ALIGNED HEMP YARN REINFORCED BIOCOMPOSITES: POROSITY, WATER ABSORPTION, THERMAL AND MECHANICAL PROPERTIES

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Abstract

In this paper, hemp composites using uniaxial aligned hemp/PLA wrap spun yarns were fabricated with 30 mass-% hemp using compression moulding. The properties of composites in terms of hemp fibre orientation (aligned and random), off-axis angle (0, 45 and 90°) and alkali treatment were investigated. Fabricated composites were characterised regarding porosity, water absorption at room temperature and at 80°C, tensile, flexural, impact strength, as well as DMTA and SEM. Compared with all the fabricated composites, the aligned alkali hemp/PLA yarn composite possessed the best mechanical properties, low porosity and low water absorption. The water absorption for all composites was higher than for neat PLA, both at room temperature and at 80°C. Based on SEM observation and theoretical analysis of DMTA data, there was a favourable interfacial adhesion in all composites.

1. Introduction

Hemp is an upcoming European industrial crop [1], with good mechanical fibre properties, which can be cultivated with a low consumption of fertilizers and almost no pesticides [2]. Concerning the matrix in the composites, the industrial trend for natural fibre composites is to use thermoplastic matrix resin, rather than a thermosetting matrix resin [1]. Polylactic acid (PLA) is the most important bio-based thermoplastic for applications requiring biodegradability. The mechanical properties of PLA can be improved by using reinforcements like natural fibres in order to allow use in structural industrial applications [3]. Therefore, because of the attractive properties of hemp fibre, it was used as reinforcement for PLA composite in the presented study.

The main application of natural fibres is today mainly in non-structural composites as they are mostly available as randomly oriented nonwovens [1]. The fibre orientation must be controlled to ensure that the fibre mechanical properties are efficiently utilized in order to attract industrial interest as an alternative to the traditionally applied synthetic fibres (e.g. glass fibres). Previous studies have demonstrated that the full reinforcement potential of natural fibres can be exploited in bio-composites if an aligned fibre orientation is used [4]. Natural fibres are naturally discontinuous; therefore natural fibre reinforcements reported so far are based on twisted spun staple yarns. These spun yarns tend to be highly twisted, which leads to fibre misalignment due to their helical paths around the yarn axis. This misalignment contributes negatively to the mechanical properties of the resultant composites. Therefore, in the textile industry a broad range of techniques for the alignment of natural fibres have been developed and optimised to produce yarns with controlled fibre orientations [4, 5].

In the current paper, we discuss the development new hybrid yarns with low twist for high performance natural fibre-reinforced composites suitable for use in structural or semi-structural applications and with lower amount of porosity. The overall aim was to study the mechanical properties of these novel aligned hemp fibre yarn composites and investigate the effect of a range of relevant parameters such as prepreg type such as nonwovens and hybrid yarn prepregs with different off-axis angles (0°, 45° and 90°) and fibre treatment.

2. Materials and methods

2.1 Materials

Hemp and PLA staple fibres were used in this study. The PLA staple fibre had a fineness of 1.7 dtex and a mean fibre length of 38 mm, while the average diameter of the hemp fibre was 20-40 μm and the mean fibre length was 30 mm. The hemp fibres were treated by 4 wt% NaOH solution for 1 hr, rinsed with distilled water until it was neutral and finally dried at room temperature for 48 hr and following with 3 hr. In addition, a 18-tex PLA multifilament yarn was used as wrapping yarn in the wrap spun yarns.

2.2 Methods

2.2.1 Preparation of prepreg and composites

PLA/hemp hybrid wrap spun yarns were produced by using a laboratory spinning machine and yarn twist machine. The PLA fibre and the hemp fibre were weighed to the desired proportion (30 mass-%) and the fibre mixture was then fed into the carding machine. The blended PLA/hemp web was carded three times to parallelize the fibres and to achieve sliver uniformity. Then the sliver was fed through a roving frame, where the strands of fibre were further elongated. Although it was possible to create hybrid yarns with low twist, the cohesion of the fibres was very low because PLA/hemp roving had a false twist, which means that they could not form a roving of sufficient integrity. In order to collect the roving without causing breakage in the roving machine, processable PLA filaments were used as a processing carrier for the PLA/hemp roving in the final step. Finally the roving was wrapped by PLA filaments in the twisting machine. The wrap yarn was spun to the nominal count of 550 tex, and it had a wrapping intensity of 200 turns/m. The yarn structure obtained from the wrap spinning used is shown in Fig. 1.

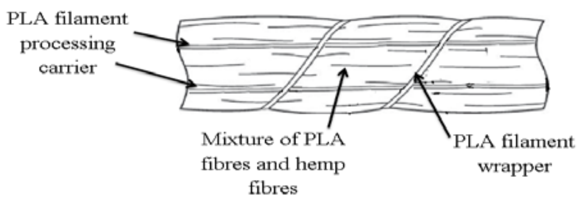

Figure 1. Structure of wrap spun hybrid yarn.

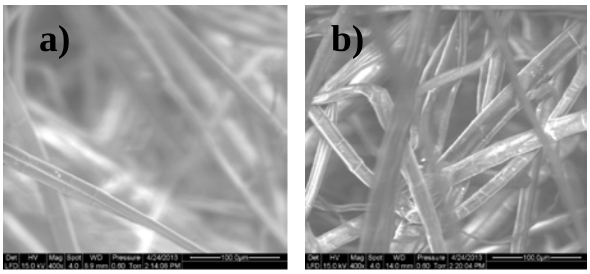

Figure 2. SEM micrographs of the surface morphology of: (a) untreated and (b) alkali treated hemp fibres.

Before compression moulding, multilayer unidirectional prepregs were prepared by winding the hybrid yarn around a rectangular steel frame. The off-axis fibres were oriented at different angles including 0°, 45° and 90°. In order to investigate the effect of random fibre orientation on composites, non-woven PLA/hemp prepreg was produced through carding. The composites were formed by pressing the prepreg at 195˚C and at 1.7 MPa for 15 min. The obtained thickness of produced laminates was between 2-3 mm. Before the testing, the specimens were conditioned for at least 24 hours at 23˚C and 50% relative humidity according to DIN EN ISO.

2.2.2 Testing

The hemp fibres were tested on a Favigraph single fibre tensile tester. To simulate the effect of composite compression moulding conditions on the hemp fibre properties, single hemp fibres were treated in a hot press at 195 ˚C and 1.7 MPa for 15 min, and then again tested for tensile properties on the Favigrapgh.
The densities of the composites were determined by the buoyancy method using ethanol as the displacement medium. The fibre volume fraction was calculated from the fibre weight fraction taking porosity into account.
The water absorption analysis was done according to ASTM D570-98. The specimens were first dried in an oven and then cooled to room temperature in a desiccator. The weight of these specimens was denoted as W_0. The specimens were further immersed in two different baths: one of distilled water at room temperature and one distilled water bath at 80°C. The amount of water absorbed was measured every 24 hours for 10 days. At each measurement, the specimen was taken out of the water and the surface was wiped dry before the weight was recorded as W. The percentage of apparent weight gain (W_G) was then calculated using equation (1).

$$W_G = \frac{W - W_0}{W_0} \times 100 \tag{1}$$

Tensile testing was done according to ISO 527, using a H10KT testing machine equipped with a mechanical extensometer. The testing parameters were: 10 mm/min for loading rate, and 1 kN for loading range. The extensometer was attached to the central portion of the test specimen with clips.
Flexural testing was performed on the same machine according to ISO 14125. At least five specimens were tested for each batch of samples. The loading rate was 10 mm/min and the load range was 1 kN. The outer span was taken to be 64 mm for discontinuous-fibre-reinforced composites and 40 mm for unidirectional composite, and the range of displacement was 20 mm.
To investigate the toughness, an un-notched Charpy impact strength test was carried out according to ISO 179 179, using a pendulum type Zwick test instrument. A total of 10 specimens were tested edgewise to determine the mean impact resistance.
The time-temperature dependency of the mechanical properties was determined by DMTA, using a Q-series instrument supplied by TA Instruments. The DMTA was run in the dual-cantilever bending mode, whereas the temperature range was from 30 to 150˚C with a heating rate of 3˚C/min, using a frequency of 1 Hz and amplitude of 15 μm. At least 3 specimens were tested for every composite composition.
Fibre morphology and composite fracture surfaces structures obtained from the tensile testing were studied using low-vacuum scanning electron microscopy.

3. Results and discussion

In order to evaluate the effect of moulding conditions on neat fibres, the mechanical properties of heat and alkali treated single hemp fibres were determined, see Table 1. The alkali treatment improves fibre tensile strength and modulus, which improves the properties of the composites. This treatment possibly orients the fibrils in the direction of the tensile forces by removing hemicelluloses from fibre surface, resulting in better load sharing between the fibrils. Heat treatments greatly reduce mechanical properties. This could be due to the high percentage of lignin removal or a result of thermal degradation of cellulose chains.

Treatment	Tenacity (cN/dtex)	E-Modulus (N/dtex)	Elongation (%)	Linear density (dtex)
As received	4.66 (1.43)	97.71 (24.92)	3.93 (0.66)	4.15
After hot pressing	3.75 (1.10)	84.62 (26.60)	3.37 (0.88)	4.27
After alkali treatment	5.18 (1.30)	99.15 (32.64)	4.05 (0.86)	3.75

Table 1. Hemp fibre properties.

The physical compositions of the composites are summarized in Table 2. The composite made from PLA/hemp nonwoven had the higher porosity. The nonwoven mat fibre has a more tortuous flow path compared with the composite made from hybrid yarn prepregs and, hence, it is more difficult for the entrapped air to flow out of the system. The formation of a stronger interface by improved hemp fibre and PLA adhesion could be the result of the reduced porosity for alkali treated hemp composites compared with the untreated hemp/PLA composites. This can be explained by the fact that alkali treatment will increase the available hydroxyl groups [6] due to removal of the noncellulosic materials covering the cellulose hydroxyl groups, and also by the increase in roughness (Fig. 2), which would largely increase the surface area of the fibre. In addition to increasing the number of hydroxyl groups for hydrogen bonding, increased surface roughness would also enable better mechanical interlocking with PLA.

Sample	Density (g/cm^3)	Fibre mass fraction (%)	Fibre vol. fraction (%)	Matrix vol. fraction (%)	Porosity vol. fraction (%)
PLA	1.2490	0.0	0.0	100.0	-
Alkali hemp/PLA yarn (0°)	1.2943	30.0	26.23 (0.03)	72.53 (0.10)	1.23 (0.15)
Hemp/PLA yarn (0°)	1.2713	30.0	25.77 (0.54)	71.25 (1.50)	2.97 (2.04)
Hemp/PLA nonwoven	1.0914	30.0	21.12 (0.31)	61.16 (0.9)	16.71 (1.17)

Table 2. Composition of the fabricated composites calculated from the density measurements.

The apparent weight gain (W_G) as a function of the square root of immersion time ($\sqrt{t}$) at different temperatures for the composites are shown in Fig. 3 a and b. In Fig. 3 a, it can be seen that for all the composites investigated, W_G increases monotonically by $\sqrt{t}$. After reaching the maximum value, W_G decreases when immersion time is increased. The fibre-based composites had significantly higher water absorption than for neat PLA due to the hydrophilic nature of hemp with polar groups such as hydroxyl and carboxyl groups on the fibre surfaces. The composite from PLA/hemp nonwoven showed the highest water absorptions compared with the composite made from PLA/hemp yarn. The compact and close packing of PLA/hemp yarns reduces the porosity inside the composites, which in turn contributes to the reduction in water absorption [7]. As a result of alkali treatment, the interfacial adhesion in PLA/hemp fibres improved, which is necessary for the reduction of interfacial wicking of the water molecules. Furthermore, as shown in Fig. 3 b, it can be observed that increasing the immersion temperature leads to increased water absorption of the neat PLA and composites as well as shortening of the saturation time. The weight gain was found to decrease after passing through a maximum. This could be due to the neat PLA layer peeling on the surface as a result of biodegradation and dissolving with time together with the removal of some substances from the hemp fibres during the immersion.

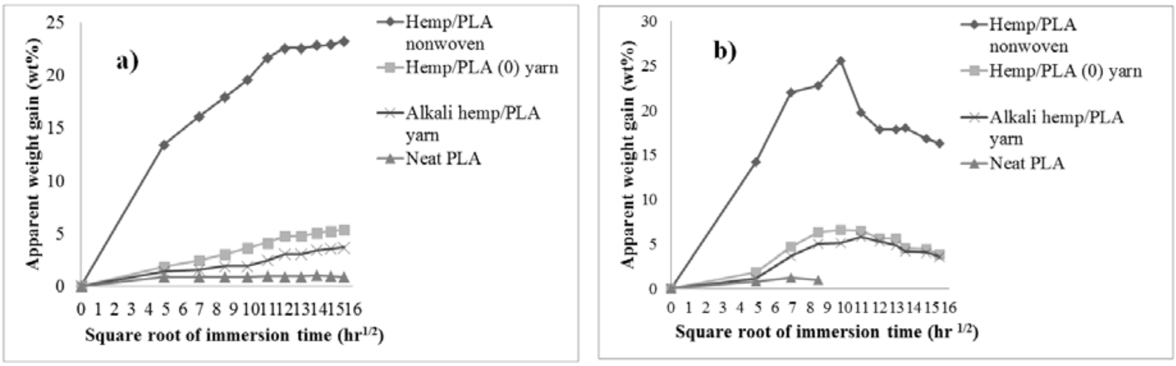

Figure 3. Apparent weight gain against √t for the different PLA/hemp composites at: (a) room temperature and (b) 80˚C.

The tensile strength and modulus of the composites are compared with the values of the neat PLA matrix in Fig. 4. The composites fabricated from PLA/hemp yarns (both untreated and treated) had considerably higher tensile strength and modulus in the longitudinal direction than for composites made from corresponding nonwoven mats. The composite strength and stiffness decreased with increasing fibre orientation angle. When the external load is directed at a significant angle to the primary fibre axes, large reductions in key composite properties such as ultimate tensile strength can occur. The tensile properties in the perpendicular direction (90˚) for the PLA/hemp yarn composites were in almost the exact opposite order to those in the principal fibre direction (0˚). The composite made from the nonwoven demonstrated higher tensile properties in the principal fibre direction compared with hemp/PLA yarn composite with fibre orientation angles 45˚ and 90˚. Tensile strength of composites made with fibre orientation angles 45˚ and 90˚ were lower than for pure PLA. because the on-axis properties are strongly dependent on fibre properties, and that off-axis properties are strongly dependent on matrix properties, particularly on their stiffness and load-carrying ability, which are typically related to their porosity content. For example, when a composite with porous matrices were tested off-axis, relatively weak strengths were observed because the porous matrix could not carry significant load compared to the pure matrix which has low porosity [8]. In the case of treated hemp/PLA yarn composites, the stronger interface formed due to increased potential hydrogen bonding.

The results of the flexural test are shown in Fig. 5. The flexural modulus of the composites is higher than that of neat PLA, which is especially evident for the treated hemp/PLA. It is also obvious that composites made from PLA/hemp yarn (0˚) showed an evident improvement in flexural modulus over the composites produced from PLA/hemp nonwoven. However, the composites from nonwoven exhibited the optimum tensile and flexural strength of 52.3 and 70.9 MPa, respectively. The reason for the reduction of mechanical properties could be the fact that all fibres with off-axis orientation failed at the particular point, and cannot contribute furtherer in the composite failure. So, the remaining number of on-axis (0˚) fibres almost exhibited more than 50% of the mechanical properties of uniaxial composites [9]. The flexural properties of unidirectional composites followed the reduction trend in their value when the fibre orientation changed from 0˚ to the off-axial direction. The lowest value of flexural strength was observed for the composites with fibre orientation angle 90˚. Alkali treatments enhanced the flexural strength and modulus of the composites. These results are consistent with the tensile properties described previously.

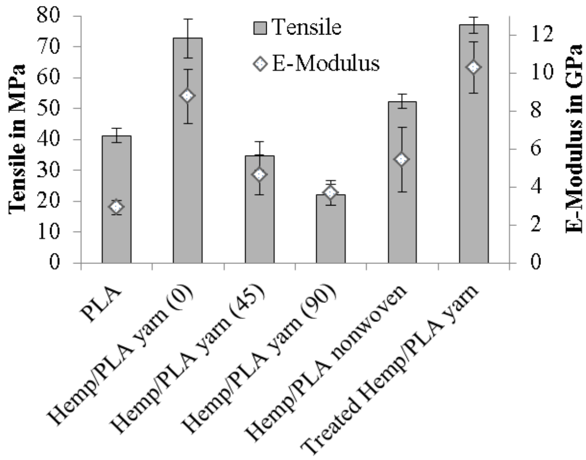

Figure 4. Tensile properties of the composites.

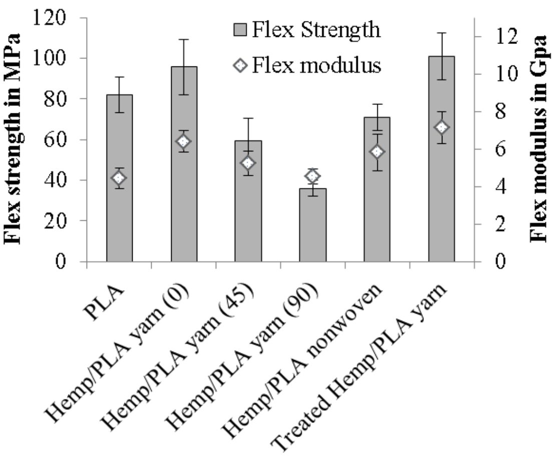

Figure 5. Flexural properties of the composites.

The results of the Charpy impact test are shown in Fig. 6. A significant reinforcement effect was determined for the treated PLA/hemp yarn composite with an impact value of 18.8 kJ/m^2 and for untreated PLA/hemp yarn composite (0˚) with the value of 16.0 kJ/m^2, while the value of the PLA/hemp nonwoven composites (9.7 kJ/m^2) was lower than that of the neat PLA matrix which is similar to flexural strength analysis. Further increment of fibres angle caused a decrease in impact strength of the composites, which is likely to be due to decreased dissipation of energy by less fibre pull-out. For an equivalent amount of hemp fibres (30 mass-%), the impact strength of the nonwoven composites was 128 and 237% higher than that of the yarn composites with 45˚ and 90˚ off-axis. Similar to the tensile properties, it can be observed that the alkali treatments enhanced the impact strength. In the case of alkali treated fibres, the dissipation of energy by fibre pull-out is much less, and debonding occurred followed by fibre breakage rather than by interfacial debonding usually associated with high energy absorption [10]. Moreover, the increased PLA crystallinity of the alkali treated hemp fibre composites compared with untreated hemp fibre composites could be another factor leading to increased impact strengths [11]. The impact resistance of the nonwoven composites was lower than that of neat PLA.

Fig. 7 a and b show how fibre treatment and orientation influenced the storage modulus and damping factor (tan δ) of PLA and its respective composites. As expected the storage modulus of the composites showed remarkable dependence on fibre orientation (Fig. 7 a). The storage modulus was highest for the hemp/PLA (0) yarn composite, followed by the hemp/PLA (45) yarn composite and the hemp/PLA (90) yarn composite. The sharp decrease in the storage modulus around 57–61˚C corresponds to the α-relaxation of the amorphous regions in PLA. The T_g seems to increase as hemp fibres are added to PLA. This shows that the presence of fibre restricts the segmental motion of the PLA polymer chains [12].

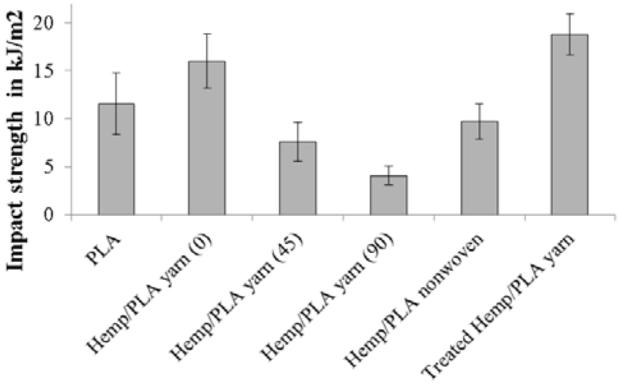

Figure 6. Impact strength of the composites relative to their proportion of fibre mass.

The storage modulus started to increase again around 100°C, which is the result of the cold crystallization typical for PLA. The decrease in modulus around 140°C indicates the softening of the sample before the onset of melting. The tan δ peak in the glass transition region is the most dominant feature, corresponding to high damping due to initiation of motion in long segments of the main polymer chain. For a composite, the molecular motion in the interface will contribute to the dampening. A larger area under the α-relaxation peak in the tan δ curves of a polymer indicates that the molecular chains exhibit a higher degree of mobility i.e. better damping properties. The area under this peak for PLA composites (Fig. 7 b) seems to be smaller especially for alkali treated hemp fibre composite. A possible explanation is that there is a strong interaction between the fibre and the matrix. The fibre/matrix interfacial adhesion can be indirectly quantified by estimating the damping term as it is a true indicator of the molecular motions in a material. The magnitude of tan δ values is also seen to increase in the case of composite from nonwoven compared to the composites from yarn. Actually, the storage modulus favours long fibres (large l/d), and damping favours short fibres (small l/d). It is also interesting to note that, for high aspect ratios l/d, damping for randomly oriented short fibre composites is higher than that of either aligned short fibre or continuous fibre composites. Higher damping of composite from nonwoven compared to composite from yarn could be because of its higher porosity. Damping properties of composites from yarn were improved by increasing fibre off-axis angle. Our experimental investigations indicated that composite with fibre off-axis 90° showed better damping than composite with 45° and 0°.

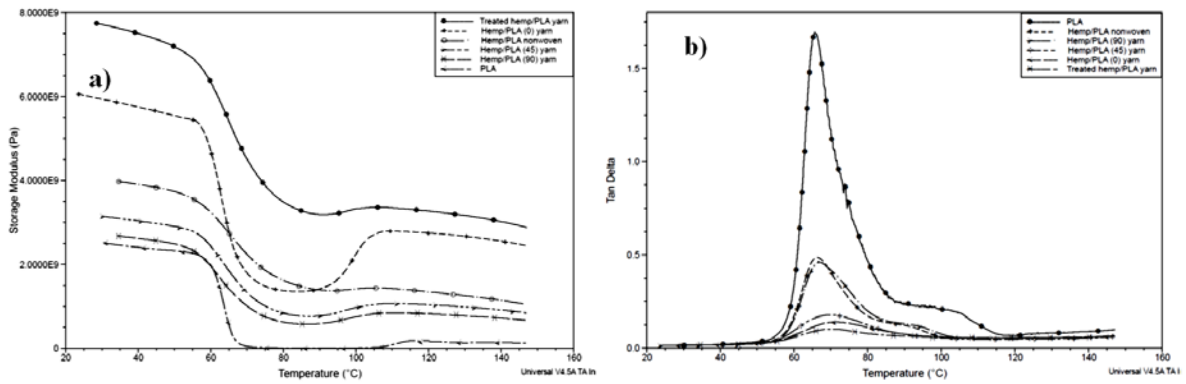

Figure 7. DMTA analysis of thermoplastic PLA reinforced with various orientaion and type of hemp fibre. a) storage modulus vs. temperature; b) tanδ curves.

4. Conclusions

We investigated the effect of different hemp fibre orientation as well as fibre alkali treatment; focusing on the determination of void percentage, water absorption, mechanical and thermo-mechanical properties. The best overall properties were achieved with aligned alkali treated hemp/PLA yarn. The results showed that the mechanical properties of the composites were highly affected by the fibre direction. Tensile, flexural, and impact values of the composites showed the decreasing trend for off-axial composites compared to 0˚, axial-oriented composite. Furthermore, the nonwoven PLA/hemp composites had an evident improvement in mechanical properties over the composites produced from yarn with off-axis angle of 45°and 90°. The thermo-mechanical tests showed that composites containing alkali treated hemp fibres had improved storage modulus due to enhanced interfacial bonding. The damping properties were highly affected by the testing direction; it was increased at an off-axis angle of 45°and 90°. Composites made from PLA/hemp nonwoven showed an evident improvement in viscoelactic properties over the composites produced from yarn with off-axis angle of 45°and 90°. From water absorption test results, it was found that higher temperature generally increased the W_G% of the neat PLA and all of the composites, as well as shortening the saturation time.

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