

Preparation, processing and characterization of biodegradable wood flour/starch-cellulose acetate compounds

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A novel biodegradable material was prepared by compounding, in different proportions, pine wood flour (WF) and a commercial starch-cellulose acetate blend on a configurable co-rotating twin screw extruder. After pelletizing, the compounds were injection moulded and the mechanical and rheological properties of the mouldings determined. As the content of wood flour increases up to 50% (wt/wt), the tensile strength and the modulus improve significantly, whereas the toughness drops gradually. The effect of the wood flour content on the shear viscosity is complex, being impossible to establish a linear relationship between the two. The shear viscosity decreases with shear rate, but for a level of 40% and 50% of WF there is evidence of a quasi-Newtonian behaviour, irrespective of the test temperature. Compounds with 50% WF present the highest tensile strength and modulus but are difficult to process. However, the processability can be improved by using glycerol as plasticizer, without paying a too severe penalty in mechanical properties. In fact, by adding 15% glycerol (wt/wt), compounds with 50% WF can be successfully injection moulded into specimens with good mechanical properties.

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1. Introduction

For almost twenty years there has been a continuous trend to make polymeric materials, namely reinforced ones, more recyclable and environment friendly. In the case of long fibre composites, the initial aim was to change from thermoset to thermoplastic matrices, without significant losses in mechanical performance. This has been achieved by a number of techniques [1, 2], leading to materials that can be easily subjected to mechanical recycling. The process continues nowadays, as the market for thermoset-matrix composites remains still important. However, as most of the fibres used are inorganic, it is not possible to

subject the new thermoplastic-based composites to a complete thermal/chemical or energy recycling. On the other hand, there is also a great interest in the use of natural materials in engineering applications, as alternatives to traditional synthetic ones. Glass fibres, extensively used in reinforced plastics (GFRP), are one example. Besides the limitation in recyclability, they also lead to abrasive wear of the processing equipment. Hence, natural vegetable fibres (NVF), such as flax, jute, hemp or sisal, appear as interesting alternatives in specific applications. NVF reinforced thermoplastics (such as polyethylene and polypropylene) have been extensively studied [3–6], aiming at saving weight and

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costs, primarily in automotive and construction structures, where lightweight is an important specification [7]. Additionally, these materials can now be subjected to mechanical, thermal/chemical and energy recycling. However, due to the synthetic nature of their matrix, they still lack one important characteristic: they are not biodegradable.

Thus, the final step in this route to natural, environment friendly materials is the production of NVF composites with biodegradable or compostable polymeric matrices. Potential alternatives for these matrices are polysaccharides or micro-organism generated polymers such as poly-hydroxybutyrate (PHB) and poly(hydroxybutyrate-co-valerate) (PHBV). Limited work has been done so far with these novel materials, often called biocomposites. Investigations by Herrmann and co-workers [8] revealed that hemp and flax fibres are suitable reinforcements for biopolymers, leading to mechanical properties comparable to those of GFRP. Luo and Netravali [9] found that the longitudinal tensile strength and modulus of pineapple fibre/PHBV laminates improve with increasing fibre content. In spite of a poor fibre-resin adhesion, evidenced by the low interfacial shear strength (around 8 MPa), the mechanical properties are still much higher than those of real wood, such as cherry- and walnut-tree [10].

The composites obtained in this way are now fully recyclable and/or degradable by natural agents. They also fulfil a more philosophical consideration, which is, they may lead to new useful materials, if buried on earth, thus closing the natural cycle. On the negative side, however, they also have a number of limitations. On one hand, the use of biocomposites is still limited, as their properties usually cannot compete with those of traditional composites, namely in structural applications. On the other hand, they normally present significant processing difficulties. Amongst these, the possibility of thermo-mechanical degradation is paramount.

Starch-based biodegradable materials are among the best matrix candidates for biocomposites, due to their intrinsic performance, and the extensive availability of the starch sources [11]. Furthermore, their processing is relatively simple and reliable, via conventional technologies such as single- or twin-screw extrusion and injection moulding [12]. Consequently, there is a need for technological developments that will allow the easy fabrication of starch based biopolymers with adequate properties.

In this paper, we report the preparation and processing of pine wood flour/starch-cellulose acetate based blend compounds, and their mechanical and rheological characterisation. The results evidence the potential of these compounds for structural applications.

2. Experimental

A commercial starch-cellulose acetate based blend (SCA) from Novamont SPA, Italy, and regenerated pine wood flour (WF), with particle size ranges from 0.02 to 3.0 mm, provided by Casca, S.A., Portugal, were used as raw materials. The respective compounds were produced on a co-rotating twin-screw extruder (LSM 34GL, Leistritz), at a processing temperature of

180–190°C, and consequently pelletized. The experimental plan included composites with 20, 40 and 50% (wt/wt) of WF. The initial moisture content of SCA and WF was, respectively, 10.9 and 6%.

The configuration of the screw and the operating conditions were optimized in order to minimise the residence time in the barrel and avoid high shear fields. This optimization procedure was based on a preliminary experimental work and supported by a design of experiments approach.

The resulting pellets were injection moulded at 190°C into round disks, of 120 mm in diameter and 3 mm in thickness, in a Krauss Maffei KM60-210A machine.

Special precautions were also taken in the injection moulding process to avoid material degradation. The back-pressure was kept lower than 0.5 MPa (value in the hydraulic circuit) and a mould with a direct sprue gate was used.

The mouldings were conditioned in ambient conditions (23°C, 50% RH) for at least 48 hours. Rectangle bars (55 mm × 10 mm) were then cut in the tangential and radial directions, according to the scheme shown in Fig. 1. Subsequently, they were shaped into dumb-bell tensile bars (ISO) using a Ceast shaping machine.

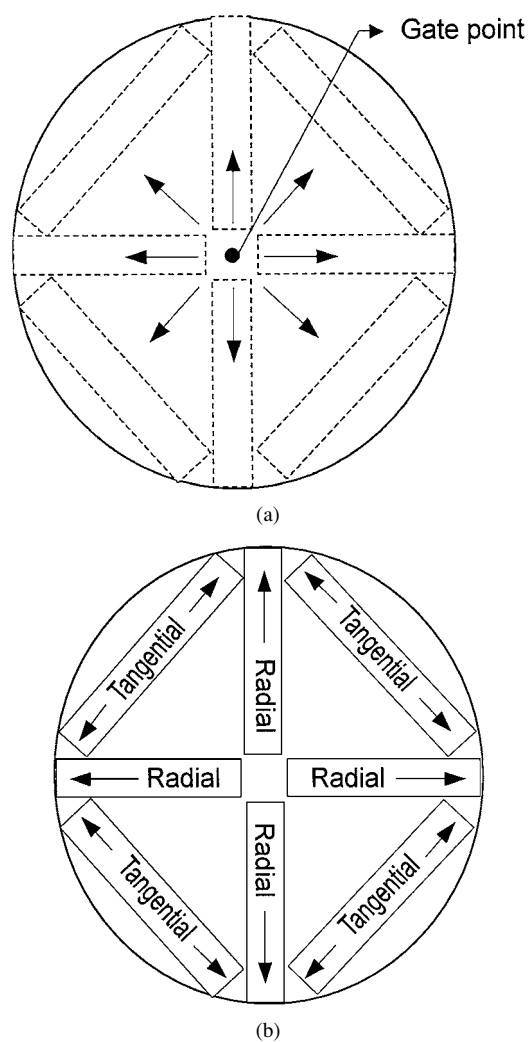


Figure 1 (a) Gate point and flow direction (b) Specimens lay-out Schematic of the cutting of test specimens from the injection moulded plates. The arrows in (a) indicate the flow direction and preferential WF alignment.

A Rosand RH8-2 advanced capillary rheometer system was used to assess the rheological behaviour of the compounds at 180–200°C. The Rabinowitch correction was performed automatically throughout the test. All the rheometric tests were performed on compounds dried at 115°C for 12 hours.

The moulded specimens were microtomed to obtain cross sections in the radial direction, that were examined in an Olympus BH-2 optical microscope, equipped with an image analysis system (Quantimet 500 QWIN, Leica Cambridge Ltd.). The respective software was used to precisely determine various geometrical parameters of the wood particles (namely length, area and aspect ratio).

The tensile tests were carried out at 23°C at 50% RH on an Instron 4505 testing machine, with a 50 kN load cell. The measurement procedure was in accordance with ASTM D-638M-87b. A cross-head speed of 1 mm/min (1.67×10^{-5} m/s) was used, and the strain determined using a 10 mm resistive extensometer. Mechanical performance was evaluated by the maximum tensile stress (referred as tensile strength) and by the materials toughness (quantified by the integration of the force over the displacement until the breakage).

The respective fractured surfaces were examined in a Leica S360 scanning electron microscope.

3. Results and discussion

3.1. Raw materials

In a composite system, the fibres sustain the applied loads within the structure and stiffen it, whereas the matrix holds the fibres together, transmits shear forces between them and prevent the fibres from being damaged by environmental agents. In the present work, a starch-cellulose acetate (SCA) based blend was used as matrix. SCA is a biodegradable and compostable injection moulding polymer blend, which can be used to make rigid and dimensionally stable items. Its mechanical properties and mouldability are very close to those of standard polystyrene, as can be seen in Table I [9].

Morphologically, the SCA blend exhibits a two-phase structure, in which cellulose acetate domains, of about 20 μm in diameter, are dispersed in a continuous phase of thermoplastic starch (Fig. 2).

The composition of the wood flour (WF) reinforcement is presented in Table II. As can be seen in the

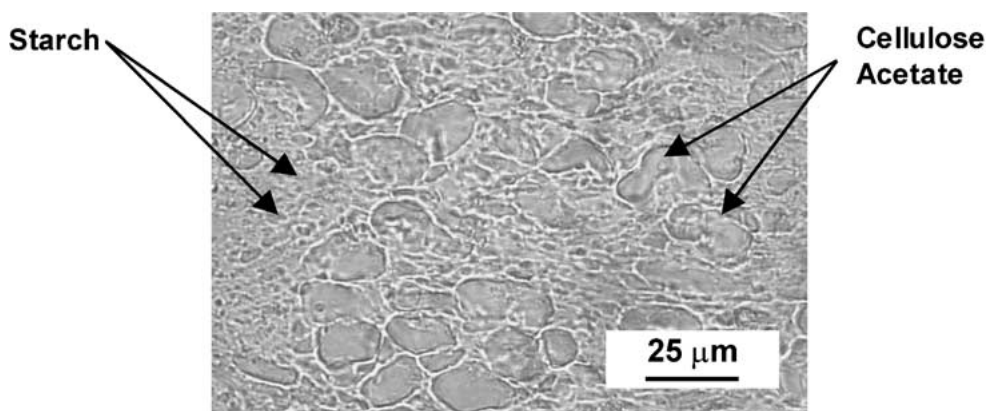


Figure 2 Optical micrograph of SCA.

TABLE I Main physical properties of SCA and polystyrene [9]

Property	SCA	PS
Density ($\text{g} \cdot \text{cm}^{-3}$)	1.35	1.04–1.09
Melt flow index ($\text{g} \cdot 600^{-1} \cdot \text{s}^{-1}$)	10–15	8–12
Tensile strength (MPa)	25–30	35–64
Elongation at break (%)	2.0–6.0	1.0–2.5
Tensile modulus (GPa)	2.1–2.5	2.8–3.5

TABLE II Composition of the wood flour reinforcement [10]

Constituent	Content (%)
Cellulose	42
Lignin	30
Galactoglucomannan	20
Xylan	8

Table, the nature of the material is complex, less than half of it being made up of hydrophilic cellulose.

The remaining part, in which lignin prevails, corresponds to hydrophobic substances. Unlike glass or carbon fibres, that have relatively uniform shapes, namely a quasi-constant diameter, the wood flour particles used in this investigation have an irregular geometry and unequal dimensions. In fact, any wood flour particle is a bundle of cellulose fibrils connected by non-cellulose components (Fig. 3), with aspect ratios no greater than 6–8. For simplicity, these elongated particles will be

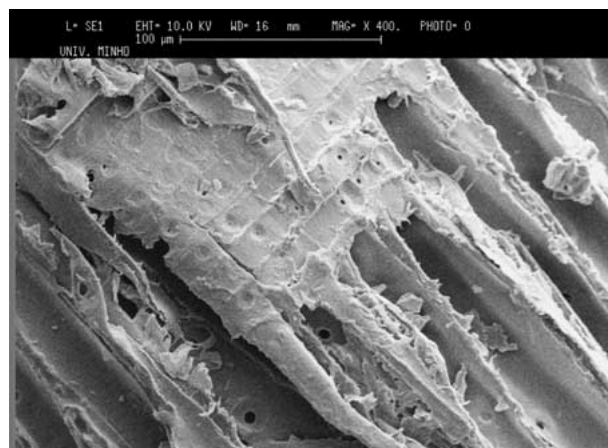
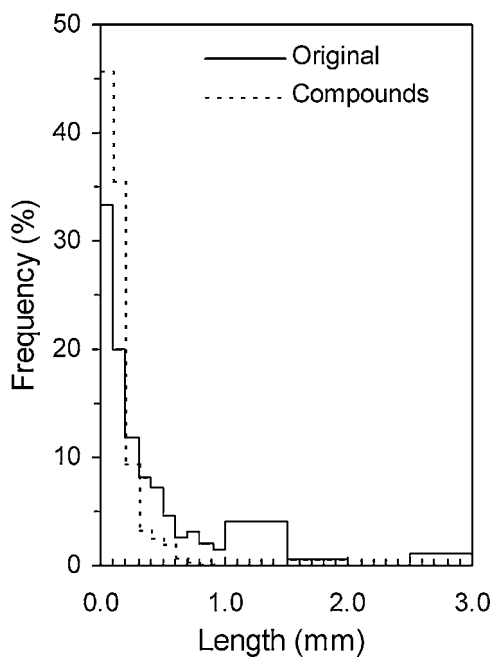


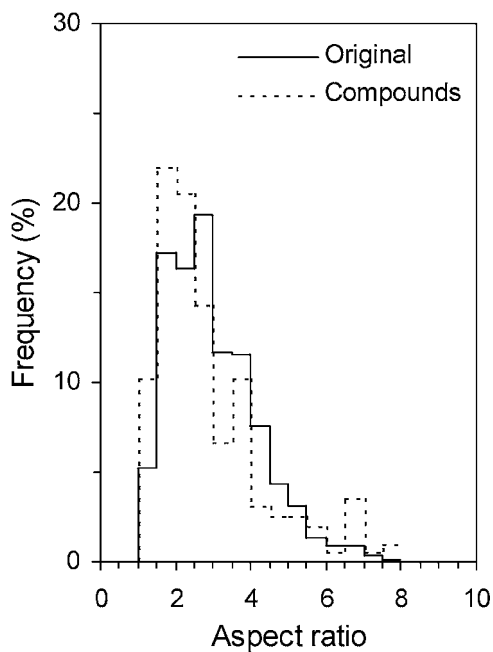
Figure 3 SEM micrograph of the wood flour supplied by Casa, SA.

referred to in the text as wood “fibres”. The vascular and tubular structure provides excellent insulation against heat, as evidenced by its extremely low thermal conductivity ($0.05\text{--}0.07\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) [13]. The rough surfaces with many tubular flaws may also benefit the interfacial adhesion.

Fibre length and aspect ratio distributions are determinant on the mechanical properties of any fibre-reinforced composites. In Fig. 4 it can be observed that an exponential drop type histogram fits better the length distribution than a Gaussian one, as more than 80% of the fibres are less than 0.5 mm in length. The median aspect ratio of wood flour is ca. 3, which is very small, compared with a value of 20–50 for flax or regenerated paper pulp fibres.



(a)



(b)

Figure 4 Fibre length and aspect ratio distributions of the wood flour fibres, as obtained (original) and after twin screw extrusion compounding (compound). (a) Length; (b) Aspect ratio.

Although the wood fibres are relatively soft, thermo-mechanical effects during processing can decrease both their length and aspect ratio distributions. In particular, the tail corresponding to the higher lengths disappears, whilst the fraction less than 0.2 mm in length increases drastically. The fibre attrition, albeit small, indicates that the fibres are more likely to fracture than to split.

3.2. Rheology

The knowledge of the shear viscosity of a given thermoplastic system is one of the more important factors in the optimisation of its injection moulding conditions. Henceforth, the rheology of the wood flour/starch-cellulose acetate based blend system was studied in detail in the present work. Capillary rheometry was selected, as it allows making experiments in a shear rate range close to that prevailing in the processing equipment. Fig. 5 shows the shear viscosity of the compounds, with different weight contents of wood flour, determined at 180°C and shear rates from circa 1 to 10^4 s^{-1} . The effect of the wood flour content on the viscosity is complex, being impossible to establish a linear relationship between the two.

For low WF levels, a shear-thinning behaviour is observed. However, at 40 and 50% WF, a quasi-Newtonian behaviour is evidenced. In practice, this means that increasing the screw speed in extrusion or employing high injection velocities will fail to improve the processability. The alternative of increasing the processing temperature is also inadequate, as evidenced in Fig. 6, which shows the viscosity of the 40 and 50% WF compounds from 180 to 200°C .

A quasi-Newtonian behaviour of the melt is observed for both compounds, irrespective of the temperature. Moreover, the shear viscosity almost does not decrease when the temperature increases. The latter behaviour should be associated to the excellent heat resistance and low thermal conductivity of the wood fibres, as the respective tests were based on dried compounds. On the other hand, the quasi-Newtonian behaviour may be due to the strong bonds that can be formed between the macromolecules of the compound. In fact, as constituents of the matrix and the reinforcement (cellulose in the SCA and WF, and starch in SCA) share the same glucose unit and pendant hydroxyl groups, hydrogen bonds can occur between them. The hydrogen bonds

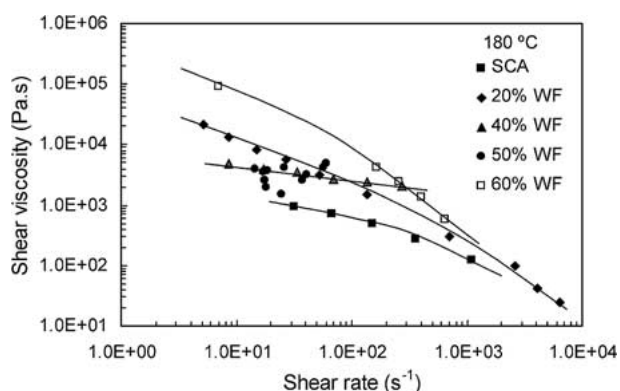


Figure 5 Effect of the WF content on the shear viscosity of the compounds.

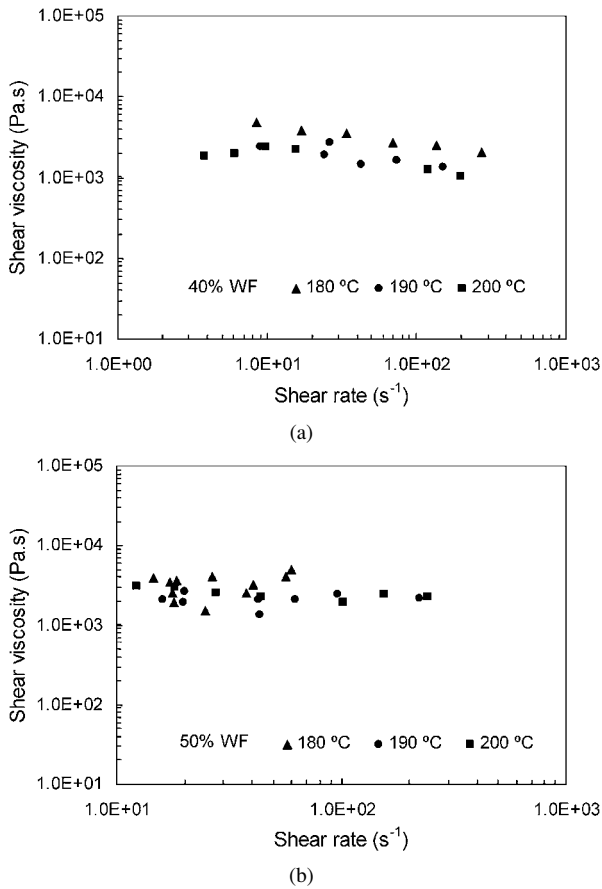


Figure 6 Shear viscosity at 180, 190 and 200°C. (a) 40% WF; (b) 50% WF.

become stronger for higher quantities of hydroxyl groups in the two constituents, preventing the occurrence of a shear-thinning mechanism.

This means that adding a plasticizer such as glycerol, a small molecule with three hydroxyl groups, should not only reduce the viscosity but also restore the shear-thinning behaviour. In fact, when 15% glycerol were added to the 50% WF compound at 180 and 190°C a clear pseudo-plastic behaviour was observed when the shear rate increased (Fig. 7). The viscosity values also decreased, in absolute terms, due to the plasticizer effect. For instance, at 190°C and with a shear rate of 100 s⁻¹, the viscosity is around one sixth ($\cong 190$ Pa · s) of that shown in Fig. 6 for the corresponding unplasticized compound ($\cong 1200$ Pa · s).

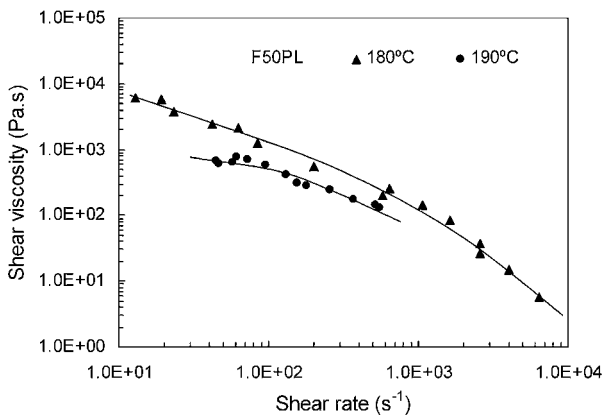


Figure 7 Shear viscosity of the compound containing 50% WF and 15% glycerol (F50PL).

3.3. Mechanical properties

The mechanical properties of short fibre reinforced composites are primarily determined by the fibre orientation, and the adhesion between fibre and matrix. Unidirectional fibre composites are known to evidence higher tensile strength and modulus in the longitudinal direction than in the transversal one. Due to the production method of the test specimens used in the present work, the reinforcements are expected to align preferentially in the radial direction, thus making the tangential direction the transversal one. Intriguingly, as can be seen in Fig. 8, the tangential samples have noticeably higher tensile strength and modulus than the radial ones. The distinction, however, is not significant in the tensile toughness data (Fig. 9).

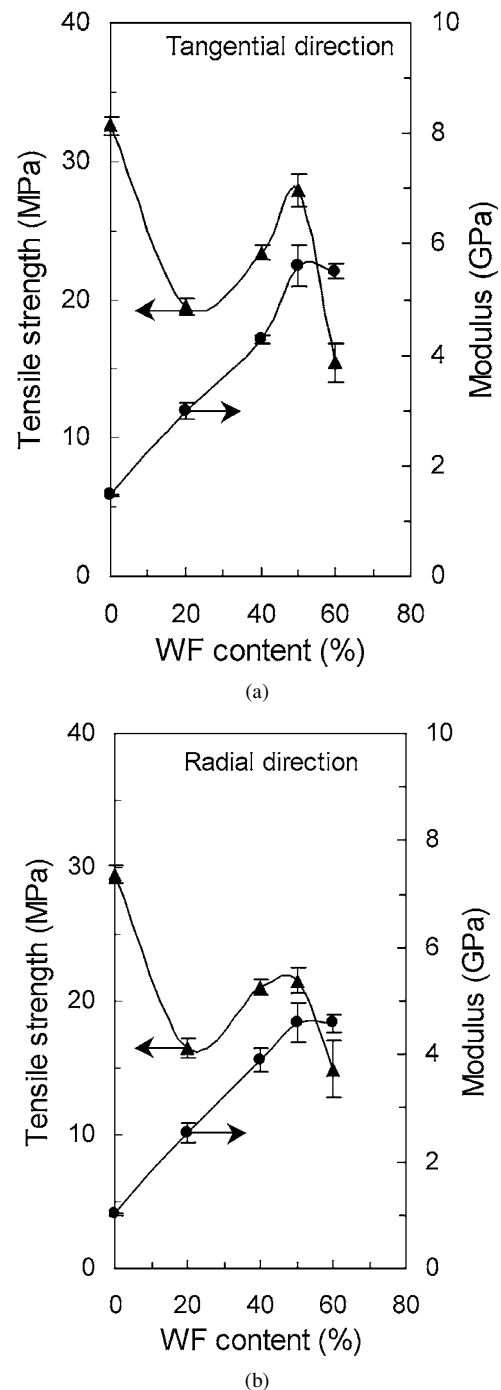
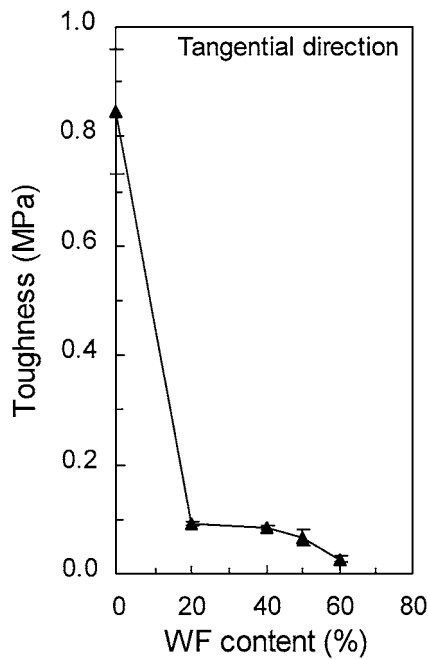
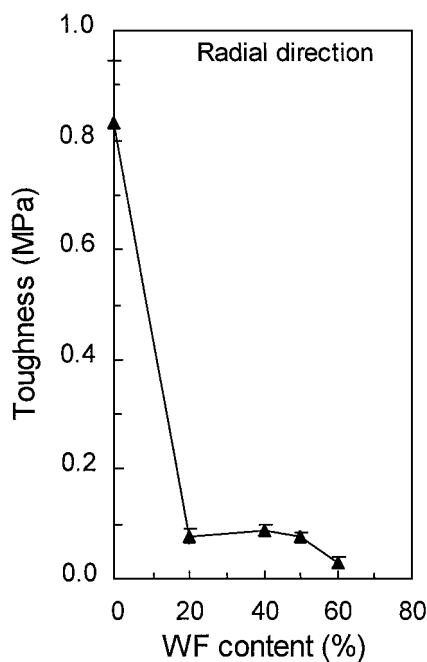


Figure 8 Effect of the cutting direction and WF content on the tensile strength and modulus. (a) Tangential direction; (b) Radial direction.



(a)

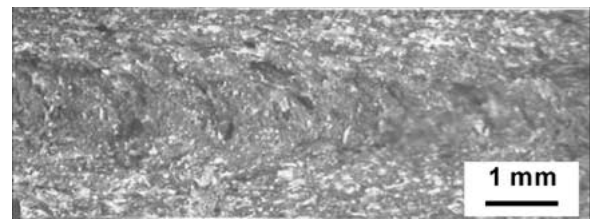


(b)

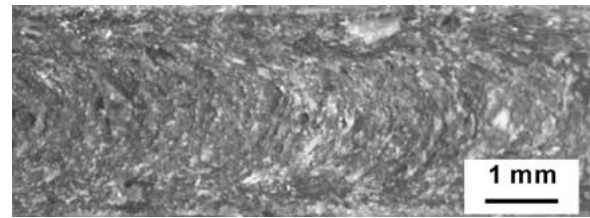
Figure 9 Effect of the cutting direction and WF content on the toughness. (a) Tangential direction; (b) Radial direction.

This observation may result from the fact that the tangential samples were cut from the edge of the mouldings. This zone is more compact or void-free than the area around the gate, from where the radial samples were cut. Fig. 10 shows the microphotographs of cross-sections in both zones. Apart from the same fountain-like flow pattern, a higher compactness of the section near edge is apparent, compared to the area near the gate (this qualitative analysis was not confirmed by density measurements due to the hydrophilicity of the materials).

From Fig. 9 it can be concluded that introducing 20% WF into SCA leads to a sharp decrease of the toughness in both the radial and tangential directions. This



(a)



(b)

Figure 10 Optical micrographs of the fracture surfaces of an injection moulded disk. (a) Near the gate; (b) Near the edge.

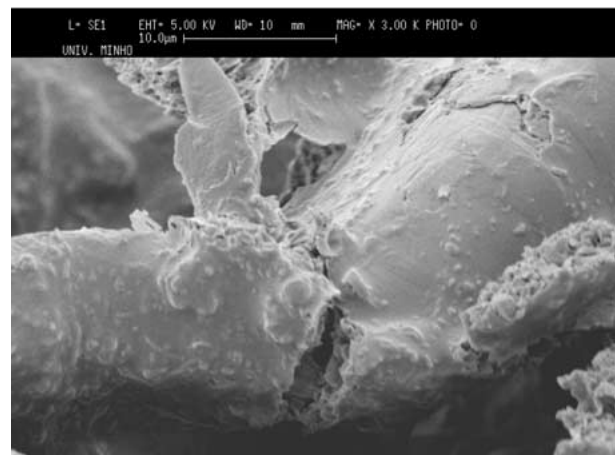


Figure 11 SEM micrograph of a compound containing 60% WF.

behaviour is common in compounds randomly filled with small amounts of fibres with low aspect ratio, in which stress concentrations occur in the vicinity of the particles. Fig. 8 shows that the dependence of the tensile strength on wood flour content is more complex, decreasing until 20%, increasing up to 50% and then decreasing again. On the other hand, the modulus is almost a positive linear function of the wood flour content, in agreement with the general rule of mixtures.

In any case, introducing more than 50% WF never benefits, and in some circumstances deteriorates, the mechanical performance. This is probably associated with severe thermomechanical degradation, as well as the fibre attrition during processing, owing to localised overheating induced by friction. One example is a compound with 60% WF, in which a fractured fibre can be observed, as shown in Fig. 11. It can also be observed that the fibres are completely coated with the polymer, which normally implies a good fibre-matrix adhesion. This supports the idea that the decrease of the aspect ratio of the wood fibres is the dominant mechanism responsible for deterioration of the mechanical properties.

The mechanical properties of compounds unplasticized and containing 15% of glycerol were determined

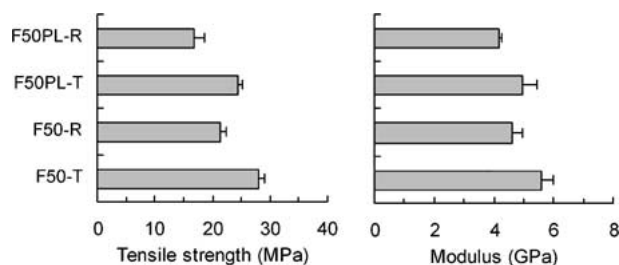


Figure 12 Effect of glycerol on the compounds' mechanical properties. F50: 50% WF; F50PL: 50% WF + 15% glycerol; R: radial direction; T: tangential direction.

and compared. In the case of the 50% WF compounds, the presence of 15% glycerol does not reduce the mechanical properties significantly in both the radial and tangential directions (Fig. 12).

It should be noticed that the rheological studies evidenced that, at high temperatures and high shear rates, glycerol acts as an effective hydrogen bond destructor, leading to a striking viscosity reduction. However, at ambient temperature and small deformation levels, its action is apparently not as effective, and the mechanical properties do not deteriorate significantly.

4. Conclusions

The present work reports the preparation and processing of a new, wholly biodegradable, reinforced thermoplastic material. The material was prepared by compounding pine wood flour and a commercial starch-cellulose acetate blend on a configurable co-rotating twin screw extruder. The compound was then injection moulded into test specimens, whose rheological and mechanical properties were characterized. Wood flour is prone to some thermomechanical degradation upon processing. A linear relationship could not be derived between the shear viscosity and the wood flour content. Compounds with 40% and 50% WF exhibit a quasi-Newtonian fluid behaviour, irrespective of the temperature. Additionally, for these compounds, the shear viscosity does not decrease by increasing the temperature.

In both the radial and tangential directions the mechanical properties improve with wood flour content up

to 50%. Above that content the mechanical properties deteriorate, possibly due to the severe fibre breakage induced by enhanced friction during the processing. Introducing 15% glycerol in the compounds with 50% WF leads to significant viscosity reduction and restores the pseudo-plastic behaviour. The compound containing 50% WF and 15% glycerol could be easily injection moulded. The mechanical properties of the resulting mouldings were only slightly lower than those of the corresponding unplasticized compounds.

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