wt% polyester	–	1.35	1.35
TPS_1/15% MF + 25 wt% polyester	–	1.33	1.31

4. Conclusion

Various formulations based on plasticized starch matrix have been carried out, varying matrix formulation (glycerol/starch ratios = 0.257 and 0.538), fibres length (from 60 μm to 1 mm), filler content (till 30 wt%) and fibres nature. The fibres show distinct surface tensions, cellulose fibres are more polar compared to lignocellulose fibres. Compared to the net matrix, DMTA analysis shows on these biocomposites some important variations in the main relaxation temperature, which can be linked to interactions resulting in a decrease of starch chain mobility and to a regular reinforcing effect. These results are consistent with the variation of static mechanical (tensile test) behaviour. By fitting these latter values on some common mechanical models, we can show that filler-matrix adhesion is high. Comparison between lignocellulose and cellulose fibres seems to show, that for these latter the interface adhesion with the starchy matrix is higher. If we compare the behaviour of both TPS matrixes, we can show that the less plasticized matrix shows higher mechanical behaviour. The highest plasticized matrix is more heterogeneous with glycerol rich domains. These micro-domains seem to decrease the behaviour of the corresponding composites. At the interface filler-matrix, glycerol decreases the quality of the adhesion with subsequent reduced static and dynamic mechanical behaviours. Besides, we have also shown by thermogravimetric analysis, that the addition of these agro-fillers improves the thermal resistance of the biocomposites. Compared to cellulose fibres, lignocellulose fibres bring higher degradation temperature, to the corresponding composites. Finally, to minimise the matrix ageing, we have tested the impact of the addition of biodegradable polyesters into these composites without significant result on the post-processing stability.

Further investigations have to be carried out, to predict the mechanical loss angle for TPS-cellulose composites, using an accurate model. Such an approach should allow removal of the filler reinforcement effect, keeping only the interfacial effect. Another direction of the investigation will be to develop complementary approaches to give further insight into the molecular structure.

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