Reinforcement of Poly (Lactic Acid) with Spray-dried Lignocellulosic Material

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Effects of the addition of spray-dried lignocellulosic material in polylactic acid (PLA) were evaluated in this work. The lignocellulosic material was produced by spray-drying unbleached fibrous material provided by a paper mill. Beforehand, this material was made hydrophobic in the sizing step of the papermaking process. We propose that size present on the lignocellulose powder may act as a potential alternative to commonly-used coupling agents in the compounding of cellulosic filler with PLA. The lignocellulose powder was compounded with PLA in various amounts by extrusion and injection-moulding. Homogeneous dispersion of the lignocellulose powder in PLA was achieved. However, comprehensive mechanical and microscopic characterisation revealed only minor positive effects of the filler on PLA in a limited number of cases. Further investigation by gel permeation chromatography (GPC) showed a reduction of the average molar mass of the PLA matrix with increasing filler content, partly due to the residual inorganic matter in the spray-dried powder. This effect overshadowed the homogeneous dispersion and resulted in composites with weaker mechanical properties in most cases.

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INTRODUCTION

Even before the industrial revolution, fibre-reinforced materials such as straw reinforced plaster for construction were used. The combination of plastic with fibres to take advantage of the properties of both components in a new composite material emerged soon after the invention of fully synthetic plastics (Baekeland 1909). Due to their high stiffness, glass fibres were very often the first choice for reinforcing purposes in the past decades. However, these synthetic fibres have high production costs and a substantial carbon footprint; the glass-melting step requires high temperatures and therefore a high energy input. Thus, natural fibres have been considered as alternative reinforcing materials. For example, laminated sheets of phenolic resin-impregnated paper have been used in planes and cars (Lee *et al.* 2014).

Environmental sustainability is widely established as one of the biggest challenges to science and industry. Since the negotiation of the United Nations Framework Convention on Climate Change at the Rio de Janeiro Earth Summit in 1992 (United

Nations 1992) and its extension in the Kyoto Protocol in 1997 (United Nations 1997), more ambitious goals in terms of global warming limitation and sustainable technology development are regularly fixed (the last example being the 2015 United Nations Climate Change Conference in Paris (United Nations 2015)). This is favourable to research dealing with natural materials for technical applications. There are many studies investigating the reinforcement potential of several kinds of unprocessed or processed fibres as well as the use of nanocellulose. For further information, the reader is referred to the numerous reviews on the topic (Pandey *et al.* 2010; Siró and Plackett 2010; Abdul Khalil *et al.* 2012; Leung *et al.* 2013; Miao and Hamad 2013; Shah 2013; Lee *et al.* 2014; Thakur and Thakur 2014).

Sustainability is relevant in terms of reinforcement fibres and to an equal extent with regard to the polymeric matrix used. To minimize the environmental impact of polymer/fibre composites, the matrix itself should also be biodegradable. Polylactic acid (PLA) and polycaprolactone (PCL) are examples of biodegradable synthetic polymers. The combination of these polymers with natural fibres is more environmentally friendly than the use of non-biodegradable, oil-based plastics and synthetic fibres. Especially since the late 1990's, interest in this topic has risen. Levit *et al.* (1996) extruded and compression-moulded PLA with different kinds of cellulosic fillers, finding that some of the obtained composites had improved mechanical properties and biodegradability compared to neat PLA.

Oksman *et al.* (2003) investigated the potential of PLA/flax composites as an alternative to polypropylene/flax composites. PCL emerged a few years later and is less popular than PLA. Composites made of PCL and cellulosic products have increased thermal stability (Ruseckaite and Jiménez 2003).

Even though the use of these so-called "green" polymers and natural fibres is a step towards meeting the requirements of the previously cited climate conventions, the performance of the obtained materials often remains under the standards established by their more pollution-generating competitors.

One of the main challenges is the natural incompatibility between the non-polar polymer matrix and the polar cellulosic fibres. Coupling agents such as maleic anhydride are used to overcome this limitation (Maldas and Kokta 1991). Their role is to create a chemical bond between the resin and the fibre by reacting with both of the components. Here also, higher sustainability can be reached.

For example, the use of lignin as coupling agent has been studied (Rozman *et al.* 2001a, b). It is naturally present in the wood cell walls and is expected to provide compatibility because it contains both polar and non-polar groups.

Another possibility is the use of sizing agents like alky ketene dimer (AKD) (Zhang 2014). These chemicals are originally used to provide a hydrophobic coating on paper sheets, and they can be found in various side- or waste streams of the papermaking process. Even if they are synthetic (unlike lignin), their use as potential coupling agents is a good recycling opportunity.

In this study, a hydrophobic lignocellulosic material provided by a paper mill was spray-dried and evaluated as a potential polymer reinforcement. This material was expected to provide good inherent compatibility with PLA due to the presence of hydrophobising sizing agent on its surface.

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EXPERIMENTAL

Materials

Never-dried, unbleached hydrophobic lignocellulose material containing fibres was obtained from a paper mill running a softwood kraft process. Polylactic acid (Ingeo Biopolymer 3251D) was purchased from NatureWorks (Naarden, The Netherlands).

Production of Fibre-Reinforced PLA

The above-described lignocellulosic material was converted into powder by spray-drying a fibre suspension (solid content: 1%) with a FSD 4.0 (GEA Niro, Plainfeld, Austria) spray-drier implemented at the AGRANA Research & Innovation Center (Tulln, Austria). The inlet temperature was 240 °C, and the outlet temperature was 90 °C. A pressure of 2.5 bar was applied, and the nozzle had a diameter of 1.3 mm. The acid-insoluble lignin content of the obtained powder was 23.5%, measured according to TAPPI T222 om-11 (2011). The ash content at 525 °C was 22% measured according to TAPPI T211 om-02 (2002). The ash content at 900 °C was 19.4% measured according to TAPPI T413 om-93 (1993). After spray-drying, the fibres were oven-dried at 103 °C overnight to remove any remaining humidity. Verification of the moisture content of the fibres was performed with a moisture analyser (HS153, Mettler Toledo, Vienna, Austria) at 105 °C just before the extrusion.

PLA was dried at 60 °C overnight and then compounded with the moisture-free lignocellulosic fibre material in defined amounts (Table 1) in a cylindrical counter-rotating twin-screw extruder (ZK 25, Collin, Ebersberg, Germany) equipped with a double-die of 3 mm diameter. The screws had a diameter of 25 mm and an aspect ratio of 18. Their rotation speed was held constant at 40 rpm, and the dosage speed was set to 300 rpm during the extrusion of all mixtures. The barrel temperatures of the extruder were 150 °C in the feeding zone, 180 °C in the second zone, 165 °C in the third zone, and 165 °C in the die. The extrusion strands were conveyed on a band-conveyor and directly fed into a pelletizer (Primo 100, Rieter Automatik GmbH, Winterthur, Switzerland).

Table 1. Sample Characteristics

Sample Designation	Lignocellulose Content (%)	PLA Mass (g)	Lignocellulose Mass (g)
PLAref	0	1400	0.00
PLA0.5	0.5	1400	7.04
PLA1	1	1400	14.14
PLA2	2	1400	28.57
PLA3	3	1400	43.30
PLA5	5	1400	73.68
PLA10	10	1400	155.56

Test specimens were produced on a Battenfeld HM 60/210 injection moulding machine (Vienna, Austria) equipped with a multi-cavity mould. The standard screw had a diameter of 30 mm and a length to diameter ratio of 22. One injection-moulding shot yielded 2 tensile dog bones, 2 flexural bars, and 2 notched impact bars. The dimensions of the specimens were as follows: tensile bar: total length 150 mm, centre section length 80 mm, centre section width 10 mm, thickness 4 mm; flexural bar: length 80 mm, width 10 mm, thickness 4 mm; impact bar: length 80 mm, width 10 mm, thickness 4 mm, notch

radius 1 mm.

Mechanical Characteristics

Injection-moulded samples were stored in a standard climate (25 °C, 60% relative humidity) for several weeks. Tensile and flexural properties were evaluated on a universal testing machine (Z20, Zwick-Roell, Ulm, Germany) according to the procedures described in EN ISO 527-2 (1996) and EN ISO 178 (2003), respectively. Impact strength (EN ISO 179-1 2001) was tested with a HIT50P impact testing machine (Zwick-Roell, Ulm, Germany) equipped with a 5 J pendulum. In each case, 10 specimens per recipe were tested.

Optical Imaging

Flexural bars from all sample types were placed side by side on a white paper sheet and photographed with a commercial digital single-lens reflex camera. Moreover, images were captured with an optical microscope (AxioPlan 2, Zeiss, Jena, Germany) in transmission mode at various magnifications. The microscope was equipped with a camera (AxioCam HRc, Zeiss, Jena, Germany), and the output files were processed in AxioVision 4.9 software (Jena, Germany).

Scanning Electron Microscopy

Dry lignocellulosic fibre material, as well as fracture surfaces of neat PLA and PLA/lignocellulose composites after tensile testing, were imaged by scanning electron microscopy (SEM). The PLA samples were cut to reduce their height to approximately 1 cm. All samples were mounted on a graphite pad and sputter-coated with gold. The imaging was performed on a Quanta 250 FEG microscope (FEI, Hillsboro, Oregon, USA) in high vacuum with an acceleration voltage of 5 kV.

Melt Flow Index (MFI)

MFI was measured with a melt flow tester (CEAST MF20, Instron, Norwood, Massachusetts, USA) according to ISO 1133 (2000). Approximately 8 g of pellets were dried at 130 °C (HS153, Mettler Toledo) and placed in the heating chamber of the device, which was then pre-heated at 190 °C for 4 min. After pre-heating, a 2.16 kg load was applied, and the MFI was taken as the mean of 40 values recorded within a 3 cm load displacement.

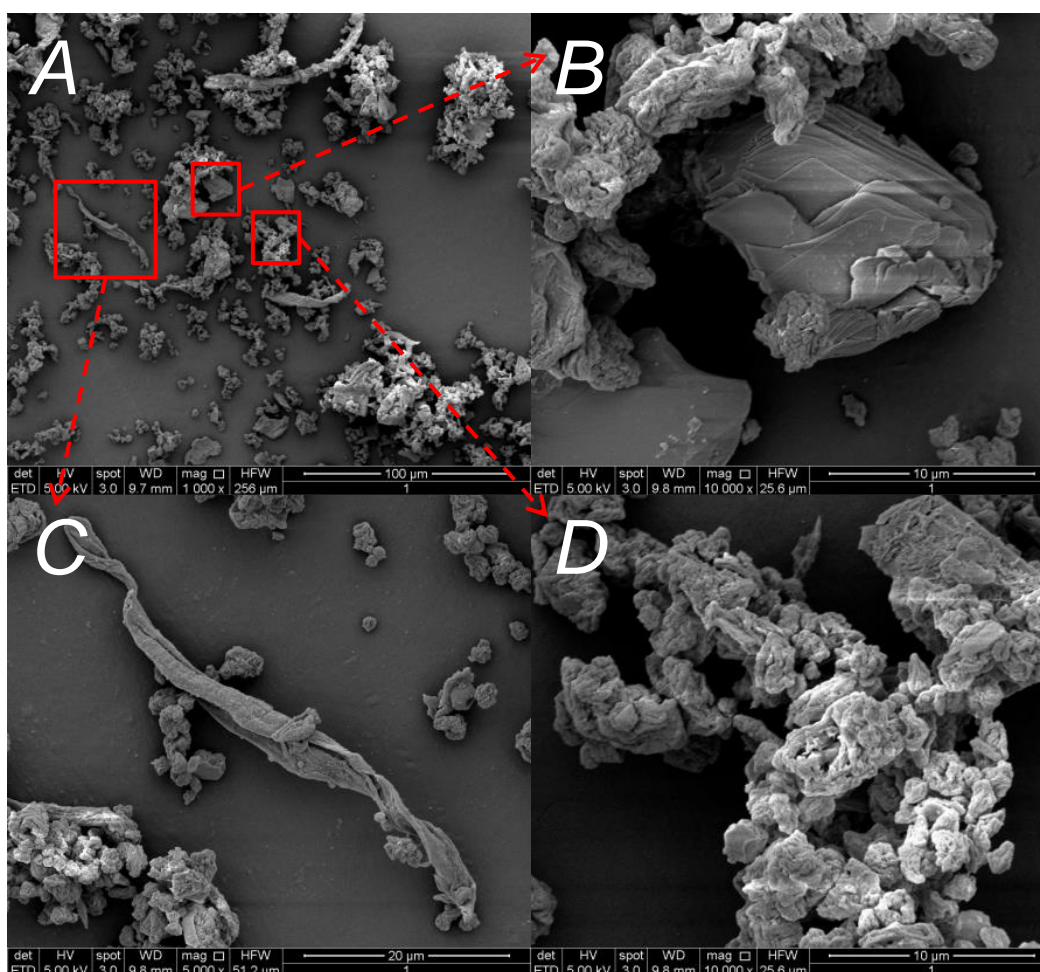## Gel Permeation Chromatography (GPC)

GPC analysis was conducted using a HT-GPC 220 chromatographic system (Agilent, Church Stretton, UK) equipped with an RI response detector. The samples were dissolved in $CHCl_3$ (~2 mg/mL) overnight. Separation took place on a 1x PL gel-mixed-A bed column (300 × 7.8 mm, 20 μm particles) + 1x PL gel-mixed-B bed column (300 × 7.8 mm, 10 μm particles) + 1x PL gel-mixed-D bed column (300 × 7.8 mm, 5 μm particles). Analyses were carried out at 40 °C in THF. The flow rate was 1.0 mL/min, and the injection volume was 100 μL. The GPC system was calibrated with narrow polystyrene standards ranging 580 to 6 120 000 g/mol (Polymer Laboratories Ltd., Church Stretton, UK). The weight average molar mass M_w, number average molar mass M_n, and molar-mass dispersity (PDI = M_w/M_n) of the tested samples were determined from peaks corresponding to the polymer fraction, these being expressed as "polystyrene-relative" molecular weights. All data processing was carried out using Cirrus software (Agilent, Church Stretton, UK).
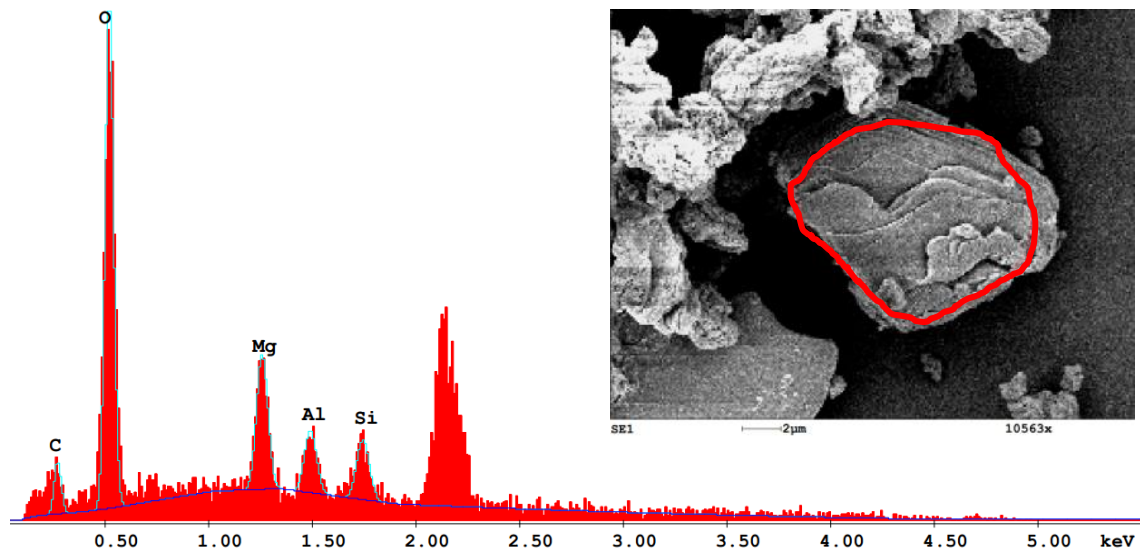
RESULTS AND DISCUSSION

Lignocellulosic Fibre Material

An overview of the material obtained is shown in Fig. 1A. Nearly undamaged fibres with lengths of around 50 µm are highlighted in Fig. 1C. However, most of the material consisted of small agglomerated particles (Fig. 1D). These may originate from the collapse of lignocellulose due to sudden water evaporation in the spray-dryer.

Moreover, layered, crystal-shaped structures were observed (Fig. 1B). The analysis of these structures by energy-dispersive X-ray spectroscopy (EDX) showed the presence of the inorganic elements magnesium, aluminium, and silicon (Fig. 2) in the proportions indicated in Table 2. While efforts have been made to replace inorganic fillers with more environmentally friendly compounds (Shen *et al.* 2011), materials such as magnesium silicate (talc) have been widely used ever since the beginning of papermaking history (Beazley 1985). The structures described here are most probably residues from fillers added in the paper mill during previous process steps.

Fig. 1. SEM images of the material obtained from a paper mill. Overview (A), inorganic layered structure (B), fibrous and particulate material (C), (D)
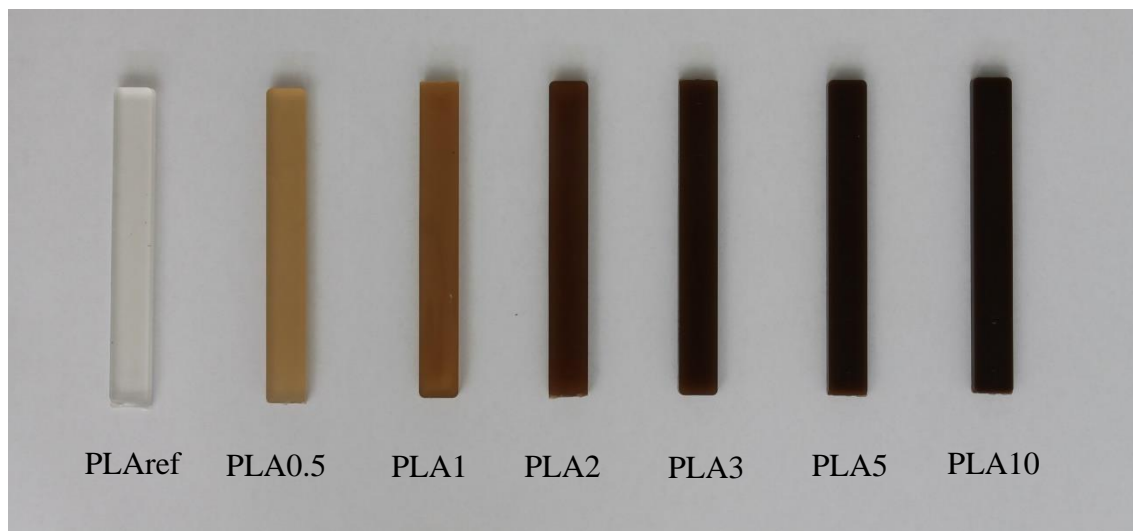
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Fig. 2. EDX spectrum of the inorganic structure shown in the insert. The unlabelled peak corresponds to the sputter-coated gold.

Table 2. Elemental Distribution of the Area Analysed by EDX

Element	Weight (%)	Atomic (%)
C	5.72	9.36
O	41.40	50.92
Mg	20.91	16.93
Al	13.67	9.97
Si	18.30	12.82

Filler Distribution in the PLA Matrix

The homogeneity of the filler distribution in PLA is analysed in Fig. 3. The change of colour, from light brown for PLA0.5 to dark brown for PLA10, was clearly visible to the naked eye.

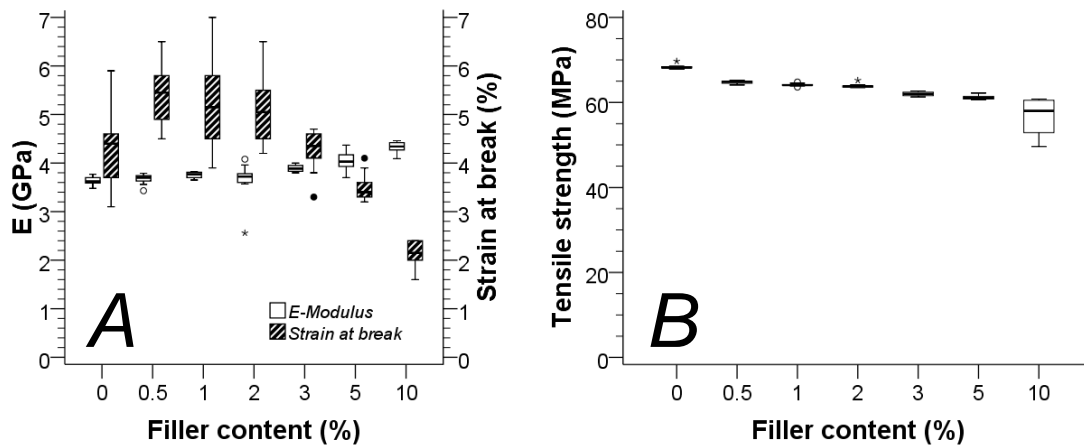**Fig. 3.** Injection-moulded test specimens (length: 80 mm, width: 10 mm, thickness: 4 mm)

As the filler used in this study was unbleached, this colour can be attributed to the lignin present on the fibres. Even if the colour of the photographed samples was uniform, the homogeneity of the filler distribution needed closer examination. For this purpose, optical microscope pictures are shown in Fig. 4. Neither fibre nor particle agglomerates were observed in the final composite. This result indicates that the filler was distributed homogeneously in the polymer matrix and that the agglomerates previously described in Fig. 1D could be de-agglomerated during extrusion and injection-moulding, due to the high shear forces occurring in these processes.

Fig. 4. PLA0.5 (A, D), PLA3 (B, E) and PLA10 (C, F) under optical transmission microscopy. The scale bar is 1 mm in the upper row and 100 μm in the lower row.

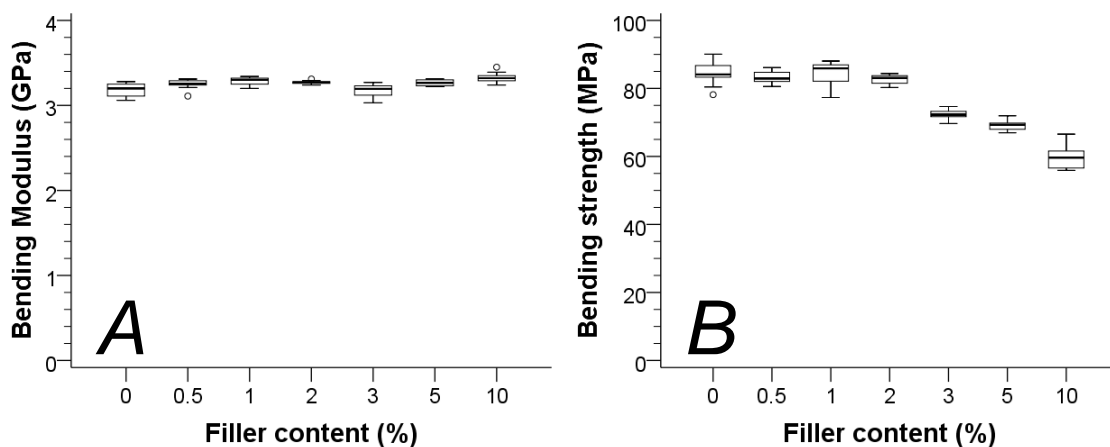## Mechanical Characteristics and Fracture Surfaces

The tensile test results are summarized in Fig. 5.

Fig. 5. Results from the tensile test. (A) E-Modulus (hollow boxes) and strain at break (hatched boxes). (B) Tensile strength. 10 samples per recipe were tested. Circles correspond to values that are between 1.5 and 3 box lengths from either end of the box. Asterisks correspond to values that are more than 3 box lengths from either end of the box. The box length is the distance between the 25% tile and the 75% tile.

The E-modulus stayed constant until the filler content reaches 2% and then increased, whereas the tensile strength decreased in parallel. In both cases, the variability of the obtained values was small, except for the tensile strength of PLA10. The strain at break tends to first slightly increase until a filler content of 3%, the scattering of the values being high. Then, less scattering is noticed and the strain at break drops down to a value of around 2% for PLA10.

The strength and the modulus measured during bending are displayed in Fig. 6. Bending strength decreased when the filler content of the composite exceeded 2%. Even though slight variations of the bending modulus were observed, it can be considered constant. Previous studies, dealing with higher natural fibre contents in the PLA matrix, found an increased flexural modulus (Shibata *et al.* 2003; Ochi 2008; Baghaei *et al.* 2014).

Fig. 6. Results from the bending test: Bending modulus (A) and bending strength (B). 10 samples per recipe were tested. Circles correspond to values that are between 1.5 and 3 box lengths from either end of the box. The box length is the distance between the 25% tile and the 75% tile.
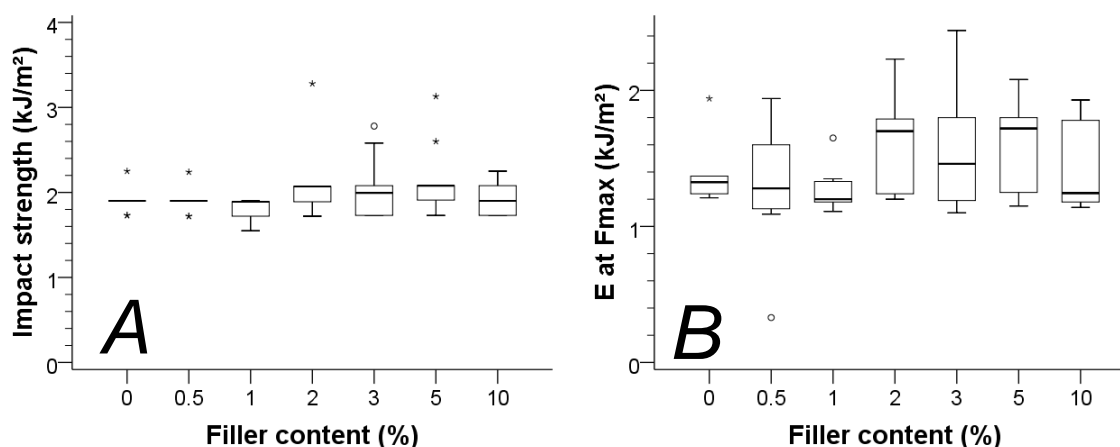
To sum up the findings presented in Figs. 5 and 6, the addition of spray-dried lignocellulosic material in the PLA matrix increased the sample stiffness and decreased the strength. This was true especially when the filler content was high. Strain at break was slightly improved by the addition of low amounts of filler. Thus, the filler can be used to partially overcome brittleness, one of the major drawbacks of PLA when compared to conventional polymers (Pandey *et al.* 2010). As a low filler content is required, other mechanical properties such as strength and stiffness would not be dramatically affected.

The impact behaviour of the composites is shown in Fig. 7. The median value of the impact strength was the same for each recipe. However, higher maximum values of impact strength around 3 kJ/m² were observed in the composites containing 2%, 3%, and 5% filler.

A similar behaviour was observed for the energy absorbed by the samples until the maximal impact force was reached; maximum values increased up to a filler content of 3%. This result shows that lignocellulose powder possesses some reinforcement potential, particularly with regard to enhancing toughness of PLA.

Overall, the mechanical characterisation demonstrated that the filler-matrix interaction in composites produced in the present study followed general trends universally observed for particulate, rather than fibrous, fillers (Fu *et al.* 2008). Due to the tendency of lignocellulose to collapse during spray-drying (Fig. 1), their geometry is particulate, rather than fibrous. As elucidated by Fu *et al.* (2008), this particulate geometry entails an increase in stiffness, a decrease in strength, and an improvement in toughness.

Fig. 7. Impact strength (A) and energy at maximal impact force (B) of the PLA/lignocellulose composites. 10 samples per recipe were tested. Circles correspond to values that are between 1.5 and 3 box lengths from either end of the box. Asterisks correspond to values that are more than 3 box lengths from either end of the box. The box length is the distance between the 25% tile and the 75% tile.

Figure 8 shows SEM pictures of fracture surfaces of samples tested under tensile load. Pure PLA exhibited large smooth surfaces without any irregularities (Fig. 8A, B), indicating a brittle fracture behaviour (Todo and Takayama 2011). The addition of filler dramatically changed the appearance of the fracture surface, which became rougher (Figs. 8C, E, and G). However, most of the observed patterns were independent of the amount of added filler.

Frequently, fibre pull-out and cavities created by debonding of lignocellulose from the surrounding PLA matrix were observed (Fig. 8D). This fracture mechanism is common for fibre reinforced composites under tensile load (Faludi *et al.* 2014). It is an indication of relatively poor surface adhesion between the lignocellulose and the PLA matrix. As local stress concentration is occurring at these defects, this explains the reduced strength of the PLA/lignocellulose composites. Moreover, PLA filaments as in Fig. 8F were often observed.

Finally, the fracture surface of the recipe containing 10% filler presented cracks (Figs. 8G, H). This particular feature was not observed in the composites containing a lower amount of filler. It may be a consequence of the high number of fibre-matrix interfaces where stresses are concentrated. Moreover, the high tensile strength scattering on this sample type (as shown in Fig. 5) could be an indication for the presence of cracks inside the polymer matrix even before the testing of the material.
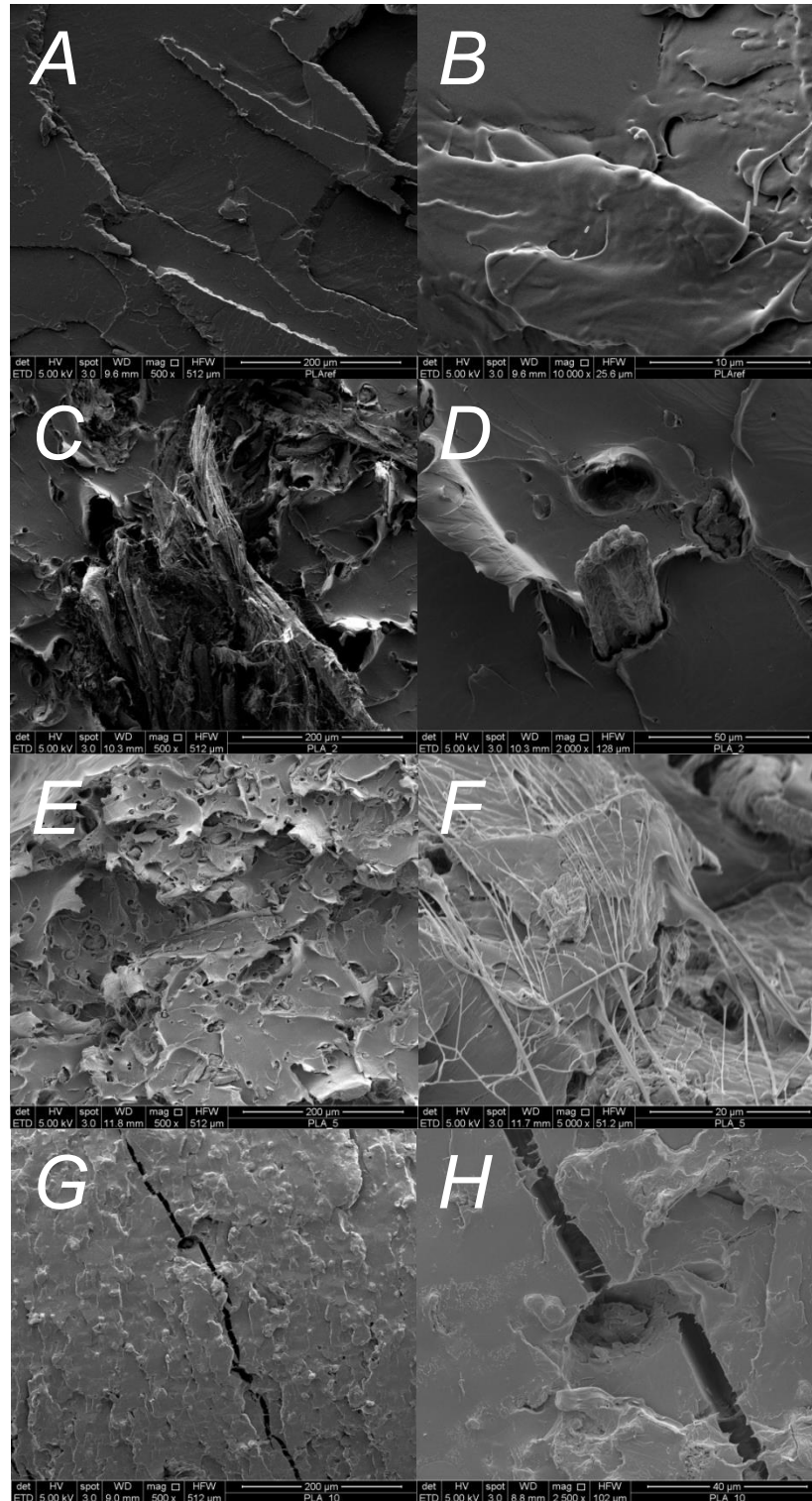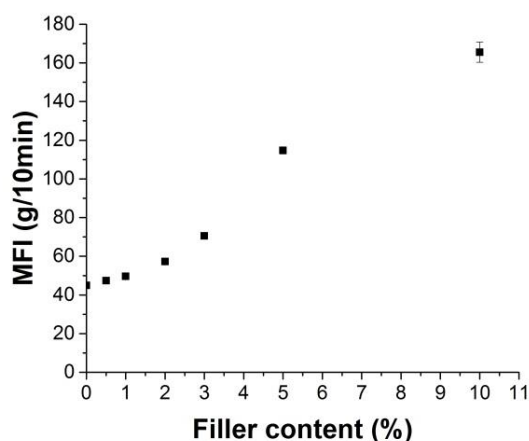
Fig. 8. SEM of fracture surfaces of PLAref (A, B), PLA2 (C, D), PLA5 (E, F), and PLA10 (G, H)

MFI and GPC

The MFI *versus* lignocellulose filler content is plotted in Fig. 9. The MFI clearly increased with the filler content. At 10% filler content, the MFI of the composite was nearly

four times higher than for neat PLA. This result is surprising, as the opposite effect (decrease of the MFI with increasing natural fibre content) has been reported in most studies (Mamun *et al.* 2013; Alam *et al.* 2014; Jaszkiewicz *et al.* 2016). As with any other kind of material, interactions between natural fibres and PLA are likely to occur. For example, the biodegradation of PLA is faster in the presence of natural fibres in the polymer matrix, which is related to the facilitated distribution of hydrolysis-causing water (Bayerl *et al.* 2014). However, this scenario can be excluded in the present study, as the sizing chemical cannot be hydrolysed and stops water from coming into contact with the fibres (Hubbe 2007), which were dry during the extrusion and injection-moulding steps. The most probable factor responsible for the increased MFI is hydrolysis caused by the release of residues during thermal decomposition of the filler, leading to chain length reduction in the polymer matrix (Jaszkiewicz *et al.* 2016). GPC measurements confirmed the degradation of PLA after the addition of filler and injection-moulding. The obtained molar mass distributions are shown in Fig. 10A. The curves shifted to the left (towards lower molecular masses) with increasing filler content. This effect is even clearer when the mass average molar mass M_w is plotted against the filler content (Fig. 10B); M_w linearly decreased when the filler content increased.
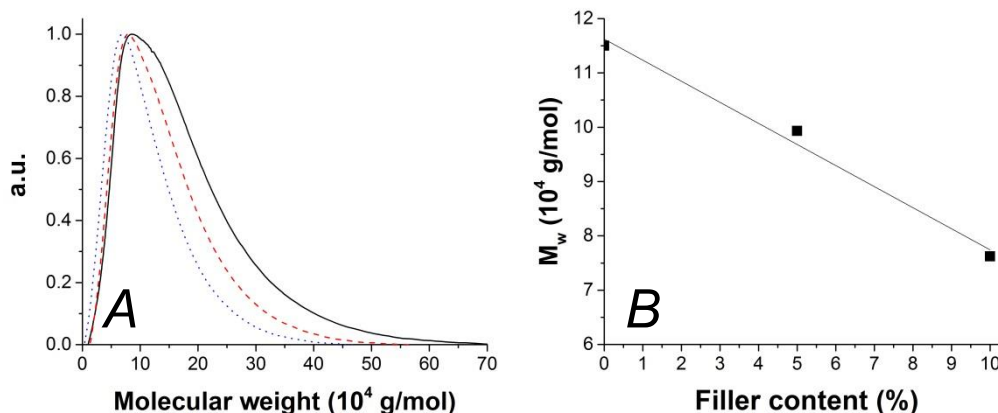

Fig. 9. Melt flow index (MFI) of the PLA/lignocellulose composites. Bars represent the standard deviation.

The previously cited studies report decreasing MFI after filler addition, but these results seem to contradict the present findings. This can be explained by the occurrence of two competing effects. Reduced chain length is often counterbalanced by the entanglements of the fibres in the polymer matrix (Jaszkiewicz *et al.* 2016). These entanglements are an obstacle for the flow of the melted polymer and decrease the MFI even if the polymer chains are shorter. In this case, the length of the lignocellulose fibres and their comparably high rigidity did not allow the formation of entanglements. Therefore, the fibres can orient in the flow without hindering it. From the processing point of view, this makes the PLA/lignocellulose composites an attractive material on the condition that sufficient mechanical performance is preserved.

Another reason for the MFI increase could be the residual inorganic content in the spray-dried powder, as already shown in Fig. 1B and Fig. 2. These inorganic fillers could act as nucleating agents increasing the crystallinity of PLA (Petchwattana *et al.* 2014, Ouchiar *et al.* 2015, Piekarska *et al.* 2016) and therefore have a lubricant effect on the

polymer chains of the matrix. As a consequence, the viscosity of the polymer matrix at high temperature is lower (Cipriano *et al.* 2014) and it can flow more easily during the MFI measurement.

Fig. 10. Normalised molecular weight distribution of PLAref (plain), PLA5 (dashed), and PLA10 (dotted) obtained by GPC (A) and mass average molar mass M_w *versus* filler content in the composites (B)

CONCLUSIONS

1. The compatibility between hydrophobic lignocellulosic spray-dried matter and PLA was assessed. Optical and microscopic investigations showed a homogeneous distribution of the filler in the PLA matrix.

2. Mechanical characterisation of the samples showed that the addition of lignocellulose during extrusion and injection-moulding resulted in composites with a lower strength and a higher stiffness than neat PLA.

3. The strain at break was increased after the addition of a small amount of filler (max. 2%).

4. The maximum values of impact strength were shown to increase after the addition of filler.

5. Further observation of the fracture surfaces with SEM showed fibre pull-out for all PLA/lignocellulose composites. Cracks parallel to the load direction were observed for samples with the highest filler content.

6. The hypothesis that size would act as compatibiliser between the polymer matrix was confirmed in the sense that homogeneous dispersion in PLA was achieved. In terms of clear improvements of composite mechanics, the results shown here are less conclusive, as only slight improvements in toughness were observed.

ACKNOWLEDGMENTS

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