Foam-Laid Thermoplastic Composites Based on Kraft Lignin and Softwood Pulp

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ABSTRACT: This article presents a new method of producing thermomoldable nonwoven materials based on kraft lignin (KL) and softwood kraft pulp (KP). A mixture of starch acetate (SA) and triethyl citrate (TEC) was used as a water insoluble plasticizer for KL. The thermoplastic lignin (TPL) material with the optimized ratio of KL, SA and TEC was prepared in a twin-screw extruder. The TPL compound was ground and mixed with KP fibers to produce thermoformable sheets using foam-laid technology. The formed webs were compression molded (CM) into plates and mechanically tested. The foam-laid composites had tensile strengths and modulus of 67 MPa and 5.2 GPa, respectively. Scanning electron microscopy (SEM) was used to analyze the dispersion of the fibers and the matrix in the composites. As a comparison, injection molded (IM) TPL-KP composites were also prepared.

KEYWORDS: Foam-laid technology, thermoplastic lignin, Biocomposite, kraft pulp

1 INTRODUCTION

Global annual plastics production currently stands at around 250 million tonnes, of which thermoplastic materials account for 65% [1]. The largest thermoplastic segments by far are petroleum-based PE, PP and PVC at 33, 21 and 17%, respectively. The share of non-petroleum-based materials is still highly marginal (< 1% of all produced thermoplastics). Furthermore, current renewable materials are almost exclusively based on starch, and thus compete directly with global food production. There is therefore a clear demand for low-cost, non-food-based plastics from renewable feedstock. One of the most promising candidates is thermoplastic lignin, of which over 50 million tonnes are produced annually as a byproduct in modern biorefineries (e.g., pulping mills and bioethanol plants) [2]. At present, lignin is almost exclusively incinerated at the production site.

Lignin is a heterogenic polyaromatic polyol whose structure depends on the wood species and processing conditions [3]. Because of the multiple free phenolic and alkylic hydroxyl groups, lignin has been actively studied as an inexpensive replacement for more expensive phenols and polyols in thermosetting systems [3,4,5]. In thermoplastic applications, lignin has been employed as a compatibilizer between lignocellulosic fibers and the matrix polymer [6]. In addition, thermoplastic lignin/polymer blends have been actively studied [3,6,7,8]. High stiffness and low ductility are characteristic for the lignin-based materials. To improve the ductility, both external as well as internal plasticizers have been employed [9,10]. So far, the most promising plasticizers such as polyethylene oxide (PEO) are water soluble as well as petrol-based, which limits their applicability. There is therefore a clear demand for sustainable water-insoluble plasticizers. In this study, lignin was plasticized with a mixture of starch acetate (SA) and triethyl citrate (TEC), both of which are scarcely soluble in water and are based on renewable materials.

Thermoformable composite materials are typically used in applications in which high mechanical strength is needed. Traditionally, glass fibers

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(GF) have been employed as the reinforcements but natural cellulose fibers are gaining more popularity. Wood fibers are especially interesting because of their abundance, constant and defined quality and lower price. Wood fiber-based nonwovens are manufactured employing air- and wet-laid techniques. The latter technique is particularly suitable for the relatively short (1–3 mm) fibers because of the good homogeneity of the formed webs and the high production rates. However, because of the low forming consistency, high amounts of water need to be circulated. Additionally, the process requires an additional drying step after web forming that further increases the cost.

In this study, foam-laid technology, also used in nonwoven industry, was utilized to manufacture thermoformable nonwoven composite materials. The technology offers several benefits from the process and product points of view compared to conventional water-forming technology. Firstly, in foam technology foam is used instead of water as a carrier phase of fibers enabling higher forming consistencies and lower water consumption [11]. Secondly, dewatering of the foam-laid sheets is easier with respect to wet-laid sheets [12]. From the product point of view the most significant benefit is the even distribution of the lignin particles in the formed sheets. In water systems hydrophobic lignin particles have a tendency to phase separate and form clusters that when big enough attach to, e.g., surfaces of pipelines and paper machine clothing. In foam-laid technology, the lignin particles go to air-water interfaces of the foam bubbles. The bubbles keep the lignin particles evenly distributed in the fiber-foam system, and further, force the particles into close contact with the fibers. During the formation of a fiber network, the lignin particles attach to fiber surfaces by surface forces. Another benefit from the moldability point of view is that bubbles also prevent flocculation of fibers, resulting in excellent formation of the sheets [13]. Additionally, the porosity of the formed webs can be tuned, further enhancing the molding properties [14].

In this study, the foam-laid sheets were made from a mixture of softwood KL and TPL. The TPL was manufactured by blending softwood KL with a mixture of SA and TEC in a twin-screw extruder, after which it was ground and mixed with KP fibers. The thermoformable nonwovens were then prepared using a foam-laid handsheet mold. The formed sheets were compression molded into rigid plates and mechanically tested. Additionally, KP-reinforced TPL composites were prepared by twin-screw extrusion and injection molding.

2 EXPERIMENTAL

2.1 Materials

Refined chemical pine pulp (kraft pine pulp, KP1) provided by Metsä Fibre was used in the foam-laid trials. Refined chemical softwood pulp (a mixture of pine and spruce, KP2), provided by Metsä Fibre, was used in the injection molding experiments. Softwood kraft lignin (LignoBoost, KL) was supplied by Metso. Starch acetate (SA) with a degree of acetylation of 2.6 was synthesized at VTT Rajamäki using corn starch (Cerestar Amylogel 03003) from Gargill as the starting material. SA was synthesized according to the previously published procedure [15]. Commercial grade triethyl citrate (TEC) (tradename: Citroflex2) was purchased from Morflex Inc. (North Carolina, USA) and obtained from OneMed (Finland). Polyvinyl alcohol (PVA) Mowiol 40-88 was purchased from Kuraray.

2.2 Thermoplastic Lignin Compounds

2.2.1 *Compounds for the Foam-Laid Trials*

The TPL compound was prepared by first pre-plasticizing KL with15% TEC. The pre-plasticized KL and SA were then dried in an oven at 70°C for at least 12 h. After drying, SA and the pre-plasticized KL as well as the rest of TEC were combined in a Papenmeier high speed mixer and subsequently compounded in a twin-screw extruder (ZE25 x 48D, Berstorff GmbH, Hannover, Germany). The extruder was equipped with modified co-rotating mixing screws of which diameters and lengths were 25 and 1200 mm, respectively. A temperature gradient from 40°C in the feeding section to 160°C in the melting zones and the die was employed. The screw speed and the feeding rate were 100 rpm and 1.5 kg/h, respectively. The TPL compound was extruded on a belt in air, cut into granulates and stored in heat sealed PE bags. The composition of TPL was 51% KL, 29.4% SA and 19.6% TEC.

2.2.2 *Compounds for the Injection Molding Trials*

The KP2 fibers were dried in an oven at 70°C for at least 12 h. The dried KP2 fibers were then pelletized in a modified planar matrix pelletizing machine (Amandus Kahl) [16]. The SA, TEC and KL blend was prepared as described above. The formed blend was then mixed with the KP2 pellets in a twin-screw extruder (ZE25 x 48D, Berstorff GmbH, Hannover, Germany). The temperature gradient was 40 (feeding zone) – 160°C (mixing zones and the die). The screw speed and the feeding rate were 100 rpm and 2 kg/h, respectively. The extruded compounds were cooled on a belt, cut into granulates and stored in heat sealed PE bags.

2.3 Foam-Laid Process

The foam-laid sheets were prepared using TPL and KP1. Prior to the foam-laid step, the extruded TPL granulates were ground using a Polymix PX-MFC 90D laboratory mill equipped with a blade grinder and a 2 mm screen. The foam-laid handsheets were then prepared using a special sheet former planned for forming of heavier and thicker web structures, as seen in Figure 1. The target basis weights of the foam-laid sheets were 200–1000 g/m^2.

The procedure for the foam-laid handsheets was as follows (Figure 2): Aqueous fiber suspension was mixed with the pre-fabricated foam, which was produced by stirring water and foaming agent (PVA) at 3500 rpm. The amount of PVA was 0.6 g/L, leading to 60–70% air content of the foam. When the foam was stabilized, the ground TPL powder was mixed into the foam. The obtained mixture was decanted into the handsheet mold and filtrated through a wire using vacuum. A low vacuum level was used in the dewatering phase in order to avoid collapsing the structure. Finally, the sheet was air-dried in an oven at 70–80°C.

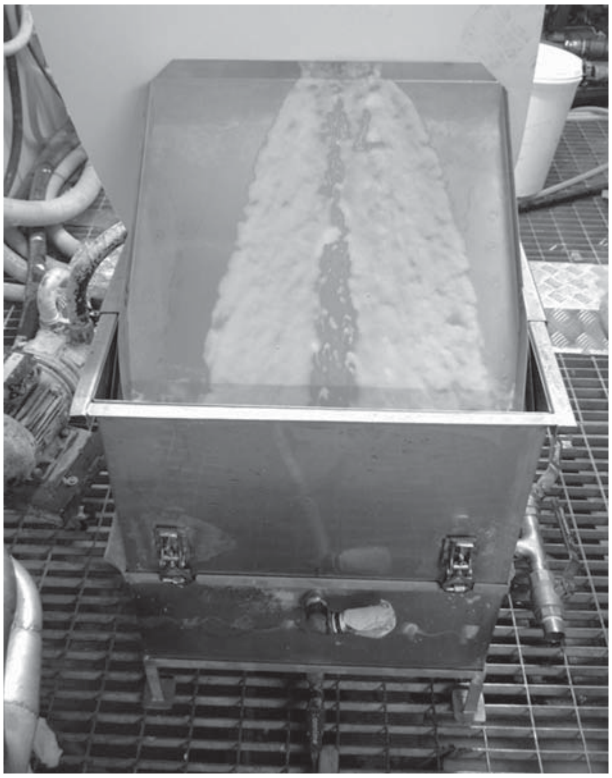

Figure 1 Vacuum assisted foam-laid sheet former.

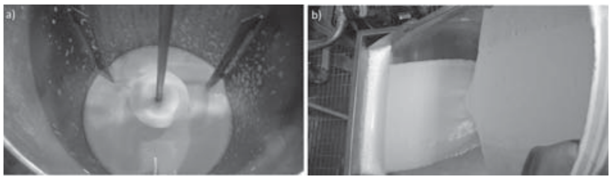

Figure 2 The procedure used to prepare foam-laid sheets. **a)** Example of an aqueous fiber suspension foam. **b)** The prepared fiber foam is decanted into the handsheet mold and dewatered.

2.4 Compression Molding of the Formed Sheets

The foam-laid sheets (see Fig. 1) were cut into 100 mm × 100 mm patches and compressed between hot molds. The temperature of the molds was 185°C, applied pressure 80 kN and the hold time 5 min. Samples with the thickness varying from one to three layers were prepared. It was observed that the foam-laid sheets had a preferred fiber direction. Therefore, the samples were pressed such that the preferred fiber orientation axis was parallel in every layer. Tensile test specimens were prepared by cutting the compressed plates into strips with the dimensions of 80 mm x 10 mm.

2.5 Injection Molding of the Thermoplastic Lignin Composites

The TPL-KP2 compounds were injection molded (ES 200/50HL, Engel Austria GmbH) into tensile test specimens according to the ISO-3167 standard. The melt-zone and the mold temperatures were 160 and 25°C, respectively.

2.6 Characterization

2.6.1 *Tensile Testing*

Tensile tests were performed on an Instron 4505 Universal Tensile Tester machine (Instron Corp., Canton, MA, USA) and operated at crosshead speed of 5 mm/min. Cross-sectional dimensions were determined for each tensile specimen with a slide gauge. Values of elastic modulus (linear regression between the strains of 0.0005 and 0.0025 mm/mm) and tensile strength at maximum load were determined from the average of five stress-strain curves.

2.6.2 *Impact Strength*

The impact strengths of the injection molded and the compression molded samples were determined using a Charpy Ceast Resil 5.5 Impact Strength machine (CEAST S.p.a., Torino, Italy). The tests were performed on unnotched specimens. Dimensions of the IM specimens were 80, 10 and 4 mm, respectively. The dimensions of the CM samples were 80 and 10 mm and only the three-layer-thick samples were analyzed. The exact dimensions were determined by a slide gauge.

2.6.3 Scanning Electron Microscopy

Scanning electron microscopy (SEM) analysis was carried out for the fracture surfaces of the samples. Prior to fracturing, the composites were frozen in liquid nitrogen. The fracture surfaces were sputter coated with gold before the analysis.

3. RESULTS AND DISCUSSIONS

Table 1 describes the characteristics of the foam-laid sheets. Figure 3a shows two examples of the sheets with the basis weights of 200 and 900 g/m^2 and TPL contents of 50%. The composition of the TPL matrix (51% KL, 29.4% SA and 19.6% TEC) was selected based on the previous trials [17].

The KP (KP100) foam-laid sheets with the basis weight of 1000 g/m^2 were compression molded into plates. The pressed plates were cut into 80 mm x 10 mm sample strips with the long axis parallel (pa-KP100) and perpendicular (pe-KP100) to the preferred fiber orientation axis. The prepared samples were then tensile tested. The tensile strengths (TS) of the pa-KP100 and pe-KP100 samples were 2.1 and 1.5 MPa, respectively. The modulus of elasticity (E) of the corresponding samples was 0.020 and 0.016 GPa, respectively. Following these results, the fiber orientation ratio of the neat KP sheets was estimated to be 1.5:1.

Table 1 Basic information of the foam-laid sheets.

Sample	KP1 (wt%)	TPL (wt%)	Weight (g/m^2)[a]
TPL50-KP50	50	50	199
TPL60-KP40	60	40	254
TPL50	50	50	900
KP100	100	0	1046

[a] Basis weight of the foam-laid sheets.

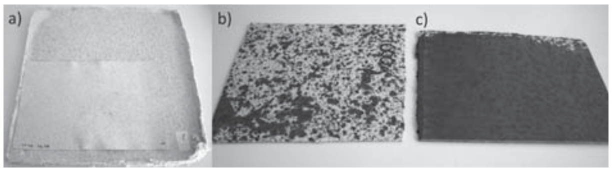

Figure 3 **a)** Foam-laid TPL50-KP50 and TPL50 sheets with the basis weights of 200 and 900 g/m2 and the sizes of 310 mm × 280 mm and 500 mm × 500 mm, respectively. CM samples (100 mm × 100 mm) with **b)** one and **c)** three layers. The weight of a single layer was 900 g/m2.

Thermoformable foam-laid sheets with the TPL contents of 50% (TPL50-KP50) and 60% (TPL60-KP40) were prepared. The formed sheets were compression molded into plates with one to five layers. Figure 4 describes the tensile properties of the prepared samples. Increasing the thickness of the samples substantially improved the performance. The TS of the one-layer-thick sample 1-TPL50-KP50 was 21 Mpa, whereas the four-layer-thick sample 4-TPL50-KP50 had the TS of 61 MPa. However, further increasing the thickness did not improve the TS. Also the stiffness of the samples improved with the thickness. The E of 1-TPL50-KP50 was 1.0 GPa, whereas 4-TPL50-KP50 had the E of 4.9 GPa. A similar trend was observed for the samples with the TPL content of 60%. Both the TS and E improved substantially when the thickness of the samples increased. The five-layer-thick sample 5-TPL60-KP40 had the highest TS of 67 MPa. In turn, the four-layer-thick 4-TPL60-KP40 had the highest E of 5.2 GPa.

To further evaluate the foam-laid materials, sheets with the basis weight of 900 g/m^2 and the TPL content of 50% were prepared. The sheets were compression molded into 100 mm x 100 mm patches with one to three layers. The prepared samples were tensile tested parallel (pa-TPL50) and perpendicular (pe-TPL50) to the preferred fiber orientation axis. Figure 5 shows the results of the tensile tests. pa-TPL50 with two layers (2pa-TPL50) had the highest TS of 58 MPa. However, further increasing the thickness to three layers (3pa-TPL50) did not improve the TS (52 MPa). As expected, the samples with the perpendicular fiber orientation had substantially lower TSs. The one layer thick sample (1pe-TPL50) had the TS of 21 Mpa, whereas the sample with three layers (3pe-TPL50) had TS of 41 MPa. A similar trend was also observed in stiffness. The 2pa-TPL50 had the highest E of 4.5 GPa, whereas the stiffness of 3pa-TPL50 reduced to 4.0 GPa. Perpendicular to the fiber orientation, the three-layer-thick 3pe-TPL50 sample had the highest E of 3.8 GPa. The tensile strength ratio parallel/perpendicular to the fiber orientation was for the one-layer-thick samples 2:1. However, the difference diminished as the thickness increased.

As shown above, the tensile properties of the compression molded sheets improved as the thickness or the TPL content of the samples increased. The improvements are attributed to the improved homogeneity of the samples as seen in Figure 3b and c. The dark brown

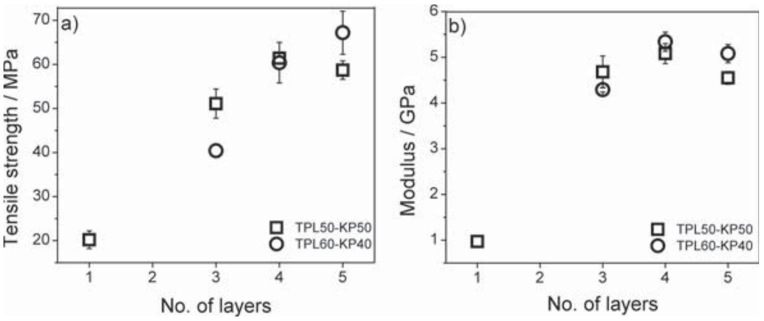

Figure 4 **a)** Tensile strength and **b)** stiffness of the compressed samples with the TPL content of 50 and 60%. The samples were measured parallel to the preferred fiber orientation.

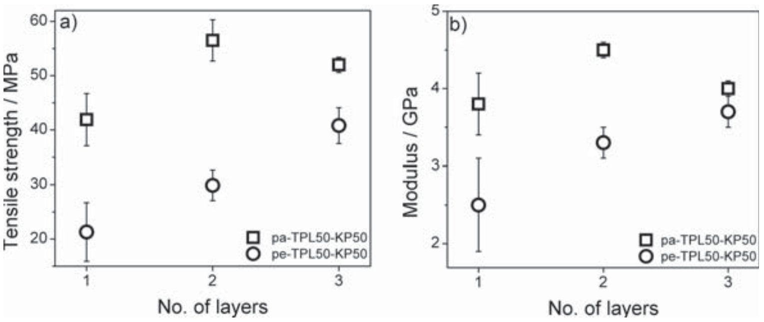

Figure 5 **a)** Tensile strength and **b)** stiffness of the compressed samples measured parallel and perpendicular to the preferred fiber orientation. The basis weight of a single layer was 900 g/m^2.

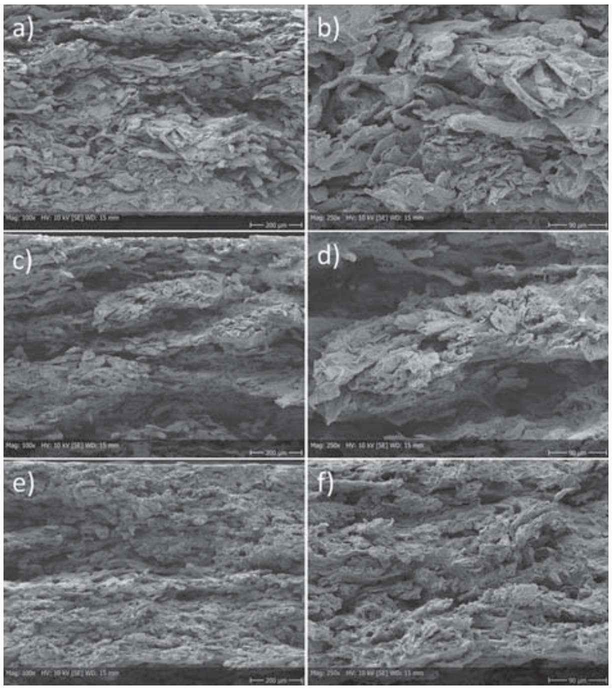

Figure 6 SEM images of TPL50 samples with one **(a-b)**, two **(c-d)** and three **(e-f)** layers. The magnifications were 100 (left) and 250 (right) times.

dots in the one-layer-thick TPL50 sample are attributed to the TPL particles. Instead the dark brown color of the three-layer-thick TPL50 samples is suggestive of a more homogeneous distribution of the matrix. This is also seen in the SEM images of the fracture surfaces of the compression molded TPL50 samples (Figure 6). The one-layer-thick samples have porous structures in which the fibers clearly stand out from the matrix. In turn, the porosity is decreased in the two- and three-layer-thick samples, suggestive of improved distribution of the TPL matrix. The improved dispersion of the fibers and the matrix also explains the better performance of the thick TPL60-KP40 samples with respect to the TPL50-KP50 materials.

3.1 Comparison with the Injection Molded Composites

As a comparison, injection molded composites with the TPL matrix and the KP2 contents of 0% (i-TPL100) and 30% (i-TPL70) were manufactured (Table 2). The TS and E of i-TPL100 were 9.9 MPa and 2.9 GPa, respectively. In turn, the corresponding values for i-TPL70 were 28 MPa and 6.2 GPa.

Table 2 Mechanical performance of selected IM and CM samples.

Sample	Method	TPL %	KP %	TS (MPa)	E (GPa)	IS (kJ/m^2)	Toughness (MJ/m^3)
i-TPL100	IM	100	0	9.0 ± 2.2	2.90 ± 0.24	1.13 ± 0.22	0.018 ± 0.009
i-TPL70	IM	70	30[a]	27.8 ± 0.6	6.16 ± 0.28	2.54 ± 0.38	0.075 ± 0.008
3pa-TPL50	CM	50	50[b]	52.0 ± 1.4	4.00 ± 0.10	10.9 ± 1.9	0.71 ± 0.10
3pe-TPL50	CM	50	50[b]	40.8 ± 3.3	3.70 ± 0.20	8.72 ± 2.18	0.42 ± 0.06

[a]KP2; [b]KP1

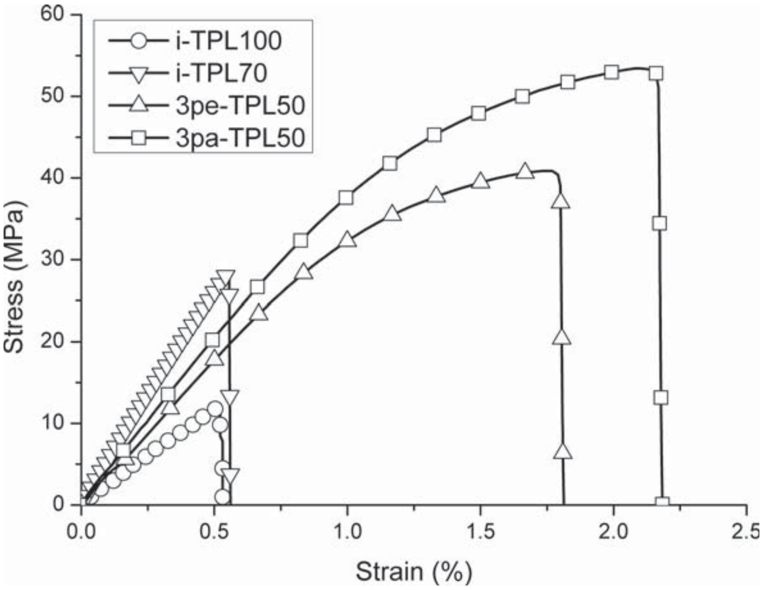

Figure 7 Stress-strain curves of the IM and CM samples.

Compared to the IM samples, the foam-laid composites show significant improvements in mechanical performance. Particularly, the TS is notably improved and is among the highest that have been published for the TPL-based composites. Furthermore, ductility of the materials is substantially improved. Figure 7 presents the stress-strain curves of the IM and CM samples. The curves of i-TPL100 and i-TPL70 are typical for brittle materials. In turn, the CM samples have notably higher strength and strain. Because of this, the toughness of the foam-laid samples is an order of magnitude higher than that of the IM samples. The improved toughness is also seen in the impact strengths (IS) of the composites. The IS of the CM samples 3pe-TPL50 and 3pa-TPL50 was 11 and 8.7 kJ/m^2, respectively, whereas the corresponding values for i-TPL100 and i-TPL70 were only 1.1 and 2.5 kJ/m^2, respectively. The main reason for the improved mechanical performance is the processing methods employed. It is well known that the attrition of cellulosic fibers is notably high in the twin-screw extrusion and injection molding processes due to the high shear forces [18]. In turn, in the foam-laid and compression molding processes, the fibers are exposed to very low shear forces, and therefore, the fiber breakage is minimal.

High-performance thermoformable nonwovens based on TPL matrix and KP fibers were prepared using foam-laid technology. The prepared samples demonstrated impressive mechanical properties, outperforming the corresponding IM composites. However, the developed method is not limited to TPL. In turn, it is suitable for various different kinds of matrix materials such as polyolefins, PET and PLA. Furthermore, the thermoplastic material can be added as particles or fibers. In addition, longer fibers such as regenerated cellulose or plant fibers can also be employed.

Finally, the developed foam-laid technique is potentially suitable for production of various different kinds of products. By altering the matrix and the fiber materials and ratios as well as the porosity of the formed webs, it is possible to design moldable composites for packaging applications or rigid and tough materials for structural or semi-structural products.

CONCLUSIONS

In this article, a new method to manufacture high-performance thermoformable wood pulp fiber sheets was presented. The studied materials were thermoplastic lignin and softwood kraft pulp. The mechanical properties of the compression molded sheets were substantially better compared to the corresponding injection molded samples. Particularly, the toughness was improved. The developed method is not restricted to thermoplastic lignin matrix and wood pulp. In turn, various different kinds of thermoplastic materials and cellulose fibers can be utilized in the developed process.

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