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Improving mechanical properties of novel flax/tannin composites through different chemical treatments

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ABSTRACT

Due to the inherent environmental benefits of using renewable materials, mimosa tannin resin (a natural phenolic resin) reinforced by flax fibres could offer desirable characteristics (lightweight, economic and low environmental impact) aiming at reducing carbon footprint of superlight electric vehicles. The non-woven flax mats were chemically treated (alkali, acetylation, silane and enzymatic treatment) to prepare tannin composites through compression moulding (130 °C/35 min/1.5 MPa). The change in fibre morphology was seen in SEM (scanning electronic microscope) images. The treatments (except enzymatic) showed significant improvement in tensile properties, along with enhancement (acetylation) in flexural properties, but little effect on impact resistance for all treatments. APS (aminopropyl triethoxy siloxane) treated composites showed highest tensile strength of 60 MPa and modulus of 7.5 GPa. BTCA (butanetetracarboxylic acid) treatment led to the highest flexural strength of up to 70 MPa. NaOH treatment retained the impact failure force of about 0.5 kN and sustained the saturation energy (4.86 J) compared to untreated composites (4.80 J).

1. Introduction

To date, crude oil-derived composites (glass/PP, glass/epoxy etc.) have been commercially used to produce lightweight parts, such as doors, panels, chassis pillars etc., for vehicles and other means of transportation (Fan et al., 2011). However, the interest in renewable raw material based composites has been increasing on account of their perceived eco-credentials and the foreseen future scarcity of oil and oil-derived products (Mohanty et al., 2000; Schuh, 1999). According to the life cycle assessment, for example, about 80% production energy can be saved by replacing glass fibre mats with flax fibre mats (Kosbar et al., 2000; Patel et al., 2005). Natural fibres (e.g. bast, leaf and seed) are employed as reinforcement because of their competitive specific properties to synthetic fibres like glass fibres, by considering the fibre cost, production yielding and mechanical properties (Yan et al., 2014). They also give a nice 'natural' look, warmth and grip to composites along with reduced environmental impact. In addition, the use of bio-matrices derived from renewable sources (e.g. soybean oil, pine oil waste, castor oil, cellulose and proteins etc.) to replace synthetic plastics could further develop the ecological and sustainability credentials of the final product (Mohanty et al., 2000).

Among the bast fibres, flax has relatively high tensile strength in the range of 345–1100 MPa due to the high cellulose content and the low microfibril angle. The high tensile strength, high specific strength, low cost and renewability of flax composites become the reasons for its wide use in natural composites (Rosa et al., 2009; Xie et al., 2010). The mechanical properties of flax fibre reinforced polymer composites depend on the nature and orientation of the fibres, the nature of the matrix and the fibre/matrix adhesion (Mishra et al., 2004). Tannin has lots of phenolic rings with molecular range between 500 and 2000, and is mainly extracted from plants, such as wattle, pine, and myrtle. It could be chemically grouped into hydrolysable and condensed tannin. The latter is more stable for resin and composite preparation as the di-substitute hydroxyl groups make the phenolic rings more active to suitable agent like formaldehyde (Pizzi and Mittal, 2003). Theoretically, it can partially or fully substitute phenol to form resins and the associated composites. Barbosa et al. (2010) reported that the impact strength was very low for coir/tannin–phenolic composites as a result of poor mechanical properties of coir fibres. Optimised 50 wt% sisal fibre content in tannin–phenolic composites was observed by Ramires and Frollini (2012) to present the highest stiffness and impact strength. The 100% use of tannin instead of phenol as matrix was

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Table 1
Summarised results of some treatments for flax composites.

Fibre/matrix	Treatment	Conditions	Effect on properties	Ref.
Flax/phenolic	Esterification	25 wt% MMA, 30 min, 210 W	More moisture retardant	(Kaith and Kalia, 2007)
Flax/polyester	Silane treatment	0.05 wt%, 24 h RT	Hydric fibre/matrix interface	(Alix et al., 2011)
Flax/epoxy	Alkali treatment	4 wt% NaOH, 45 s	Transvers strength, 30% increment	(Van de Weyenberg et al., 2006)
Flax/epoxy	Alkali treatment	5 wt% NaOH, 30 min	Tensile strength 21.9%; flex. strength 16.1%	(Yan et al., 2012)
Flax/PP	Esterification	MA–P coupling agent	Interphase compatibility	(Bledzki et al., 2004)
Flax/PP	Esterification	10 wt% MA, 25 h, 50 °C	Highest flexural and tensile strength	(Cantero et al., 2003)

MMA – methylmethacrylate and MA – maleic-anhydride.

initially investigated by Ndazi et al. (2006) who successfully manufactured composite panel boards from rice husks and mimosa tannins. Pizzi et al. (2009) firstly used flax fibres to produce mimosa tannin based composites. 5% Hexamine was applied as hardeners for tannin resins to eliminate formaldehyde emission.

The mechanical performance of natural fibre composites is limited by the poor interface quality between the hydrophilic fibre and the hydrophobic polymer matrix (Zhu et al., 2013b). The hydroxyl groups from its components could be modified for hydrogen bonding with cellulose groups or to introduce new moieties that form effective interlocks within the system (Summerscales et al., 2010). The hydroxyl groups could be modified for hydrogen bonding with cellulose groups or to introduce new moieties that form effective interlocks within the system. Mercerization, acetylation, silane treatment and other fibre pre-treatments are commonly used for flax modifications to improve the composite performances (Van de Weyenberg et al., 2003). Some example results are summarized in Table 1. Alkali treatment of natural fibres, also called mercerization, is used to produce high-quality fibres (Bledzki et al., 2004). Alkali treatment of flax fibre in 5 wt% NaOH for 30 min resulted in a 21.9% and 16.1% improvement of tensile strength and flexural strength of flax/epoxy composites (Yan et al., 2012). Acetylation is a well-known esterification method originally applied to wood cellulose to stabilize the cell walls against moisture, improving dimensional stability and environmental degradation. Tensile and flexural strengths of flax/PP composites were found to increase with increasing degree of acetylation up to 18% and then decreased (Van de Velde and Kiekens, 2001). Proper treatment of fibres with silane can increase the interfacial adhesion to the target polymer matrices and improve the mechanical performances of the composites. The suitable silane modification for fibres in epoxy composites was aminopropyl triethoxy siloxane (APS) and for methacryloxypropyl trimethoxysilane (MPS). 3% APS solution combined with alkali treatment was found to provide better moisture resistance (Singha and Rana, 2012). Enzymes, such as laccases or peroxidases are an increasingly interesting option and are often combined with hydrophobic compounds for modification and processing of biomaterials. (Grönqvist et al., 2003). The grafting of lauryl gallate after enzyme treatment showed significant reduction of water penetration for flax composites (Garcia-Ubasart et al., 2011, 2012).

In the previous work, the effects of production parameters and fibre configurations on properties of flax/tannin composites have been studied by Sauget et al. (2013) and Zhu et al. (2012, 2013a), respectively. With respect to the investigation of manufacturing techniques for non-woven flax/tannin composites, the best mechanical result was obtained by curing at 130 °C for 35 min. The 12 unidirectional (UD) flax layers/tannin composites showed very good tensile strength of up to 140 MPa while non-woven flax/tannin composites exhibited good damage resistance as reported by Zhu et al. (2013a). The SEM images of the fractured surface suggested that an improvement in flax/tannin adhesion could potentially increase the mechanical properties.

However there is little to no work done on suitable fibre modifications to boost the performance of flax/tannin composites. The current paper reports the research pertaining to the fibre treatments done by authors to fill this gap in the literature. Four treatments, including alkali, acetylation, silane and enzymatic methods, were adopted for non-woven flax mats to prepare flax/tannin composites through compression moulding. The effect of fibre treatments on mechanical properties was obtained through tension testing incorporated with digital image correlation (DIC) method, three point bending tests and low velocity impact tests.

2. Methodology

2.1. Materials

The Retan MD® mimosa tannin (0.4 g/cm^3) mainly extracted from black wattle was purchased from the SCRD, France. The hexamethylenetetramine (hexamine, >99.0%) was purchased from Sigma–Aldrich. The flax fibres used as reinforcement in tannin composites were provided by Ecotechnilin Ltd., in the form of non-woven fibre mats with areal weight of 600 g/mm^2 and average thickness of 3 mm. The same fibre mats with different treatments (NaOH, NaOH–BTCA, NaOH–APS and LD) were supplied by VTT, Finland (Table 2). The NaOH treatment was made by immersing the flax mats into 5 wt% NaOH solution for one hour, washing them two times thoroughly with water and drying in 50 °C for 12 h. This NaOH treatment was used as pre-treatment also for butanetetracarboxylic acid (BTCA) and aminopropyltriethoxysilane (APS) treated mats. The BTCA treatment was done by spraying 2.5 wt% BTCA–water solution on both mat surfaces to contain 5% of BTCA, followed by heating at 80 °C for 20 min and drying at 50 °C for overnight (to 24 h). APS treatment was done with ethanol (98%): water-solution (80:20) containing 1% APS. Mats were sprayed 'full' on both sides with solutions containing 1% of APS. Then the mats were placed in heat oven at 80 °C for 4 h followed by washing with ethanol–water solution and drying in heat oven in 50 °C for overnight. The laccase Doga (LD) treatments were carried out as following steps: (a) wetting of the samples with distilled water, (b) activation with laccase, (c) treatment with DOGA (phenolic dodecyl gallates), (d) rinsing with water and (e) drying.

2.2. Resin preparation

The tannin resins prior to composite manufacturing were prepared using aqueous tannin and 33 wt% hexamine/water solution

Table 2
Untreated and treated fibre used for tannin based composites.

Type	Modification	Treatment details
Untreatred	–	–
NaOH	Mercerization	5 wt% NaOH purification
BTCA	Acetylation	Alkali + butanetetracarboxylic acid
APS	Silane treatment	Alkali + amiopropyltriethoxysilane
LD	Enzyme treatment	Benzenediol + dodecyl gallate