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Research article

Cellulose kraft pulp reinforced polylactic acid (PLA) composites: effect of fibre moisture content

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Abstract: PLA offers a competitive and CO₂ neutral matrix to commonly used polyolefin polymer based composites. Moreover, the use of PLA reduces dependency on oil when producing composite materials. However, PLA has a tendency of hydrolytic degradation under melt processing conditions in the presence of moisture, which remains a challenge when processing PLA reinforced natural fibre composites. Natural fibres such as cellulose fibres are hygroscopic with 6–10 wt% moisture content at 50–70% relative humidity conditions. These fibres are sensitive to melt processing conditions and fibre breakage (cutting) also occur during processing. The degradation of PLA, moisture absorption of natural fibres together with fibre cutting and uneven dispersion of fibres in polymer matrix, deteriorates the overall properties of the composite.

In the given research paper, bleached softwood kraft pulp (BSKP) reinforced PLA compounds were successfully melt processed using BSKP with relatively high moisture contents. The effect of moist BSKP on the molecular weight of PLA, fibre length and the mechanical properties of the composites were investigated. By using moist never-dried kraft pulp fibres for feeding, the fibre cutting was decreased during the melt compounding. Even though PLA degradation occurred during the melt processing, the final damage to the PLA was moderate and thus did not deteriorate the mechanical properties of the composites. However, comprehensive moisture removal is required during the compounding in order to achieve optimal overall performance of the PLA/BSKP composites. The economic benefit gained from using moist BSKP is that the expensive and time consuming drying process steps of the kraft pulp fibres prior to processing can be minimized.

Keywords: poly(lactic acid); bleached softwood kraft pulp; degradation; mechanical properties; compounding; injection moulding

Abbreviations

Fibre Reinforced Polymer	FRP
Poly(lactic acid)	PLA
Glycerol triacetate	GTA
Bleached softwood kraft pulp	BSKP
Size exclusion chromatography	SEC
Number average molecular weight	M_{n}
Weight average molecular weight	$M_{\rm w}$
Polydispersity index	PD

1. Introduction

Currently, the majority of the commercial available Fibre Reinforced Polymer (FRP) composites in e.g. automotive industry are based on petroleum-based polymers (either thermoset or thermoplastic) reinforced with synthetic fibres such as carbon fibre, aramid fibre and glass fibre [1]. However, environmental concerns are pushing industries for the use of renewable and bio-based materials. The focus of environmentally friendly composites has led to investigations of alternative constituents for composites. For example, poly(lactic acid) (PLA), a thermoplastic biopolymer, has been considered as one of the most promising material to replace petroleum-based plastics in a wide range of applications. PLA offers a competitive and CO₂ neutral basis to polyolefin and bulk polymer based composites. Moreover, use of PLA reduces dependency on oil for the production of composite materials. However, the major concerns of PLA biopolymers are their low impact strength, narrow processing window, poor fibre-matrix compatibility and moisture absorption [2,3]. Another drawback related to PLA is its tendency to hydrolytic degradation under melt processing conditions in the presence of moisture [4], which remains a challenge when processing PLA reinforced natural fibre composites.

Natural fibres are hygroscopic by nature with 6–10 wt% moisture content at 50–70% relative humidity conditions [5]. Moisture absorption of natural fibres often leads to swelling and presence of voids at the interface. In general, to avoid drawbacks related to moisture, PLA and natural fibres have been dried prior to processing biocomposites to remove most of water [2,6–10]. Some studies do not mention drying PLA and natural fibres prior to processing [11,12]. Besides fibre drying, cellulose fibre modification is another way to decrease moisture absorption of the produced PLA/cellulose composites [13].

Studies on the influence of moisture in natural fibres on the properties of PLA composites have been published. Fujiura et al. [14] demonstrated the decrease of the average molecular weight of PLA as the moisture content of the jute fibre increased in the composite. The mechanical properties of the composites were also decreased due to the hydrolysis. Eliminating moisture from the long jute fibres (LJF) in the preparation process of the LJF/PLA pellets was found to be important for preventing the deterioration in the molecular weight of PLA and the mechanical performance of the

composites. Another study concluded that 6–9 wt% moisture present in the natural fibres did not cause fatal PLA degradation during compounding time of 13 min [5]. A low moisture content of 0.2–0.4 wt% in the fibres did not have large impact on the morphological and mechanical properties of the PLA/natural fibre composites. Molar mass analysis revealed that not all water molecules available in the fibres caused PLA cleavage in the melt compounded PLA/natural fibre samples. This was explained by the variable fibre-PLA contact surface area, which is related to the fibre or the fibre bundle diameter.

Cellulose fibres are sensitive to melt processing conditions and suffer morphological changes caused by the high processing temperatures and high shear forces of the extruders and injection moulding machines [15]. The fibre breakage during the composite manufacturing process causes of the reduction of the composites' mechanical properties. Therefore, several papers have investigated natural fibre damage (cutting) during the melt processing of thermoplastic composites. Longer cellulose fibres have exhibited higher length reduction during the compounding than shorter fibres [16,17,18]. In most cases shorter cellulose fibres showed better fibre dispersion in the thermoplastic matrix than longer fibres [16,19]. The improved performance of the composite has been explained by the even dispersion of natural fibres in polymer matrix, good fibre-matrix adhesion and higher stiffness of the fibres. The viscosity of the melt, which determines shear forces, can be influenced by the polymer [20], the fibre and plasticizer content [21], and the compounding system [22]. Peltola et al. [18] succeeded to reduce the wood fibre degradation in the polypropylene composites by using lower shear forces during the melt processing. However, low screw rotation speed during compounding hindered the formation of good dispersion of wood fibres in the polymer matrix. Generally, use of tougher compounding conditions, better fibre dispersion and interfacial adhesion between fibres and polymer matrix can be achieved at the cost of greater degradation of cellulose fibres [23–26].

Mechanical properties of wood pulp fibres depend on their moisture content. Considerable stiffening of fibres takes place with decreasing moisture content, which is often called hornification. Hornification can be reversible or irreversible. Hornification phenomenon is associated with the formation of irreversible or partially irreversible hydrogen bonds in cellulose upon drying or water removal [27,28]. Drying of wood pulp fibres is accompanied by shrinkage of the internal fibre volume due to structural changes in wood pulp fibres caused by the removal of water molecules [27]. In the case of irreversible hornification the original water-swollen state is not regained after resuspension of fibres in water [29]. Hornification is especially well-known in papermaking processes. The use of stiff, hornified and once-dried fibres results in reduced strength properties of paper to be made of them [27]. On the other hand, when the shrinkage is prevented during drying of paper, the water removal results in increased shrinkage stresses, higher elastic modulus and strength of fibres and paper [30]. This takes place regardless of possible irreversible hornification.

When studying the hornification phenomenon of the never-dried kraft pulp fibres during water removal, Weise et al. [31] showed that the fibre shrinkage occurs in two different phases. Even the removal of "free" water in the initial phase of drying results in some hornification and leads to shrinkage of fibre wall thickness, when the gaps between the lamellae of the fibre cell wall become dewatered. In the second phase, removal of bound water causes a rapid and isotropic shrinkage of the fibre cross-section. Hornification was also detected when removing the last few percent of water from the air-dried fibres, which restricted the fibre re-swellability regarding the fibre width. The hornification was especially high with the never-dried bleached kraft pulp fibres [31].

Using moist fibres of kraft pulp in the melt processing of PLA could be the ideal, simple and cost-effective route to fabricate composites. However, there is lack of research dealing with this topic and detailed analysis is needed to gain a deeper understanding on how those compounds behave during the melt processing and how the optimal performance of the composites could be reached. Herrera et al. [32] succeeded to reinforce PLA using aqueous dispersion with 9.5 wt% of the nanofibres for the liquid feeding in the extrusion. Glycerol triacetate (GTA) was used as a processing aid to facilitate the nanofiber dispersion and as a liquid medium for their feeding. Recently, a simple and efficient method for the manufacturing of the thermoplastic composite using wet natural fibres was invented by Nikkilä and Ture [33]. In this method a wet mixture of natural fibres was compounded with a thermoplastic polymer and a compatibility improving agent in an extruder followed by mechanical pressing. By using high pressures and temperatures, water can be efficiently removed from the inner structure of the fibre and fibre may be worked into a more advantageous form in the melt mixing.

In this study, never-dried bleached softwood kraft pulp (BSKP) was used for feeding in the compounding with PLA without any processing additives. Moisture content of the BSKP was adjusted to 1, 3, 16 and 25% in a conditioning chamber and/or flow dryer before the compounding stage. Subsequently, the PLA/BSKP specimens were prepared by the injection moulding. The properties of the composites were investigated from a viewpoint of clarifying the effect of the moist kraft pulp fibres on the average molecular weight of PLA after processing and the mechanical performance of the composite. The study also evaluates the advantage of using the moist BSKP to prevent damage to the BSKP fibres during the melt processing. The fibre dispersion in the PLA matrix was also examined.

2. Materials and Methods

2.1. Materials

Poly(lactic acid) (PLA) (Natureworks[®], 3052D grade) was used a matrix polymer for the preparation of the PLA/bleached softwood kraft pulp (BSKP) composites. Never-dried bleached softwood kraft pulp made from spruce was delivered by Stora Enso. The PLA samples containing 30 wt% of BSKP with 1, 3, 16 and 25% moisture contents were prepared and denoted as PLA/BSKP1, PLA/BSKP3, PLA/BSKP16 and PLA/BSKP25, respectively.

2.2. Processing

PLA composites with bleached softwood kraft pulp content of 30 wt% were prepared using a co-rotating twin-screw extruder (Berstorff GmbH ZE 25x33 D). Diameters and lengths of the screws of the twin-screw extruder were 25 mm and 870 mm respectively. The extruder zone temperatures ranged from 60 to 195 °C.

The moisture content of the bleached softwood kraft pulp was adjusted prior to compounding:

- BSKP1 sample was dried in the flow dryer at 50 °C for 30 minutes. Drying of BSKP1 was continued in an oven at 50 °C for 4 hours and in a vacuum-oven at 50 °C for 2 hours.
 - BSKP3 sample was dried in the flow dryer at 50 °C for 30 minutes.

- BSKP16 sample was kept in a conditioning chamber (WTB Binder KBF-115) at 30 °C and 75% RH for 24 hours. Drying of BSKP16 was continued at 25 °C and 50% RH overnight. Finally, BSKP16 sample was dried in the flow dryer at 30 °C for 15 minutes.
- BSKP25 sample was kept in a conditioning chamber (WTB Binder KBF-115) at 30 °C and 75% RH for 24 hours. Finally, BSKP25 sample was dried in the flow dryer at 30 °C for 15 minutes.

Vacuum was used during the compounding to remove excess water. Samples were compounded under nitrogen and a vacuum of 500 mbar was applied. The compositions of the prepared composites and the initial moisture contents of bleached softwood krat pulp before compounding are presented in Table 1. The moisture contents of BSKP were determined with a moisture analyser Precisa XM 50. After compounding, the PLA/BSKP samples were injection moulded with an injection-moulding machine (Engel ES 200/50 HL) to dumbbell shape specimens according to ISO 3167. At least 25 injection moulded specimens for each sample material were prepared. Neat PLA specimen was prepared following the same processing parameters and used as reference. Figure 1 illustrates the injection moulded PLA and PLA/BSKP samples.

Table 1. Compositions of the produced composites and moisture contents of the bleached softwood kraft pulp (BSKP) before compounding.

Sample code	Bleached softwood kraft pulp (wt%)	PLA (wt%)	Moisture content of bleached softwood kraft pulp before compounding (%)
PLA	-	100	-
PLA/BSKP1	30	70	1
PLA/BSKP3	30	70	3
PLA/BSKP16	30	70	16
PLA/BSKP25	30	70	25

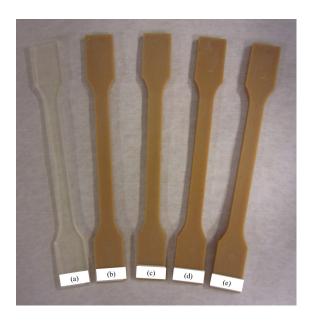


Figure 1. Injection moulded tensile test specimens of PLA composites containing 30 wt% of BSKP with four different moisture contents: (a) neat PLA, (b) PLA/BSKP1, (c) PLA/BSKP3, (d) PLA/BSKP16 and (e) PLA/BSKP25.

2.3. Fibre Length Analysis

For determination the BSKP fibre lengths, the fibre fraction of injection moulded PLA samples was Soxhlet-extracted. A small amount of composite sample was placed into the Soxhlet thimble and continuously fluxed with a hot solution of chloroform for 48 h. The remaining kraft pulp fibre fraction was collected and the fibre lengths were determined using a Kajaani Fiberlab analyser. Some 0.23–0.30 g of each sample was soaked in 500 ml deionized water and they were dispersed using a high shear laboratory blender (IKA Ultra-Turrax T18) for five minutes. After dispersing the samples were left in deionized water overnight. Next day the samples were further mixed in five litres of water with an impeller for 10 minutes. Some 50 ml of dispersed sample was pipetted into the analyser and fibre analysis was performed with two repeat measurements. Fibre length results were reported according to TAPPI standard method T271.

2.4. Size Exclusion Chromatography (SEC)

The average molar masses and polydispersity index of the samples before and after the melt processing steps were determined using size exclusion chromatography (SEC) coupled with a refractive index detector (Waters 2412).

The PLA/BSKP samples were prepared for SEC analysis by dissolving in chloroform overnight at room temperature. Each solution concentration was 1 mg/ml. Before injection, the samples were filtered through a 0.45 μm GHP filter. Styragel HR 4 and 3 columns with a pre-column were used in the SEC measurements. Separations were performed at 30 °C using chloroform as eluent at a flow rate of 0.6 mL min⁻¹. Three parallel samples were analysed for each composite. The data obtained with Waters 2412 detector were analysed with Waters Empower 3 software. The molar mass distributions (MMD) were calculated against 8 x polystyrene (PS) (1260–1030000 g mol⁻¹) standards, using Waters Empower 3 software. The average molar masses and polydispersity of the samples were calculated using the following equations:

The number average molecular weight, M_n

$$Mn = \frac{\Sigma N_i M_i}{\Sigma N_i}$$

where M_i is the molecular weight of a chain and N_i is the number of chains of that molecular weight.

Weight average molecular weight, M_w

$$Mw = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i}$$

Polydispersity index, PD

$$PD = \frac{M_w}{M_n}$$

2.5. Mechanical Testing

Tensile tests were performed using an Instron 4505 Universal Tensile Tester (Instron Corp., Canton, MA, USA) and an Instron 2665 Series High Resolution Digital Automatic Extensometer (Instron Corp., Canton, MA, USA) with a 10 kN load cell and a 5 mm/min cross-head speed. The ISO-527 and ISO-179 standards were used in the mechanical testing of the specimens. Five specimens were tested for each sample material to obtain the average values of the tensile properties. Impact strengths were determined by using a Charpy Ceast Resil 5.5 Impact Strength Machine (CEAST S.p.a., Torino, Italy). Charpy impact strength tests in edgewise orientation was applied to the unnotched specimens. Impact testing was conducted in sets of ten replicates to obtain an average value and variance. The test specimens were kept in standard conditions (23 °C, 50% relative humidity) for at least five days before testing.

3. Results and Discussion

3.1. Fibre Length

Damage of the natural fibre during the composite melt processing steps is one of the main reasons of the reduction of the composites' mechanical properties such as strength and stiffness. For this reason, retaining fibre length is desirable for the improved strength and stiffness of the composite. In the present work by using moist BSKP less hornification and kraft pulp fibre cutting is expected. The BSKP fibre lengths were determined from the compounded and injection moulded PLA samples (Table 2).

Table 2. Fibre lengths of the bleached softwood kraft pulp (BSKP) before and after processing.

Sample code	Fibre length of BSKP L(l) (mm) ^b	Fibre length of BSKP L(l) (mm) ^c		
Unprocessed BSKP ^a	1.79	-		
PLA/BSKP1	0.69	0.29		
PLA/BSKP3	0.68	0.35		
PLA/BSKP16	0.84	0.28		
PLA/BSKP25	0.96	0.29		

^a Bleached softwood kraft pulp fibre length before compounding and injection moulding.

Less cutting to BSKP fibres in the melt compounding is observed as the moisture content of fibres for the feeding is increased as shown in Table 2. By using wet BSKP with higher moisture contents (up to 25%) for feeding in the compounding, the damage (cutting) to fibres is decreased by 39% as compared to the kraft pulp fibres with 1% moisture content in the feeding. This may be due to the fact that never-dried BSKP fibres are not hornificated and thus less brittle than the dried BSKP fibres. Another explanation for this phenomenon is the formation of water vapour on the surface of the kraft pulp fibres during the compounding. This so-called "vapour bed" acts as a protective layer and decrease shear forces subjected to the fibres from polymer melt. Phenomenon is similar to

^b BSKP fibre lengths determined from compounded samples.

^c BSKP fibre lengths determined from injection moulded samples.

Leidenfrost effect [34–37]. On the other hand, the formation of the vapour bed restrains the heat transfer into the fibre. In addition, moisture evaporation from the kraft pulp fibre creates a cooling effect and thus fibres are able to retain moisture for a longer period of time.

As shown in Table 2 injection moulding effectively cuts the BSKP fibres. After injection moulding the kraft pulp fibre lengths of different samples are almost the same. In injection moulding step moisture is already removed from the fibre and thus do not protect the fibres from cutting anymore.

3.2. SEC

The average molar weights and polydispersities of neat PLA and PLA/BSKP samples are presented in Table 3. The initial number average (M_n) and weight average (M_w) for the molecular weights of the neat PLA granulates before processing are 154.751 kg mol⁻¹ and 228.181 kg mol⁻¹, respectively. The polydispersity of neat PLA is 1.5. The weight average of the molecular weight of neat PLA granulates decreases through the compounding and injection moulding steps as shown in Table 3. After compounding with BSKP with 1, 3, 16 and 25 wt% moisture contents, lower weight average molecular weights of PLA are recorded. However, after injection moulding Mw values of the PLA/BSKP specimens increase when compared to Mw values of the compounded PLA/BSKP samples. In the melt stage of PLA there exist reactive end groups due to thermal and hydrolytic degradation occurring in the process. This can lead to transesterification and chain coupling in the polymer melt. On the other hand, the use of vacuum for the removal of water from the extruder may to some extent lead to longer polymer chains in the next melt stage [38,39]. PLA tends to degrade when there is excess water in the compounding stage. We suggest that by removing excess water the acidic conditions can be retained which initiates the polymerisation reaction during injection moulding. There is a balance between esterification and transesterification reactions in the melt stage and it can be in relation to the moisture content.

The polydispersity values of all samples remain relatively constant.

Table 3 The average molecular weights (M_n, M_w) and polydispersities (PD) of the PLA/BSKP samples after the compounding and injection moulding.

Sample F	Process	M_n	$M_{ m w}$	PD	Eluent/HPSEC
	Process	$(kg mol^{-1})$	$(kg mol^{-1})$	ΓD	system
Neat PLA	-	154.8	228.2	1.5	Chloroform
PLA	compounding	149.3	223.0	1.5	Chloroform
	injection moulding	143.0	216.0	1.5	Chloroform
PLA/BSKP1	compounding	139.5	212.6	1.5	Chloroform
	injection moulding	123.7	221.5	1.8	Chloroform
PLA/BSKP3	compounding	139.0	212.1	1.5	Chloroform
	injection moulding	141.5	226.8	1.6	Chloroform
PLA/BSKP16	compounding	128.0	198.8	1.6	Chloroform
	injection moulding	130.8	217.6	1.6	Chloroform
PLA/BSKP25	compounding	126.4	197.6	1.6	Chloroform
	injection moulding	128.2	217.5	1.7	Chloroform

3.3. Morphological Analysis

The morphology of the cryo-fractured surfaces of the injection moulded PLA/BSKP composites was studied by SEM. The micrographs indicate that the BSKP fibres were partly attached with the PLA matrix as shown in Figure 2a–d. Some void spaces between the BSKP fibre and the PLA matrix were detected. SEM studies revealed that by using moist never-dried pulp fibres in the compounding resulted in a moderate fibre-matrix adhesion in the injection moulded specimens. PLA/BSKP1 and PLA/BSKP3 showed improved tensile strength and modulus, which may indicate a better fibre-matrix interaction or an improved fibre dispersion when compared to PLA/BSKP16 and PLA/BSKP25 samples. However, SEM micrographs do not reveal a clear fibre-matrix adhesion difference when using never-dried fibres with various moisture contents in the melt processing.

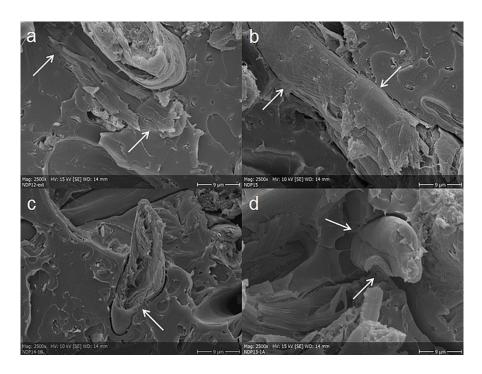


Figure 2. SEM images of the cryo-fractured surfaces of the PLA/BSKP dumbbell specimens with the same magnification: (a) PLA/BSKP1, (b) PLA/BSKP3, (c) PLA/BSKP16 and (d) PLA/BSKP25.

3.4. Mechanical Properties

The mechanical properties of the PLA/BSKP composites with standard deviations are summarized in Table 3. The addition of 30 wt% BSKP with various moisture contents resulted in improved strength and stiffness of all the composites when compared to the neat PLA. Tensile strength improved from 62.7 MPa for neat PLA to 73.1 MPa for PLA/BSKP3. Similarly, strength enhanced from 62.7 MPa for neat PLA to 72.8 MPa, 70.6 MPa and 70.4 MPa for PLA/BSKP1, PLA/BSKP16 and PLA/BSKP25, respectively. The highest improvement in Young's modulus was obtained from the PLA/BSKP16 composite in comparison with the neat PLA. The incorporation of the BSKP with various moisture contents deteriorated the strain and impact strength of PLA. Lower strain and impact strength can be explained by the voids between the kraft pulp fibres and PLA

matrix resulting in reduced fibre-matrix adhesion in the composite. After the injection moulding BSKP3 retained the highest fibre length among other fibres. The longer fibre length together with the higher molar mass of PLA in the PLA/BSKP3 sample may explain the superior tensile strength. We believe that the tensile modulus or the material stiffness is related to good fibre dispersion in a polymer matrix. We suggest that the degradation of PLA decreases the molecular weight while water acts as a plasticizer for the kraft pulp fibres during the compounding. Degraded PLA together with water decreases the viscosity of the polymer melt which may lead to improved fibre dispersion during the compounding stage and also reflects the better properties of the composites after injection moulding.

Sample code	Tensile strength	Young's modulus	Elongation at	Impact strength
	(MPa)	(GPa)	max stress (%)	(kJ/m^2)
PLA	62.7 ± 0.3	3.38 ± 0.1	2.28 ± 0	16.4 ± 1.1
PLA/BSKP1	72.8 ± 0.7	6.19 ± 0.1	1.85 ± 0.1	14.3 ± 1.6
PLA/BSKP3	73.1 ± 0.3	6.21 ± 0.1	1.87 ± 0.1	13.9 ± 1.7
PLA/BSKP16	70.6 ± 1.2	6.67 ± 0.1	1.50 ± 0.1	13.1 ± 1.7
PLA/BSKP25	70.4 ± 0.8	5.91 ± 0.3	1.75 ± 0.1	14.2 ± 1.3

Table 4. Mechanical properties of PLA and PLA/BSKP composites.

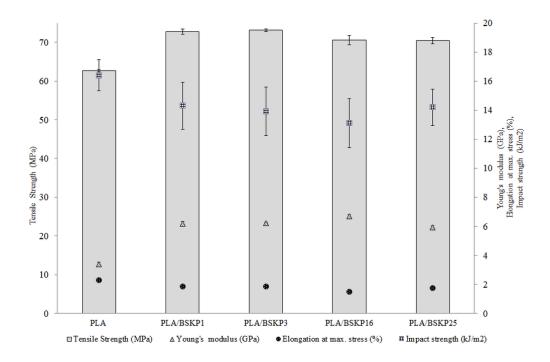


Figure 3. Effect of bleached softwood kraft pulp (BSKP) moisture contents on the mechanical properties of PLA.

4. Conclusion

Kraft pulp fibres are mainly used in the form of dried pulp sheets or never-dried pulp in thermoplastic composites. Prior to compounding pulp sheets need to be grounded and pelletized. In the first place, wetting of pulp fibres is required for the pellet production. Secondly, pulp fibres need to dried after pelletizing. When never-dried pulp is used it can be pelletized wet and dried. It is common practise to dry natural fibres as dry as possible prior to processing with PLA. This usually requires use of vacuum dryers and non-humid feeding system with protective gas in processing. In this way, the degradation of PLA during processing can be minimized. Dried cellulose has a very high moisture absorption tendency directly from the air. Usually this behavior complicates the use of cellulose in thermoplastic composite processing.

Pulp drying consumes a huge amount of energy. It is estimated that the energy consumption in pulp drying is about 2.8–4.0 gigajoule/ton evaporated water. However, the energy consumption is determined by the drying method [40]. The average cost of energy across Europe was 0.08 €/kWh [41].

This paper presents a promising and advantageous route to produce bleached softwood kraft pulp reinforced PLA composites via compounding and injection moulding. By using moist neverdried bleached softwood kraft pulp for feeding, the kraft pulp fibre cutting during the melt processing is decreased. This phenomenon can be explained by the less brittle features of moist never-dried BSKP fibres when compared to dried BSKP fibres. On the other hand, water present in the BSKP fibres during compounding may act as a plasticizer for the fibres. It is suggested that water together with degraded PLA reduces the viscosity of the polymer melt. The reduction of melt viscosity leads to reduction in shear forces in the latter stage of compounding before the vacuum treatment and thus less cutting to BSKP fibres occurs.

According to these trials it seems that moist BSKP could be successfully used in PLA compounding and there is no need for intensified drying of the kraft pulp fibres. moist present in the kraft pulp does not necessarily deteriorate the final properties of PLA. By avoiding the use of additional drying steps or protective gas facilitates processing and results in cost savings. First of all, this study demonstrates that the cellulose fibre length can be retained in the compounding stage when using never-dried fibres for feeding. We suggest that with the optimum initial moisture content of BSKP (for example 3 wt%), the most cost-effective processing method for injection moulded PLA/BSKP composites is achieved.

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Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

References

1. ABC's of FRP Materials, Automotive Composites Alliance, American Composites Manufacturers Association (2016) Available from: http://www.autocomposites.org/composites101/abc.cfm.

- 2. Bledzki AK, Jaszkiewicz A (2010) Mechanical performance of biocomposites based on PLA and PHBV reinforced with natural fibres A comparative study to PP. *Compos Sci Technol* 70: 1687–1696.
- 3. Hossain KMZ, Parsons AJ, Rudd CD (2014) Mechanical, crystallisation and moisture absorption properties of melt drawn polylactic acid fibres. *Eur Polym J* 53: 270–281.
- 4. Document on crystallization and drying of PLA, NatureWorks LLC, 2016. Available from: www.natureworksllc.com.
- 5. Oever MJAVD, Beck B, Müssig J (2010) Agrofibre reinforced poly(lactic acid) composites: Effect of moisture on degradation and mechanical properties. *Compos Part A–Appl S* 41: 1628–1635.
- 6. Penjumras P, Rahman RA, Talib RA (2015) Mechanical properties and water absorption behaviour of durian rind cellulose reinforced Poly(lactic acid) biocomposites. *Int J Sci Engg Tech* 5:343–349.
- 7. Ganster J, Fink HP, Pinnow M (2006) High-tenacity man-made cellulose fibre reinforced thermoplastics injection moulding compounds with polypropylene and alternative matrices. *Compos Part A–Appl S* 37: 1796–1804.
- 8. Jonoobi M, Harun J, Mathew AP (2010) Mechanical properties of cellulose nanofiber (CNF) reinforced polylactic acid (PLA) prepared by twin screw extrusion. *Compos Sci Technol* 70: 1742–1747.
- 9. Sippola M, Immonen K, Miettinen A (2015) Predicting stiffness and strength of birch pulp-Polylactic acid composites. *J Compos Mater*.
- 10. Huda MS, Drzal LT, Misra M (2006) Wood–fiber-reinforced poly(lactic acid) composites: evaluation of the physicomechanical and morphological properties. *J Appl Polym Sci* 102: 4856–4869.
- 11. Oksman K, Skrifvars M, Selin JF (2003) Natural fibres as reinforcement in polylactic acid (PLA) composites. *Compos Sci Technol* 63: 1317–1324.
- 12. Anuar H, Zuraida A, Fuad F (2010) Biodegradable PLA-Kenaf Fibre Biocomposite for Cleaner Environment. In: Malaysian Science and Technology Congress (MSTC 2010), Crystal Crown Hotel, Petaling Jaya, Malaysia.
- 13. Laxmeshwar SS, Viveka S, Madhu Kumar DJ, et al. (2012) Preparation and properties of composite films from modified cellulose fibre-reinforced with PLA. *Der Pharma Chem* 4: 159–168.
- 14. Fujiura T, Sakamoto K, Tanaka T (2015) A study on preparation and mechanical properties of long jute fiber reinforced polylactic acid by the injection molding process. In: Syngellakis S, *Composites: Advances in Manufacture and Characterisation*, WIT Transactions on State of the Art in Science and Engineering, WIT Press, 109–118.
- 15. Fu SY, Mai YW, Ching ECY (2002) Correction of the measurement of fiber length of short fiber reinforced thermoplastics. *Compos Part A Appl S* 33: 1549–1555.
- 16. Ariño R, Boldizar A (2013) Barrier screw compounding and mechanical properties of EEA copolymer and cellulose fiber composite. *Int Polym Process* XXVIII 4: 421–428.
- 17. Baillif ML, Oksman K (2009) The effect of processing on fiber dispersion, fiber length, and thermal degradation of bleached sulphite cellulose fiber polypropylene composites. *J Thermoplast Compos Mater* 22: 115–133.
- 18. Peltola H, Pääkkönen E, Jetsu P (2014) Wood based PLA and PP composites: Effect of fibre type and matrix polymer on fibre morphology, dispersion and composite properties. *Compos Part A–Appl S* 61: 13–22.

- 19. Peltola H, Laatikainen E, Jetsu P (2011) Effects of physical treatment of wood fibres on fibre morphology and biocomposite properties. *Plast Rubber Compos* 40: 86–92.
- 20. Sykacek E, Hrabalova M, Frech H (2009) Extrusion of five biopolymers reinforced with increasing wood flour concentration on a production machine, injection moulding and mechanical performance. *Compos Part A–Appl S* 40: 1272–1282.
- 21. Peltola H, Madsen B, Joffe R (2011) Experimental study of fiber length and orientation in injection molded natural fiber/starch acetate composites. *Adv Mater Sci Eng* 891940: 1–7.
- 22. Barkoula NM, Garkhail SK, Peijs T (2010) Effect of compounding and injection molding on the mechanical properties of flax fiber polypropylene composites. *J Reinf Plast Compos* 29: 1366–1385.
- 23. Karmarkar A, Chauhan SS, Modak JM (2007) Mechanical properties of wood–fiber reinforced polypropylene composites: effect of a novel compatibilizer with isocyanate functional group. *Compos Part A–Appl S* 38: 227–233.
- 24. Amash A, Zugenmaier P (2000) Morphology and properties of isotropic and oriented samples of cellulose fibre–polypropylene composites. *Polymer* 41: 1589–1596.
- 25. Stamboulis A, Baillie CA (2000) Environmental durability of flax fibres and their composites based on polypropylene matrix. *Appl Compos Mater* 7: 273–294.
- 26. Doan T, Gao S, Mäder E (2006) Jute/polypropylene composites I. Effect of matrix modification. *Compos Sci Technol* 66: 952–963.
- 27. Fernandes Diniz JMB, Gil MH, Castro JAAM (2004) Hornification its origin and interpretation in wood pulps. *Wood Sci Technol* 37: 489–494.
- 28. Smook GA (1990) Hornification (keyword), In: Wilde A, *Handbook of pulp and paper terminology*, Vancouver: Angus Wilde 135.
- 29. Minor JL (1994) Hornification its origin and meaning. *Progr Pap Recycling* 3: 93–95.
- 30. Retulainen E, Martikainen P, Timofeev O (2015) Drying tension and shrinkage in paper and board: Part 1 Single ply sheets of chemical and mechanical furnishes. *Appita J* 68: 51–54.
- 31. Weise U (1997) Characterization and mechanisms of changes in wood pulp fibres caused by water removal. Acta Polytechnica Scandinavica, Chemical Technology Series No. 249, Laboratory of Paper Technology, Department of Forest Products Technology, Helsinki University of Technology, 1–141.
- 32. Herrera N, Mathew AP, Oksman K (2015) Plasticized polylactic acid/cellulose nanocomposites prepared using melt-extrusion and liquid feeding: mechanical, thermal and optical properties. *Compos Sci Technol* 106: 149–155.
- 33. Nikkilä M, Ture T (2014) Method and apparatus for the manufacturing of composite material. WO 2014/181036 A1.
- 34. Eshuis PG, van der Weele K, van der Meer D (2005) Granular Leidenfrost effect: Experiment and theory of floating particle clusters. *Phys Rev Lett* 95: 258001.
- 35. Eshuis K, van der Weele D, van der Meer D, Lohse D (2005) The granular Leidenfrost effect, In: Garcia-Rojo R, Herrmann HJ, McNamara S, *Powders and Grains*, Leiden: Balkema Publication, 1155–1158.
- 36. Eshuis P, van der Weele K, van der Meer D (2007) Phase diagram of vertically shaken granular matter. *Phys Fluids* 19: 123301.
- 37. Eshuis P, van der Meer D, Alam M (2010) Onset of convection in strongly shaken granular matter. *Phys Rev Lett* 104: 038001.

- 38. Masutani K, Kimura Y (2014) Chapter 1: PLA Synthesis. From the Monomer to the Polymer, In: Jiménez A, Peltzer M, Ruseckaite R, *Poly(lactic acid) Science and Technology: Processing, Properties, Additives and Applications*, RSC Polymer Chemistry Series No. 12, 1–36.
- 39. Garlotta D (2001) A Literature Review of Poly(Lactic Acid). J Polym Environ 9: 63–84.
- 40. Kuhasalo A, Niskanen J, Paltakari J (2000) Introduction to paper drying and principles and structure of a dryer section, In: Karlsson M, *Papermaking Part 2: Drying*, Papermaking Science and Technology Series 9, Fapet Oy, Helsinki, 16–53.
- 41. Reduced energy consumption in plastics engineering (2005) European benchmarking survey of energy. Available from: http://ec.europa.eu/energy/intelligent/projects/sites/iee-projects/files/projects/documents/recipe_benchmarking_report.pdf.



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