MECHANICAL PROPERTIES OF HEMP FIBRE/EPOXY COMPOSITES. INFLUENCE OF FIBRE CHEMICAL TREATMENTS

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Abstract

Environmental and economical concerns are stimulating research in design and production of innovative materials especially for aeronautic, railway and automotive industries. New materials are particularly attractive in which a good part is based on natural renewable resources, preventing further impact on the environment. Among these materials, Natural Fibres Reinforced Composites (NFRC) are finding much interest as a substitute for glass or carbon reinforced polymer composites. In fact, they are used more frequently in technical applications such as in the automotive industry, where mechanical properties have to be combined with low weight. Natural fibres are subdivided according to their origins, coming from plants, animals or minerals. Generally, plant or vegetable fibres are used to reinforce plastics. Plant fibres may include hairs (cotton, kapok), bast (flax, hemp, jute, ramie) and hard-fibres (sisal, henequen, coir). The availability of large qualities of such fibres with well defined mechanical properties is a general prerequisite for the successful use of these materials and such lack is one of the drawbacks at the moment. In this paper the mechanical behaviour epoxy matrix composite reinforced with woven hemp was studied. Fibre-matrix adhesion was promoted by fibre surface modifications using an alkaline treatment and a silane coupling agent. The tensile and flexural strength was studied using different chemical treatments.

1. Introduction

Natural fibres are increasingly being considered as an environmentally friendly substitute for synthetic fibres in the reinforcement of polymer based composites [1-6]. In fact these fibres are already used instead of glass and carbon in some technical applications such as the automotive industry, where mechanical properties have to be combined with low weight.

Natural fibres can be sourced from plants, animals and minerals. Generally, plant or vegetable fibres are used to reinforce polymer matrices. In fact, plant fibres are a renewable resource and have the ability to be recycled. The plant fibres leave little residue if they are burned for disposal, returning less carbon dioxide (CO2) to the atmosphere than is removed during the plant's growth. Although the strength of natural fibres is substantially lower than that of glass fibres the modulus is of the same order of magnitude. However, when the specific modulus of natural fibres (modulus per unit specific gravity) is considered, the natural fibres show values that are comparable to or even better than glass fibres. Moreover the price of natural fibres is about 70% lower than that of glass fibres. Chemical composition, surface characteristics, structural defects, strength, stiffness, and costs are some of the important parameters in selecting natural cellulose fibres for use in polymer composites. Therefore natural fibres are very attractive reinforcement materials for composites, as they are readily available, renewable, cost effective, and have good specific properties. However, the processing and properties of composite materials depend on the properties and proportions of the matrix and the reinforcement.

Hemp, flax, jute and kenaf are called bast fibres and they have similar morphologies and can have similar functions in composite materials. Cellulose, hemicelluloses, and lignin are the basic

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components of natural fibres and govern the physical properties of fibres and then properties of composite materials. The adhesion plays an important role to transfer the stress from the matrix to the fibres and thus contributes towards the properties of the composites. Poor surface adhesion due to insufficient wetting is the principal reason for the formation of a weak or ineffective interface between the fibre and the matrix. Several studies [7, 8] reported that the main factor that limits the mechanical properties of natural fibre reinforced thermoplastic composites is the chemical incompatibility between the hydrophilic lingo cellulosic molecules of the natural fibre and the hydrophobic thermoplastic molecules. On the other hand even if thermosets like epoxy and phenolic are known to be able to form covalent cross-links with plant cell walls via OH groups, due to the presence of unstable non cellulosic components like hemicelluloses and lignin, composites with untreated natural fibre have performed lower mechanical properties. In order to improve the necessary adhesion between the fibres and matrix several chemical treatments of the fibres can be used.

Alkaline treatment, silane treatment, benzoylation, use of maleated coupling agents, peroxide treatment, acetylation, and isocyanate treatment were considered [8-13].

Alkaline treatment involves immersing the fibres in an alkaline solution, frequently that of NaOH, for a period of time. It is believed to work by increasing the surface roughness of the fibre which improves the mechanical bonding.

Bachtiar et al. [14] studied the effect of alkaline treatment on tensile properties of sugar palm fibre reinforced epoxy composites. It was found that the alkaline treatment improve significantly the tensile properties of sugar palm fibre reinforced epoxy composites particularly for tensile modulus. The hydrophilic nature of sugar palm fibre is reduced due to this treatment increasing the interfacial bonding between matrix and fibres. Silane treatment usually entails soaking the fibres in a weak solution of a silane diluted in a water/alcohol. In the presence of water, silane breaks down into silanol and alcohol. The silanol reacts with the OH groups of the cellulose in natural fibres, forming stable covalent bonds to the cell walls that are chemisorbed onto the fibre surface.

Franco et al. [15, 16] studied the mechanical behavior of high density polyethylene (HDPE) reinforced with continuous henequen fibres. It was found that the use of the silane coupling agent improved the degree of fibre-matrix adhesion and then the strength and stiffness of the composites. Rachini et al. [17] studied the chemical modification of natural hemp fibres treated with two organosilane coupling agents. The effect of the initial concentration and the chemical structure of the organosilane on the grafting quantity will also be discussed.

The effects of alkali and silane treatments on the tensile and flexural properties of woven hemp reinforced epoxy composites are investigated in the present study. All laminates were prepared by Vacuum Infusion Process (VIP) in a mould at room temperature thereby preventing degradation of the hemp fibre. For comparison purposes, composites reinforced by untreated fibres were also manufactured using the same process.

2. Experimental

2.1. Materials

Woven hemp fabric with plain weave and having a count of 50×50 (50 yarns in warp and 50 yarns in weft direction per inch) was used as reinforcement. The weight of the fabric used is approximately 180 g/m^2. An epoxy infusion resin Prime^{TM} 20LV produced by Gurit with density of 1.084 g/cm^3 and tensile strength of 73 MPa was used as matrix. This was used in conjunction with slow hardening agent, the weight ratio between mixing resin and hardener being 100:26.

2.2. Fibre surface treatment

The effects of surface treatment of natural fibres on their properties are usually functions of the type and concentration of the treatment solution used. The chemicals used in this study were sodium

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hydroxide (NaOH; Sigma Aldrich co.) and (3-Glycidyloxypropyl) trimethoxysilane (Sigma Aldrich co), a silane coupling agent with chemical formula $H_2COCHCH_2O(CH_2)_3Si(OCH_3)_3$.

Before any treatment the fabric was cut into 280 x 220 mm sheet having a weight of 11 g. To evaluate the effect of the sodium hydroxide solution concentration, the hemp fibres were treated using 1 wt% and 5 wt% sodium hydroxide solution in water. Each sheet was soaked in the alkaline solution for 30 min using a ratio between the volume solution and the weight of the sheet equal to 45 ml/g. Afterwards, the alkalized fibres were washed with distilled water until all the sodium hydroxide was eliminated and the pH of the water was equal to 7. The washed fibres were then dried in an oven at 70 °C for 24h. Also the effect of silane coupling agent the amount was investigated. Therefore, the hemp fibres were treated using solutions containing 1, 5, and 20 wt% of silane coupling agent (weight of silane relative to the weight of hemp fabric) in ethanol and water. Adequate amounts of the silane were previously prehydrolysed at room temperature for 1 h in an 80/20 vol % solution of ethanol/water. After that period, the fibres where soaked in the hydrolyzed silane solution for 1 h using a ratio between the volume solution and the weight of the sheet equal to 22.5 ml/g. Subsequently, the fibres were dried in an oven at 70 °C for 24h.

2.2. Laminates fabrication

Six different configurations of hemp/epoxy composites were manufactured. These were epoxy reinforced with untreated hemp fibre, epoxy reinforced with alkali treated hemp fibre with different sodium hydroxide solution concentration, and epoxy reinforced with silane treated hemp fibre with different solution concentration of the silane coupling agent. The untreated fibres were dried out before to make the composites.

All laminates were prepared by Vacuum Infusion Process (VIP) in a mould at room temperature. The mould used for preparing laminates is made from a rectangular glass sheets having dimensions of 350 x 300 mmxmm, the PVA release agent was applied to the surfaces of the mold. Resin and hardener were thoroughly mixed with a mechanical stirrer for 5 min, followed by degassing under vacuum for approximately 5 min. prior to use. Composites were formed from four plies of textile. The stacks of textile were infused with catalyzed resin and cured for 24 h at room temperature. All composites were produced at 42% (±1) fibre weight fraction. The total fibre volume fraction is calculated using Eq. (1).

$$V_f = \frac{(W_f / \rho_f)}{(W_f / \rho_f) + (W_r / \rho_r)}; \tag{1}$$

where W_f and W_r are the weights of the fibres and resin, respectively, and ρ_f and ρ_r are the densities of fibres and resin, respectively. The density of epoxy resin is 1.084 g/cm^3, which is obtained from the manufacturers test report. The hemp density, determined from the density of the composite following water displacement method is found to be 1.48 g/cm^3 which is consistent with the literature value [18].The stacking sequences of the laminates were reported in Table 1.

Table 1. Laminate stacking sequences.

Symbol	Fibre	Treatment	Test	N° ply	Stacking sequence	Thickness (t_h) [mm]	W_f %	V_f %
A	Hemp	Untreated	Tension and flexural testing	4	$[0/90]_{1s}$	1.364	42.9	34.5 (±1)
B	Hemp	Alkaline treatment NaOH 1%	Tension and flexural testing	4	$[0/90]_{1s}$	1.511	42.2	34.8 (±1)
C	Hemp	Alkaline treatment NaOH 5%	Tension and flexural testing	4	$[0/90]_{1s}$	1.679	41.9	33.9 (±1)
D	Hemp	Silane treatment 1%	Tension and flexural testing	4	$[0/90]_{1s}$	1.471	40.8	33.8 (±1)
E	Hemp	Silane treatment 5%	Tension and flexural testing	4	$[0/90]_{1s}$	1.460	42.0	34.7 (±1)
F	Hemp	Silane treatment 20%	Tension and flexural testing	4	$[0/90]_{1s}$	1.450	42.26	34.8 (±1)

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2.3. Mechanical characterization

2.3.1 Flexural testing

Three point bending tests were performed in accordance with ASTM D 790 to measure flexural properties. The tests were carried out using an electromechanical testing machine MTS with load cell of 30 kN. The specimens of 25.4 mm length and 12.4 mm wide were cut from the laminates such that warp yarns were oriented longitudinally. The specimen is placed onto two supports with a span of 25.4 mm and the speed of the jaws was set to 0.72 mm/min. A three point bending test was chosen instead of a four point bending one because the former eliminates the need to accurately determine center-point deflections with test equipment. The flexural modulus and maximum flexural stress were calculated by (2) and (3).

$$E = \left(mL^3\right)/\left(4bh^3\right); \tag{2}$$

$$\sigma_{\max} = \left(3P_{\max}L\right)/\left(2bh^2\right); \tag{3}$$

where:

P_{max} is maximum load at failure in [N];
L is span in [mm];
b is width of the specimen in [mm];
h is thickness of the specimen in [mm];
m is initial slope of the load-displacement curve.

2.3.2 Tension testing

Specimens for tension test were carefully cut from laminates using a diamond wheel saw; the specimens were cut with fabric warp yarns oriented in the loading direction. The geometry of the specimens is a plate 25.4x254xt_h (mmxmmxmm).

The tensile tests of the composites were performed on an electromechanical testing machine MTS according to ASTM D 3039/M. The tests were carried out using a load cell of 30 kN and measuring the strain by extensometer with 50 mm gage length. The specimens were tested without tabs and, to ensure proper gripping and failure in the gauge length, a folded strip of medium grade (80 grit) emery cloth between the specimen faces and the grip jaws was used, mounting at grip pressure of 1 MPa. The crosshead speed was 2 mm/min at room temperature.

Five samples were tested for each composite to evaluate the mechanical properties. All data (load, displacement and strains) were acquired. Stress-strain curves were obtained from these tests and Young’s modulus and tensile strength values were evaluated.

2. Results

The variation in the tensile strength of composites manufactured with fibres treated with alkali and silane coupling agent is reported in Fig. 1. It is evident that the tensile strength varies with the treatments. The tensile strength of composites reinforced with alkali treated fibres is lower than that of composites reinforced with untreated fibres. The reduction of the tensile strength is most noticeable for composites with fibres treated with a solution of NaOH at 5% concentration. For this treatment, the tensile strength is 25% lower than that of composite with untreated fibres. Meanwhile, the tensile strength of the 5% NaOH-treated fibre composite is lower than that of 1 % NaOH-treated composite. This may be due to the hemicellulose and lignin present on the fibre, which was substantially removed after the 5% alkali treatment causing fibril in the fibre to be easily pulled out (fibrillation). The tensile

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strengths of the silane-treated composites are lower than that of the untreated hemp fibre composites, but the tensile strength of the 20% silane treated fibre composite is 8% lower than that of untreated fibre composite. The tensile modulus of composites with fibres subjected to alkali treatment and silane treatment is presented in Fig. 2. The variation of the tensile modulus with alkali treatment concentration closely matches that of the tensile strength shown in Fig. 1. The tensile modulus of the composite with fibres subjected to the 5% NaOH treatment is lower than that of the composites with untreated fibres (about 7%) while the modulus of the1% NaOH-treated fibre composite is almost equal of untreated fibre composite. The tensile modulus of the composites with fibres subjected to silane treatment is significantly higher than that of the composites with both untreated fibres and fibres treated with alkali solution. The increase in modulus associated with the silane treatment is attributed to improved bonding between the fibres and the matrix. Sufficient load transfer between the matrix and the fibres occurs for the higher modulus of the fibres to beneficially impact on the modulus of the composite. The 1% silane treatment composite shows the highest tensile modulus value (5828 MPa) while the 5% NaOH treated fibre composite show the lowest (4947 MPa). Therefore the 1% silane treatment composite is found to have tensile modulus 15% and 10% higher than that of 5% NaOH treated fibre composite and untreated fibre composite respectively.

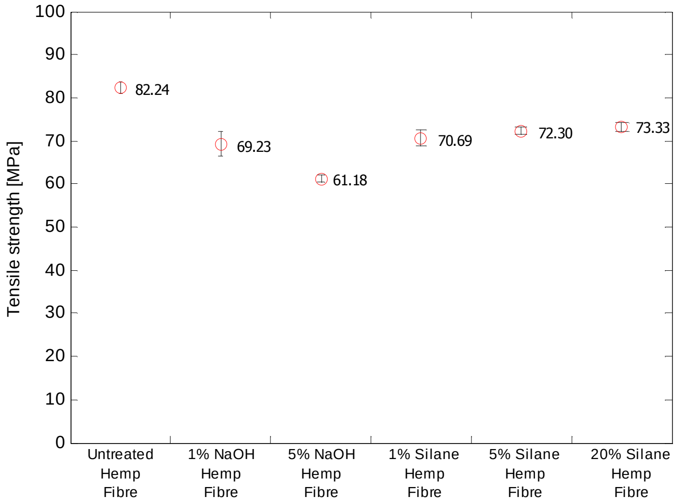

Figure 1. Tensile strength of treated fibre composites.

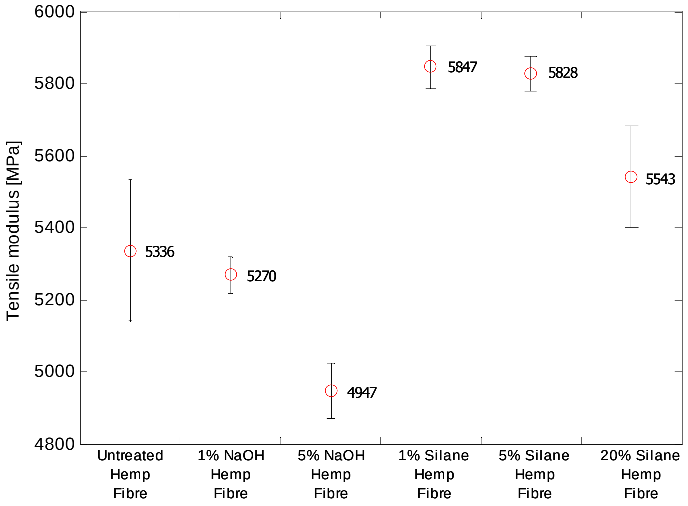

Figure 2. Tensile modulus of treated fibre composites.

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The flexural strengths and flexural modulus of the hemp fiber-reinforced composites are shown in Fig. 3 and Fig. 4. The composites with untreated fibre and with 5% silane treated fibre show the highest modulus value (around 4250 MPa) while composite with 1% NaOH treated fibre shows the lowest (3617 MPa). Moreover the composite with 1% NaOH treated fibre shows the lowest flexural strength (112 MPa). Different from the NaOH treatment, the flexural strengths and flexural modulus of the silane-treated composites are nearly equal to those of the untreated hemp fiber composites (122 MPa). This demonstrates that the silane treatment does not affect on the flexural properties of the composites.

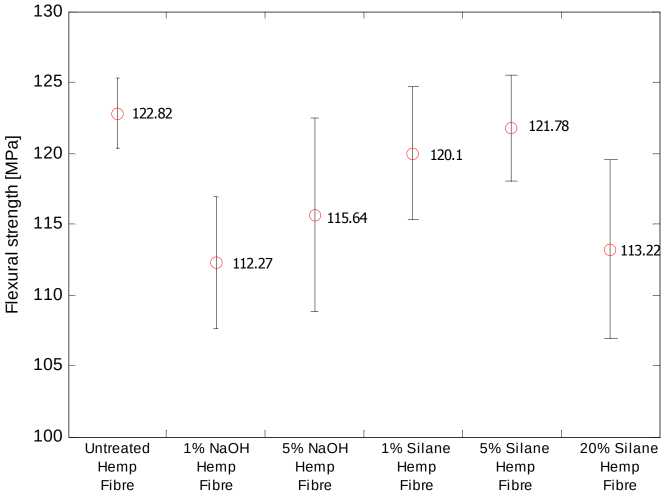

Figure 3. Flexural strength of treated fibre composites.

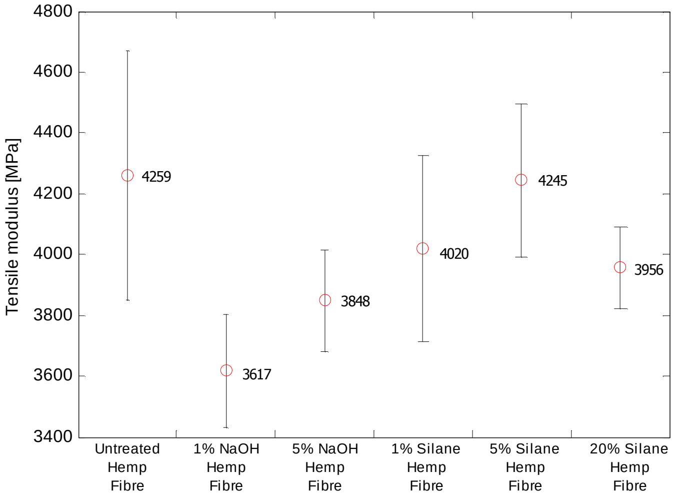

Figure 4. Flexural modulus of treated fibre composites.

3. Conclusions

Some mechanical behaviour of the epoxy matrix composites reinforced with hemp treated fibre has have been experimentally evaluated. From the results of this study, the following conclusions are drawn.

1. The tensile strength of all composites with treated fibre is lower than that of composite whit untreated fibre.

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2. The composite with 5% NaOH treated fibre displayed the lowest tensile strength. This may be due to the hemicellulose and lignin present on the fibre, which was substantially removed after the 5% alkali treatment causing fibril in the fibre to be easily pulled out (fibrillation).
3. The composite with 1% silane treated fibre shows the highest tensile modulus. The improvement of the modulus associated with the silane treatment is attributed to improved bonding between the fibres and the matrix.
4. All composites with silane coupling agent treated fibre show the tensile and flexural strengths nearly equal to those of the untreated hemp fiber/epoxy composites.

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