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Partially Compacted Commingled PLA-Flax Biocomposites

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Abstract: Non-woven materials feature unique properties that allow them to be used in different applications, such as the automotive sector that is increasingly seeking lightweight and sustainable materials. The aim of this work was to investigate the influence of reinforcement type and porosity on the properties of commingled, partially compacted composites based on polypropylene (PP) and polylactic acid (PLA). Furthermore, a model was applied to predict the properties of such composites, i.e., the elastic modulus, to aid materials development. It was found that high properties could be achieved using flax as reinforcement for partially compacted fleece biocomposites. Porosity is an important factor influencing these types of composites and was influenced by the compaction grade achieved as a result of stacking different numbers of layers during the consolidation of the composites. The modeling of the elastic modulus was found to be adequate for both PP-flax and PLA-flax composites for porosities under 20 vol.%.

Keywords: nonwovens; partially compacted composites; modeling; elastic modulus; porosity

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1. Introduction

For tailoring material properties, combining a polymer matrix with some reinforcements is a widespread approach. While carbon-fiber fabric-reinforced thermosets are quite well known for applications in sporting goods or aircraft, lesser known but similarly widespread composites are built up from nonwoven mats containing reinforcement fibers and melt binder fibers. While the former are mainly responsible for the mechanical properties, the latter are molten in the compaction process, binding the whole composite together. Reinforcement fibers are often glass fibers, but cellulose fibers such as flax or hemp are also used. Polypropylene or polyester can be utilized as melt binder fibers [1]. The production of such nonwovens is typically carried out by commingling the fibers, a carding step to orient and entangle the different fibers, and a compacting step, for example, needle punching or water jetting, to entangle the fibers in the thickness direction of the fleece. Such nonwovens are then compacted under pressure and temperature to consolidate the desired shape by melting and cooling the melt binder fibers. Such composites are found in automotive applications such as wheel well liners, interior door panels, and hat racks, due to their combination of light weight and high mechanical properties as well as their sound dampening properties [2].

Investigations on such nonwoven composites have often looked into biobased reinforcements, to produce lightweight composites. While the mechanical properties and density are minimum requirements for such composites, other properties have also been found, due to the nonwoven, porous structure, such as sound and thermal insulation [3,4]. These are beneficial for automotive structures, for example, underbody panels, to improve passenger comfort. To improve such sound absorption properties, different materials can be combined, for example, cotton and polyester have been found to be beneficial. In addition, the method of nonwoven compaction influences the properties, for example, needle bonding results in better properties than water jetting [5].

It has also been previously shown that combining different materials can also be beneficial. Kucuk and Korkmaz investigated different reinforcement fiber combinations and found that bilayered composites could alter sound absorbance for some frequencies [6]. Using layered structures for improving properties has also been found to be beneficial to kenaf polypropylene composites [7]. This concept has also been investigated further with bagasse, kenaf, and ramie as reinforcing fibers in polypropylene and building up different layered composites. These showed lower mechanical properties than the monomaterial composites, but better wet properties, thus, making them more suitable for automotive exterior applications [8]. The improvement of composite properties by adding compatibilizers [1], as well as silane treatment for improved fiber–fiber interaction [9] have also been investigated.

In our group, a previous work was carried out on the influence of processing and composite properties on polypropylene glass fiber nonwoven composites, where we found a clear influence of porosity, resulting from compaction as well as formulation, on the composite performance [10]. Similar to the previous work in which glass fibers were used, we wanted to investigate the difference in performance with flax fibers as well as with a biobased alternative for PP, namely PLA. Therefore, the aim of this work was to investigate the influence of the type of reinforcement (glass vs. flax fiber) and the porosity on the properties of commingled, partially compacted composites based on polypropylene (PP) and polylactic acid (PLA), and to investigate the possibility of applying a model to correlate composite modulus with volume fractions of the constituents, i.e., fiber, melt binder, and porosities.

2. Materials and Methods

2.1. Materials

The materials used as binder fibers in this study were PP fibers supplied by IFGAsota GmbH, Linz, Austria, in which 3% of a proprietary grade of maleic anhydride grafted polypropylene (MAH-PP) was used as additive and added to the PP before the spinning process through compounding, ensuring homogeneous distribution of the additive. The used PLA fibers were supplied by Trevira GmbH, Bobingen, Germany; both fibers featured 7 dtex (about 31 µm) with a staple length from 60 to 80 mm. As reinforcements, flax fibers with a weight per meter of 0.28 g/m were delivered by Ekotex, Namyslow, Poland, and glass fibers, sized for use in polypropylene (DS2100), for comparison purposes were supplied by Owens Corning, Belgium, with an average fiber diameter of 17 µm; both fiber types were cut to a length of 160 mm. The fibers were weighed and mixed by hand to yield reinforcement contents of 0–50 wt.%.

2.2. Fiber Web and Composite Production

Fiber mixtures were processed into fleeces using a laboratory card Maschinenfabrik Memmingen K.G., Memmingen, Germany, where 150 g of the mixtures were introduced in the carding machine operating at a constant processing speed, three times in a row, to achieve better consistency and homogeneity of the mixtures. The fleeces exhibit areal densities of about 500 g/m^2 after carding. These were subsequently processed by pressing between two plates in a hot press (Höfer H10, Höfer Presstechnik, Taiskirchen, Austria), yielding partially compacted composites with varying porosities. The tooling used was a stamp forming tool, which produced plates with 100 × 100 mm^2 (Figure 1). Pressing parameters and stacking structures were modified during the different stages of the study.

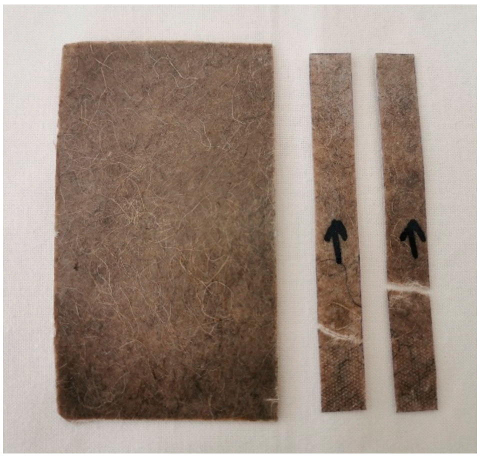


Figure 1. Compression molded plate (approximately 50 × 100 mm^2 after cutting the samples (left) and examples for cut and tested strip samples sized 90 × 10 mm^2).

For the first part of the work, different fleeces ranging from 0 to 50 wt.% of glass and flax fibers were mixed with PP and PLA fibers. Then, these four layers were pressed at 190 °C and 30 bar for 15 min and subsequently cooled down for 10 min at 20 °C and 5 bar. These processing parameters were used based on previous trials [10]. For the second part of the work, fiber content was fixed at 50 wt.% and compaction was modified through variation of layer amount for the purpose of determining the influence of compaction grade on the final properties of the composites. All the abovementioned composites were used for the modeling approach.

2.3. Testing

The tensile properties were determined in accordance with ISO-527, in a Z020 universal testing machine (Zwick Roell, Ulm, Germany), at a crosshead speed of 1 mm min^{-1} for determining elastic modulus, and afterwards with 5 mm min^{-1} until the sample broke, with three replicates per series. For this purpose, test samples with a size of 90 × 10 mm^2 were cut from the fleeces. The porosity of the composites was calculated based on density measurements, which has been found to be the most accurate method in previous studies [10]. Three measurements were carried out for each sample using the remaining material from mechanical tests for better correlation of results. First, the apparent density (ρ_{app}) was determined by weighing the specimen with known volume following Equation (1):

$$\rho_{app} = \frac{m_c}{v_c}, \tag{1}$$

where m_c is the weight of the composite and v_c its volume, determined by mechanically measuring the dimensions.

Second, the density of the composite in a liquid capable of filling the porosities had to be measured. In this case, ethanol was used as an immersion fluid and the density was measured according to ISO 1183 with a density kit YDK01 in combination with a lab scale (Sartorius, Göttingen, Germany), as shown in Equation (2):

$$\rho_{EtOH} = \frac{m_{GF} + m_{PP}}{v_{GF} + v_{PP}}, \tag{2}$$

where m_{GF} and v_{GF} are the weight and volume of the glass fibers and m_{PP} and v_{PP} those of the PP fibers, respectively.

Finally, the porosity of the composites (V_p) was calculated using the following equation:

$$V_p = 1 - \frac{\rho_{app}}{\rho_{EtOH}}, \tag{3}$$

The fiber content was determined through three different methods depending on the materials used. Samples of 2 × 2 cm^2 cut from the composites were used in all cases. For GF-based composites, the fiber content was calculated by heating the samples up to 625 °C using a Macro TGA 701 Machine (Leco GmbH, Mönchengladbach, Germany) in air atmosphere. In the case of PP-flax composites, composite and single material densities were used for the fiber content calculation using the following equation:

$$\frac{1}{\rho_c} = \frac{w_f}{\rho_f} - \frac{w_m}{\rho_m} \tag{4}$$

where ρ_c, ρ_f, and ρ_m are the densities of the composite, fiber, and matrix, respectively; and w_f *and* w_m are the weight percentages of the fiber and matrix, respectively, in the composite.

This method is suitable when the densities of the single components are not very similar. Therefore, another method was used for the PLA-flax composites, that is, Soxhlet extraction. PLA was extracted from the composite with chloroform for 24 h. Afterwards, the flax fibers were dried for 4 h at 80 °C, and then the fibers were weighed to determine the fiber content.

The morphology of composites was observed by scanning electron microscopy (SEM). Test specimens were cut diagonally in their thickness and a Vega II SEM (Tescan GmbH, Dortmund, Germany) was used for taking the micrographs after sputtering the surface with a gold layer.

3. Results and Discussion

The results of this study are presented in several sections. First, the influence of flax fiber content on the mechanical properties of PP and PLA with flax reinforcement is analyzed, followed by a comparison with glass reinforcement. In the third section, porosity content of the composites is discussed and its influence on properties as well. Lastly, a modeling approach for the mechanical properties is presented.

In Figure 2, representative stress-strain curves for the different materials are given (regardless of the composition, the stress-strain curves do not change their shape within the investigations presented here). One can see that the curves do not exhibit yielding, regardless of reinforcement (flax, glass fiber) or melt binder fiber (PLA, PP). In addition, one can see that the stress-strain curves with PLA as melt binder show steeper slopes than the ones with PP. This is emerging from the higher elastic modulus of PLA as compared with that of PP.

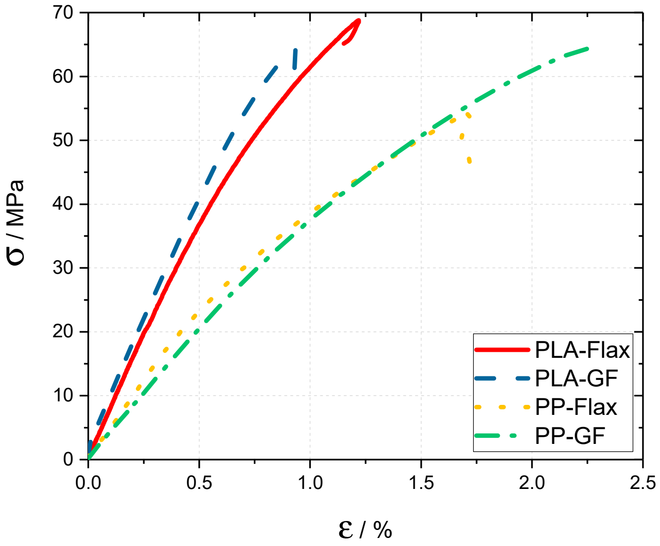


Figure 2. Representative stress-strain curves for the different material combinations (with 30 wt.% of reinforcement fibers) investigated in this study.

3.1. Influence of Flax Fiber Content

Composites with 0–50 wt.% of flax fiber reinforcement were manufactured, where porosities between 7 and 14% were achieved. The elastic modulus of the PP and PLA composites with increasing fiber content can be seen in Figure 3. The stiffness of the composites increases with increasing fiber content in both cases. It can be observed that, for the same fiber content, the PLA-flax composites show higher moduli than the PP-based composites. The difference in stiffness between PLA and PP composites can be attributed to the higher modulus of the neat PLA fibers, which are not fully molten in the consolidation process. The effect of incorporating the reinforcement is clearly seen, with an increase in modulus from 4.4 GPa to 11.3 GPa in the case of the PLA-flax composites and from 2.1 GPa to 7.1 GPa in the case of the PP-flax combination.

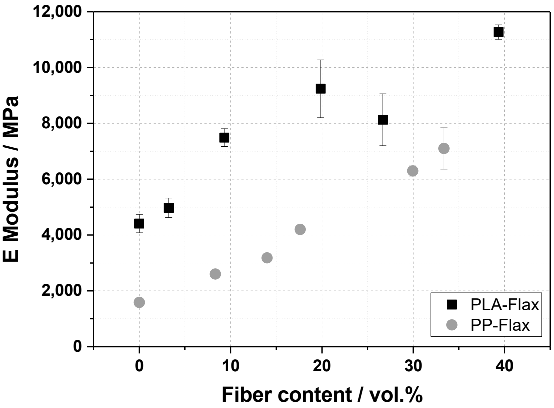


Figure 3. Elastic modulus of the flax-reinforced PLA and PP composites with different fiber content.

The same trend can be observed in the case of the tensile strength (Figure 4), which increases with increasing fiber content. In the case of PP-flax composites, a drop in the tensile strength can be observed when 10% of the fibers are incorporated with the PP fibers. This effect can be attributed to the elasticity of PP. In the case of the unreinforced composite, the strain values are around 18%. However, when reinforcement fibers are incorporated, composites become stiffer, featuring much lower strain values of 2% approximately, which gives rise to the reduced tensile strength.

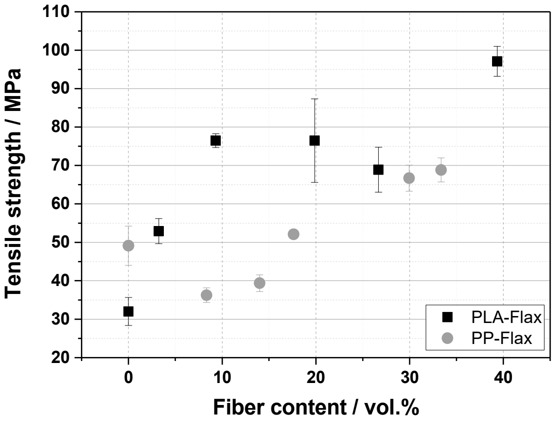
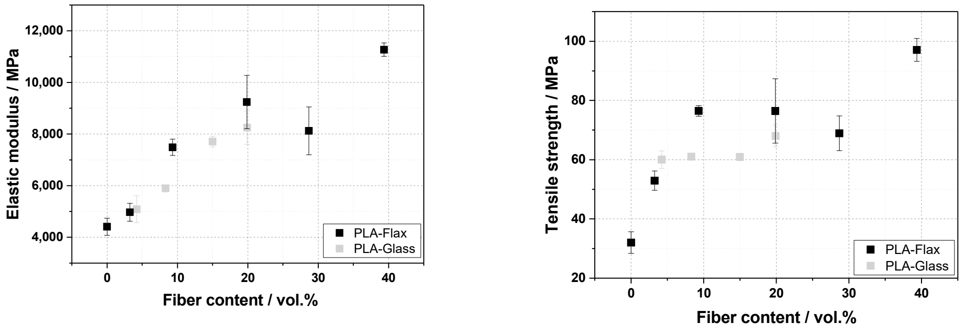


Figure 4. Tensile strength of the flax-reinforced PLA and PP composites with different fiber contents.

In the case of PLA-flax composites, an increasing trend of the tensile strength with increasing fiber content can be observed. However, the composites with 20 and 30 wt.% do not show the improvement of higher reinforcement as compared with the composite with 10 wt.%, most likely due to some inhomogeneities in the composite, as the higher scattering for these two composites might also indicate. These inhomogeneities are due to two reasons: (1) The carding operation, which has limited mixing capabilities even though three carding process repetitions are carried out to maximize the mixing of fibers and (2) the flax fibers themselves are inhomogeneous to the point that these fibers are built up from different aggregate sizes of the elemental natural fiber, i.e., the single cellulose fibers.

3.2. Comparison between Flax and Glass Fiber Reinforcements

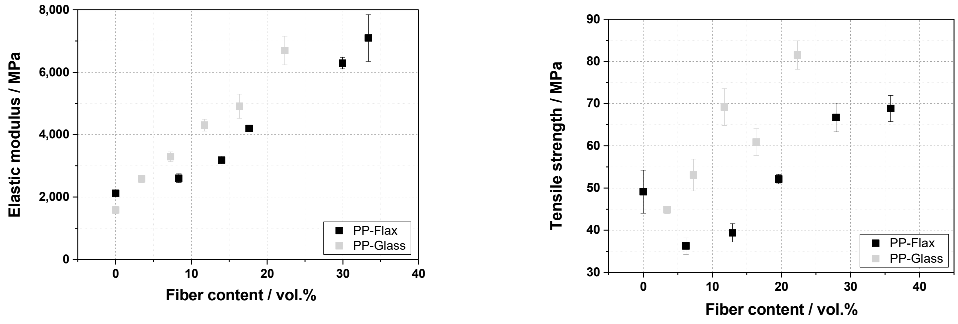
The influence of reinforcement type on the properties of partially compacted composites was studied. Figure 5 illustrates the elastic modulus and tensile strength of the PLA samples with flax and glass fiber reinforcements in relation to fiber content. These properties increase depending on fiber content, reaching high values with 40 vol.% of flax fibers. Slightly higher properties are achieved by using flax fibers as compared with glass fibers at comparable fiber volume fractions. Based on the literature, elastic modulus values have been reported to be similar for glass and flax fibers [11]. For this reason, the improved properties can be attributed to a better adhesion between PLA and flax fibers.



(**a**) (**b**)

Figure 5. (**a**) Elastic modulus and (**b**) tensile strength of the PLA composites with different content of glass and flax fibers.

In the case of the composites based on PP (Figure 6), both the elastic modulus and tensile strength increase with increasing fiber content as well, however, lower values are yielded using PP fibers instead of PLA fibers in the fleece. In this case, a difference in properties can be observed when using glass or flax fibers. Using glass fibers in combination with PP results in a 30 to 50% increase in mechanical properties as compared with flax reinforcement, showing the influence of a better adhesion with glass fibers than with flax fibers, as the former are sized to be used with PP.



(**a**) (**b**)

Figure 6. (**a**) Elastic modulus and (**b**) tensile strength of the PP composites with different contents of glass and flax fibers.

3.3. Porosity Properties

Previous studies have shown that porosity plays a decisive role in the properties of partially compacted commingled PP-GF composites [10]. The number of layers stacked during consolidation of the composite has been found to be a decisive factor influencing final void content. Therefore, this influence was also studied here in the case of PLA and PP reinforced with flax fibers, producing composites with one to five layers using fleeces with 50 wt.% fiber content. Composite thickness increased with the number of layers from 0.33 mm to 1.11 mm in the case of PP-flax and from 0.25 mm to 0.80 mm in the case of PLA-flax, which was due to the higher density of the PLA as compared with the PP. The results of porosity can be seen in Figure 7. It can be observed that porosity decreases with increasing layer number, since, with increasing layer number, the material gets more evenly distributed, and thus better compacted.

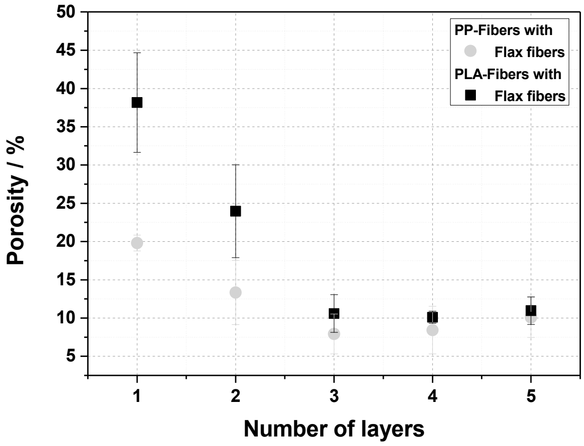
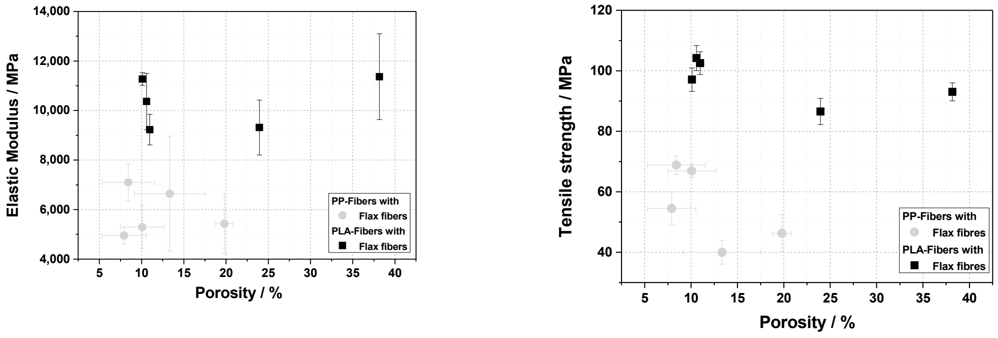


Figure 7. Porosities the PLA- and PP-flax composites processed with different numbers of stacked layers.

Figure 8 shows the tensile properties of the flax-reinforced PP and PLA composites in relation to porosity. No clear correlation can be seen between the porosity content and tensile properties of the composites, as it was seen in previous works with glass fiber-reinforced composites [10]. This could be due to differences in the porosity measurement: Flax fibers are in the form of bundles, therefore, it could be possible that those bundles contain porosities that are being measured but do not affect the mechanical properties. It could also be possible that the reinforcement effect is greater than the negative influence of the porosity.



(**a**) (**b**)

Figure 8. (**a**) Elastic modulus and (**b**) tensile strength of the PP and PLA composites depending on porosity content.

3.4. Morphology of Composites

The morphology of the composites was analyzed through SEM. Figure 9 shows the cryo-fractured surface of the PP-flax composites with 10 wt.% reinforcement. The different layers can be differentiated, and also flax fibers can be identified, both as single fibers but mostly in the form of bundles.

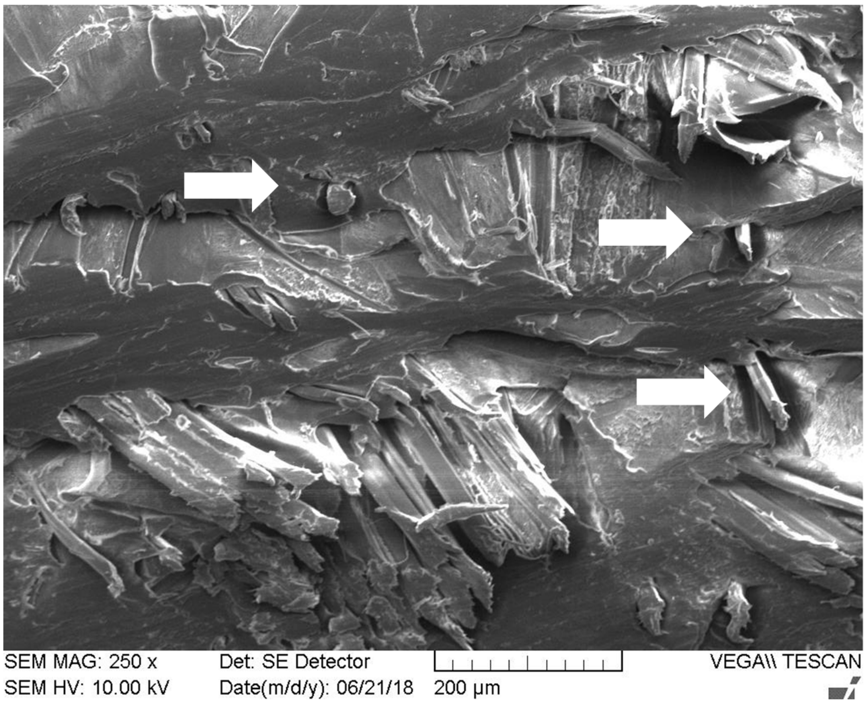


Figure 9. SEM micrographs of cryo-fractured surfaces of the PP-flax composites with 10 wt.% reinforcement at 2500× magnification (white arrows indicate single flax fibers with poor wetting).

Arrows show imperfect wetting of the flax fibers, indicating a poor adhesion between PP and flax fibers. At the lower part of the image a porous bundle of fibers can be seen, where no matrix is observed.

By increasing fiber reinforcement to 50 wt.%, as shown in Figure 10, it is possible to observe the commingled structure of the composite with flax fiber bundles surrounded by molten PP material and porosities in between.

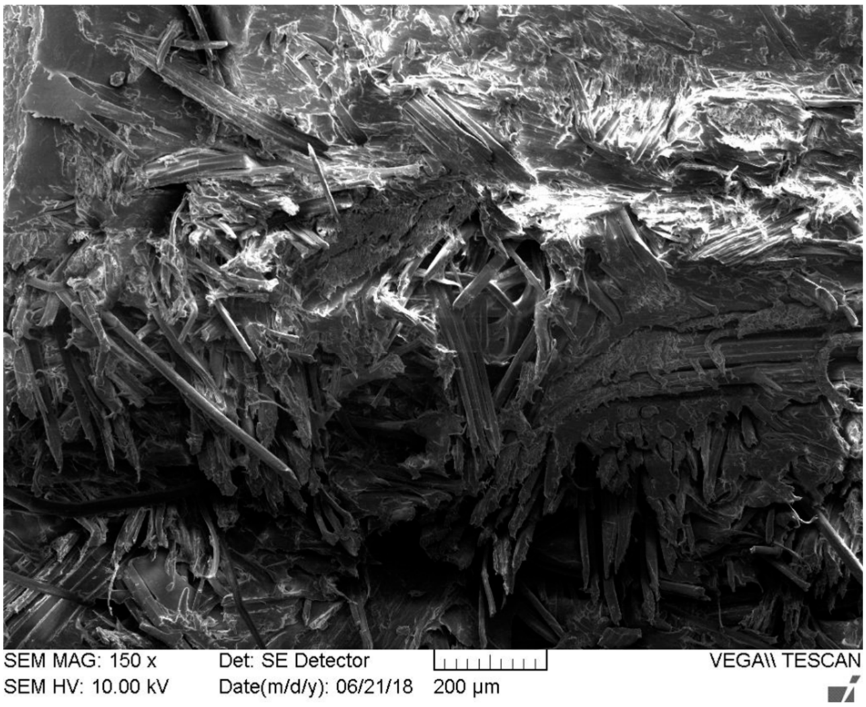


Figure 10. SEM micrographs of cryo-fractured surfaces of the PP-flax composites with 50 wt.% reinforcement at 1500× magnification.

In the case of PLA-flax composites with 50 wt.% reinforcement, as shown in Figure 11, a better wetting of the flax fibers by the molten PLA is observed, which supports the better mechanical properties observed for this combination as compared with the PP-flax composites.

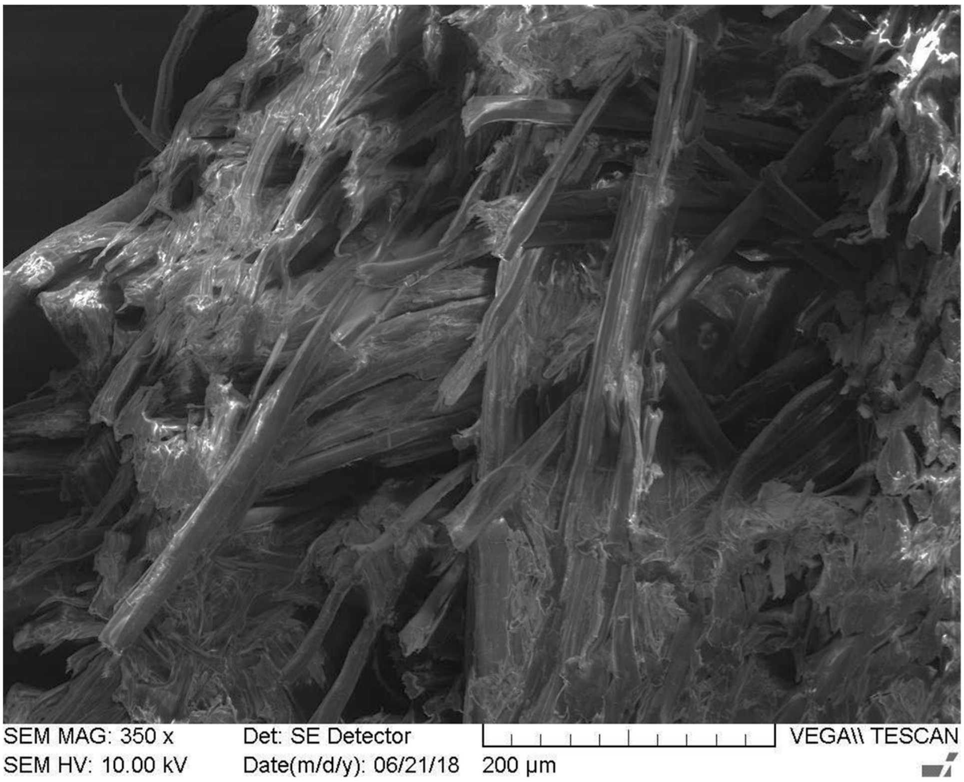


Figure 11. SEM micrographs of cryo-fractured surfaces of the PLA-flax composites with 50 wt.% reinforcement and four layers at 1500× magnification.

3.5. Modeling

The modeling approach used is based on the rule of mixtures model by Madsen and Lilholt [12] that uses a factor $(1 - V_p)^2$ to take into consideration the porosity. The following Equation (5) for the elastic modulus was applied:

$$\frac{E_c}{(1-V_p)^2} = V_f\left(\eta_0 E_f - E_m\right) + E_m \tag{5}$$

where E_c and σ_c are the ultimate modulus and tensile strength of the composite; E_f, E_m and σ_f, σ_m are the elastic modulus and tensile strength of the flax fibers and PP or PLA fibers, respectively; η_0 is a fiber orientation factor approximated with 0.375 for random in plane-oriented fibers; V_p is the volume fraction of the porosity; and V_f is the flax fiber volume fraction.

Using the model in Equation (5) to fit the data of the PP-flax composites (Figure 12), we can observe that the data can be fitted well, as long as the porosity is less than 20 vol.%. Higher porosities do not follow the trend. This is also true for the PLA-flax composites, as shown in Figure 13; both these findings are in good accordance with our findings from a previous work [10], where the PP-glass fiber composites (with compatibilizer incorporated in the PP) can be described with the same model approach.

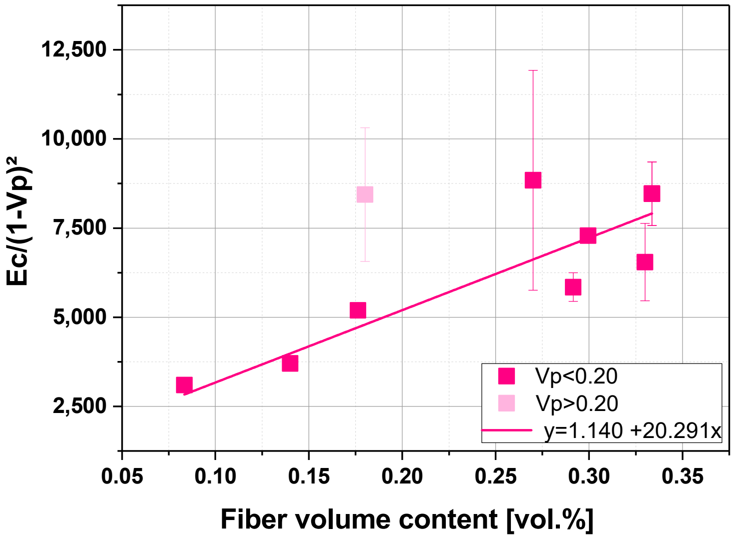


Figure 12. Elastic modulus of the PP-flax composites divided by the porosity factor vs. fiber volume content.

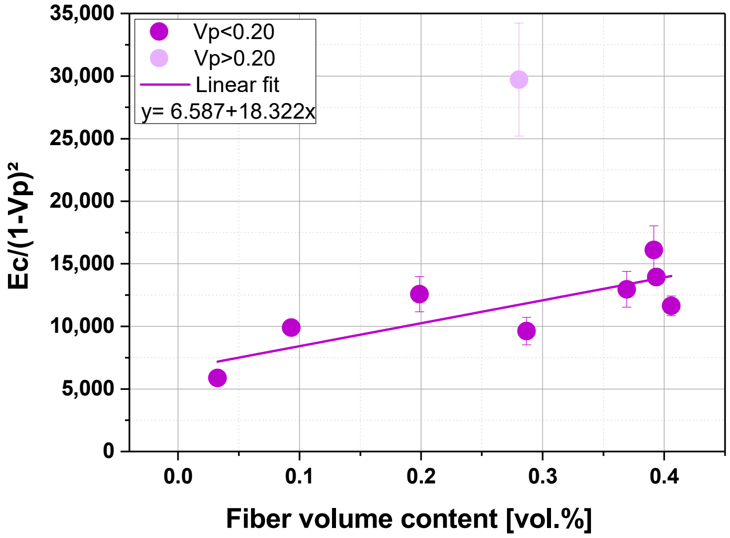


Figure 13. Elastic modulus of the PLA-flax composites divided by the porosity factor vs. fiber volume content.

4. Conclusions

In this work, we investigated the properties of partially compacted composites from different nonwovens from PLA with flax and glass fibers as reinforcements. We found that the properties can be increased by increasing the reinforcement fiber content and that these composites can give comparable performances in terms of elastic modulus and tensile strength as their counterparts based on PP. With the flax-based composites, the porosity does not seem to be such an influencing factor as, for example, with glass fibers as found in previous studies, which could be due to the inherent porosities in the flax fibers, which do not influence the mechanical properties as such. In terms of the modeling, a simple model that takes into consideration the fiber volume fractions, porosities, and elastic moduli of the constituents can be used to model the composite elastic modulus, which is useful for predicting the achievable properties. Overall, we found that, in terms of mechanical properties, PLA and flax fibers are a potential alternative to PP glass fiber composites, but other properties necessary for application, i.e., long-term stability or thermal performance, need to be investigated before application.

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