Natural fibre composites with QLD based fibres and vegetable oils

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ABSTRACT: Natural fibre composites were manufactured with epoxidized hemp oil (EHO) and epoxidized linseed oil (ELO) blended with a commercial epoxy resin. Randomly orientated short hemp fibres were used as the reinforcing fibres. The effects of EHO/ELO addition, fibre weight fraction and alkali treatment of the hemp fibre were analysed through flexural tests, dynamic mechanical analysis (DMA) and microscopic analysis. A systematic decrease in flexural stress/modulus with an increase in EHO/ELO content was observed due to the plasticising effect of epoxidized vegetable oil (EVO). Improvements in material performance were realized through the use of alkali treatment of the fibres due to enhanced fibre-matrix adhesion. In terms of cost, biodegradability and specific material properties, natural fibre composites represent an alternative to traditional synthetic fibre composites in specific applications. This study has confirmed that natural fibres and plant-oil based resins are feasible resources from which to manufacture fibre composites.

1 INTRODUCTION

Recently there has been an increasing focus towards sustainability and environmental awareness which has emerged within the fibre composite industry. This attitude has seen the emergence of research and development specifically focused on green, sustainable materials and products. Traditional synthetic composites are predominately manufactured from synthetic fibres and petro-chemical based resins. These traditional petro-chemical based composites have benefited society in numerous different ways, however there are increasing concerns over the finite nature and the unsustainably of these resources. A genuine concern is the cost increases as a result of diminished petro-chemical feedstock availability. Therefore there is a requirement to find a sustainable replacement material for use in civil engineering fibre composites, and this is where natural fibre composites are being positioned.

Natural fibres demonstrate numerous advantages over synthetic fibres. They signify an inexpensive, easy to process, renewable fibre that exhibits high specific material properties with end of life cycle recyclability (O'Donnell et al. 2004, Agrawal et al. 2000, Canché-Escamilla et al. 1999). Other advantageous properties of natural fibres are a reduced carbon footprint from the growing of the plants, and enhanced energy recovery at the end of their lifecycle (Joshi et al. 2004).

However there are also disadvantages associated with natural fibres. Saherb & Jog (1999) reported that natural fibres may have the propensity to form aggregates during processing and also exhibit a low resistance to moisture absorption. This hydrophilic characteristic may lead to poor matrix-fibre compatibility and therefore compromise material performance. Chemical treatments, such as alkali treatment aim to overcome this problem by modifying the structure and the surface properties of the fibres, thereby allowing enhanced fibre-matrix compatibility.

The majority of polymer resins used in composite applications are currently derived from non renewable petro-chemical based resources. According to Wool (2005) vegetable oil (VO) based resins, which are derived from natural sources, are a viable alternative to petroleum based resins as they are readily available in most of the world. Van Erp & Rogers (2003) have indicated that the Darling Downs region of Queensland, Australia is suitable for the production of VO based resin feedstocks, although the successful implementation of these crops will depend on the profitability of the crops and the material properties of the oil produced. The focus of this research involved using epoxidized vegetable oil (EVO) based resins and hemp fibre.

VO consists of triglyceride molecules. Triglycerides are comprised of unsaturated and saturated fatty acids. Saturated fatty acids exhibit only single carbon bonds and no carbon double bonds, whereas

unsaturated fatty acids display one to three carbon double bonds. A fatty acid chain contains a long carbon chain that is connected to a carboxylic acid group at one end. Fatty acid chains are constructed from the elements carbon, oxygen and hydrogen. According to Wool (2005) the fatty acids contained in the most commonly used oils display a variation in length of between 14 to 22 carbon atoms with 0-3 carbon double bonds per fatty acid chain. VO are predominately composed of oleic acid, linoleic acid and linolenic acid. A variation in the number and the type of triglycerides is apparent relative to the type of VO in question. The triglyceride molecules consist of three fatty acid chains and a glycerol join which can also be seen in Figure 1.

The double bonds that are present in unsaturated fatty acids are used as reaction sites in the formation of cross linking. Cross linking may be achieved by a functional reaction of the carbon-carbon double bonds (Lligadas et al. 2006) to enable use in high-molecular weight products. Van Erp & Rogers (2003) reported that the material properties of the resin are dependent on the degree of cross linking, with materials that have a high crosslink density displaying good mechanical and thermal properties.
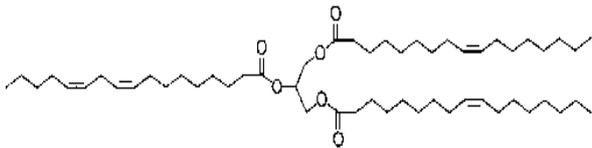
Figure 1. Triglyceride molecule, the primary component of vegetable oils.

2 EXPERIMENTAL METHODOLOGY

2.1 *Materials*

Short bleached industrial hemp (*Cannabis Sativa L*) fibre was obtained from Ecofibre, QLD, with a length range of 50mm to 100mm. Epoxidized hemp oil (EHO) was used as synthesised at CEEFC and epoxidized linseed oil (ELO) was used as supplied by Plasthall. A commercial epoxy system was used as received. Sodium hydroxide (NaOH) solutions in water were used for the alkali treatment. A summary of all experimental variables is shown in Table1.

Table 1. Summary of all experimental values.

EHO & ELO epoxy blend samples
•Epoxy/EVO (100/0, 90/10, 80/20, 70/30)
•Untreated hemp fibre (3wt% ≈5g)
Alkali treatment samples
•Epoxy
•Hemp fibre treated with NaOH solutions with concentrations of (5%, 10%, 15%, 20%)
Fibre weight fraction samples
•Epoxy/EHO (80/20)
•Untreated hemp fibre with different wt% (0.5%, 1%, 2%, 3%, 4%, 5%)

2.2 *Manufacture of test specimens*

Samples were created for flexural tests and DMA by hand mixing the required quantities of fibre, epoxy, EVO and hardener in a mould. After the epoxy/EVO was added, the hardener was added to the mixture. The mixture was thoroughly mixed for a period of five minutes to ensure uniformity and to remove any air bubbles. The weight of fibres required for each mixture was measured and then added and stirred through the mixture. The mixture in the mould was then lightly compressed. Initial curing at room temperature was performed for a period of 4 hours. The samples were then post cured at 80℃ for 4 hours. The moulds were removed and samples for testing were cut using a wet saw and polished using a rotating sander to the required dimensions.

2.3 *Alkali treatment of hemp fibres*

NaOH solutions of different concentrations in water were prepared. This treatment was chosen due to the availability of the required chemicals, the ease of the process and because of the encouraging results obtained in previous work (Mehta et al. 2005, Li et al. 2007) documented throughout the literature. The NaOH solution was then added to the fibres (5g) and then mixed together to ensure complete coverage. The fibres were then left to sit for 1 hour to allow the chemical treatment to occur. After the treatment the fibres were drained of the NaOH solution and were thoroughly washed with water three times thereby ensuring that the chemical reaction was neutralised. To ensure the fibres were completely dry they were left to air dry for six hours and then placed into an oven at 80℃ for four hours.

2.4 *Flexural tests*

Three-point bending flexural tests were conducted using a MTS RT/10 with a crosshead speed of 4mm/min to determine the peak flexural stress and flexural modulus as shown in Figure 2. Samples were approximately 14×10.5×90mm in size due to the size of the mould available at the time of the project. A span length of 64mm being used throughout the tests with three-four samples being used for each test.

2.5 *Dynamic mechanical analysis*

Dynamic mechanical analysis (DMA) was performed with a TA instruments Q800 using the dual cantilever mode with a temperature change of 3°C/min with a fixed frequency of 1*Hz*. The samples of size 58×10 ×4mm were mounted, secured and the dynamic mechanical properties were recorded. A typical DMA plot is shown in Figure 3.
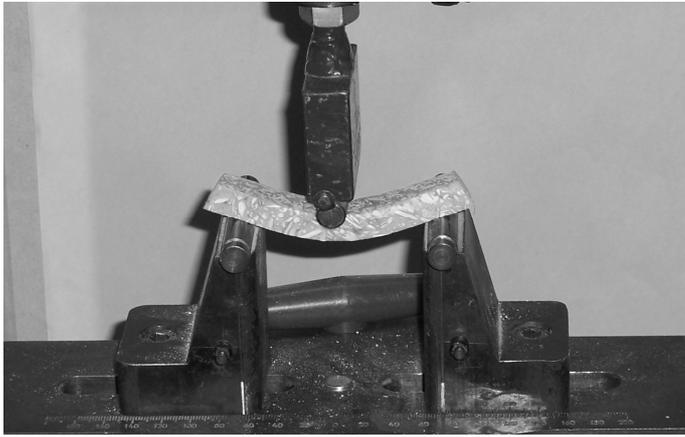
Figure 2. Specimen undergoing three-point bending flexural test.

2.6 *Microscopic analysis*

Samples were prepared for optical microscopy by sectioning and polishing with different grades of polishing paper. Coarse polishing was initially performed followed by finer grade polishing to achieve a flat reflective surface. Samples were examined with an Olympus BX41M optical microscope with image recording capabilities. The fibre-matrix interface was examined to determine the effect of alkali treatment on the fibre-matrix adhesion. Magnification from ×50 to ×200 was used to obtain the images.

3 RESULTS & DISCUSSION

3.1 *EHO & ELO epoxy blends*

When EVO was blended with the synthetic epoxy there was a noticeable decrease in peak flexural stress as the EVO percentage increased. This trend can be seen in Figure 4. The highest value of peak flexural stress was 46.31MPa observed for the hemp fibre synthetic epoxy. Samples containing EHO displayed a decrease in peak flexural stress from a maximum value of 30.32MPa at 10% EVO concentration to a minimum value of 4.02MPa at 30% EVO concentration. Similar results were displayed by the samples containing ELO. The maximum value of peak flexural stress of 24.69MPa occurred at 10% EVO concentration with the lowest value of 3.58MPa occurring at 30% EVO concentration. It was observed that samples made from EHO displayed consistently higher values of peak flexural stress than samples made with ELO throughout the data.

Flexural modulus results displayed a similar trend to the peak flexural stress results. The maximum value of flexural modulus was 970MPa observed for the hemp fibre synthetic epoxy. Samples containing EHO displayed a decrease in flexural modulus from a maximum value of 747MPa at 10% EVO concen-

tration to a minimum value of 42MPa at 30% EVO concentration. Similar results were displayed by the samples containing ELO. The maximum value of flexural modulus of 594MPa occurred at 10% EVO concentration with the lowest value of 34MPa occurring at 30% EVO concentration. From Figure 4 it can be seen that samples made from EHO displayed consistently higher values of flexural modulus than samples made with ELO throughout the data. The overall decrease in flexural modulus/stress can be attributed to the plasticising effect of EVO.

DMA showed that the maximum storage modulus value of 1452MPa occurred from the hemp fibre synthetic epoxy, with the minimum storage modulus value of 108MPa occurring at 30% ELO. The maximum loss modulus value of 166.1MPa occurred from the hemp fibre synthetic epoxy while the minimum loss modulus value of 51.6MPa occurred at 30% ELO. A trend was observed whereby the storage and loss moduli systematically decreased when the percentage of EVO increased due to the plasticising effect of EVO. The highest glass transition temperature of 65.03°C occurred from the hemp fibre synthetic epoxy while the lowest glass transition temperature of 42.56°C occurred at 30% ELO. The average glass transition temperatures for ELO and EHO were 50.23°C and 52.63°C respectively. Although the average glass transition temperature values are similar, the higher values for EHO samples may be due to the increased crosslink density of the EHO samples compared with the ELO samples. This is further supported by the consistently higher values of both peak flexural stress and flexural modulus for EHO samples when compared with ELO samples.
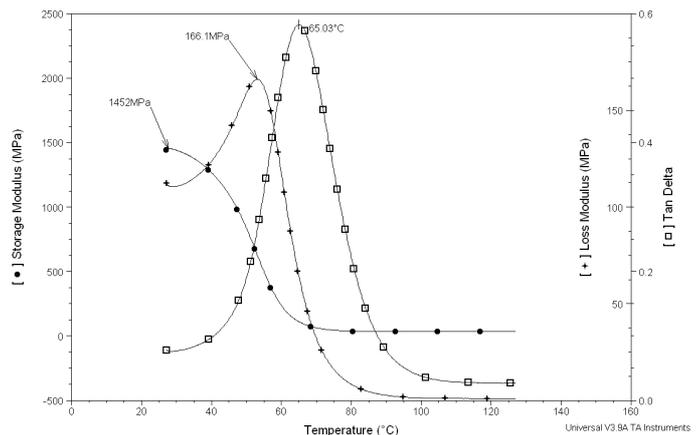
Figure 3. Sample DMA plot for hemp fibre (3wt%) synthetic epoxy composite.
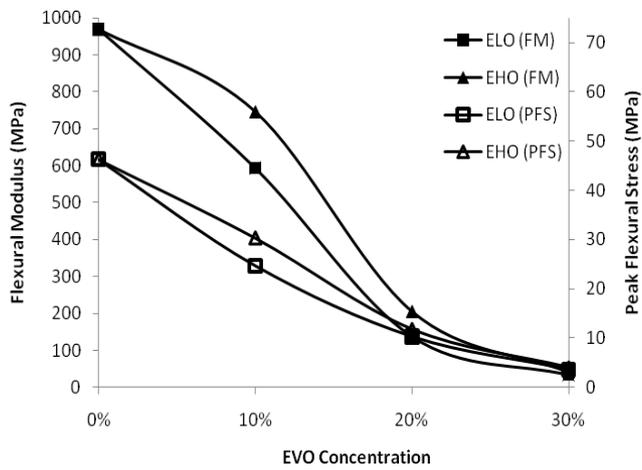
Figure 4. Flexural modulus and peak flexural stress versus EVO concentration (FM=Flexural Modulus, PFS=Peak Flexural Stress).

3.2 Alkali treatment

Peak flexural stress increased as the NaOH concentration increased up until 15% whereby a decrease was noticed as shown in Figure 5. The lowest value of peak flexural stress was 38.06MPa which occurred with the untreated hemp composite with the highest value of 47.15MPa occurring at a NaOH concentration of 15%. The flexural modulus increased from 1150MPa for the untreated hemp sample to a maximum value of 1435MPa at a 15% NaOH concentration whereby it then decreased to 1366MPa at 20 % NaOH concentration. The improvements in the flexural properties of the composites can be attributed to the alkali treatment. Alkali treatment has enhanced the fibre-matrix interface through increased surface roughness and removal of numerous impurities and waxy substances. Ultimately this has resulted in superior mechanical interlocking of the fibres with the resin. This was confirmed from microscopic analysis, Figures 6 and & 7, whereby there was a noticeable reduction in the size and number of voids, thereby suggesting increased fibre-matrix adhesion.
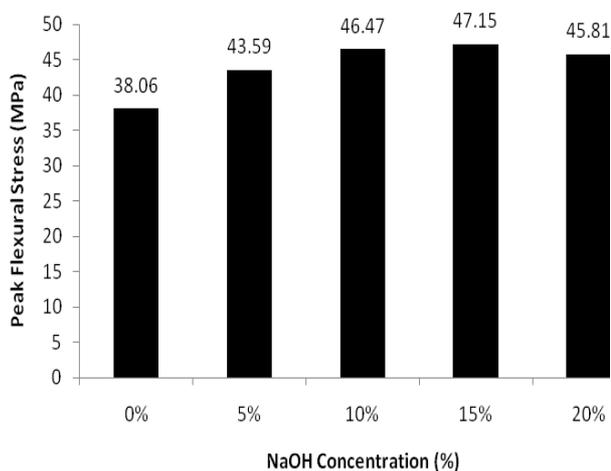
Figure 5. Peak flexural stress versus NaOH concentration.
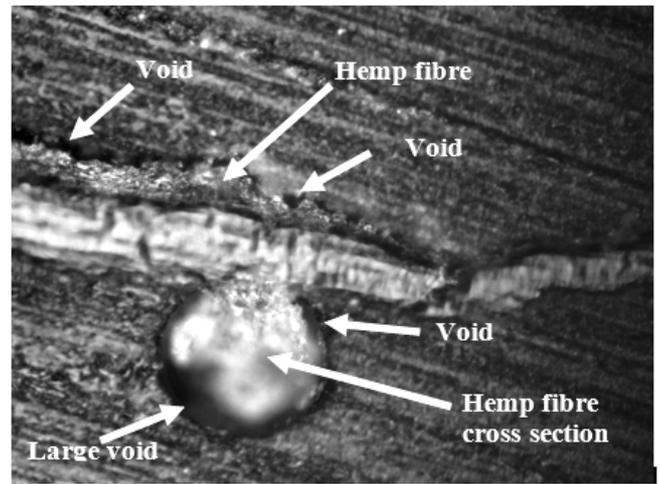
Figure 6. Micrograph of untreated hemp fibre/epoxy composite sample (×100).

3.3 Analysis of optimum fibre weight fraction

Peak flexural stress and flexural modulus as a function of fibre weight fraction were analysed. Samples were made using epoxy containing 20% EHO with varying quantities of randomly orientated short hemp fibre. From Figure 8 it can be seen that the peak flexural stress increased from 9.46MPa at 0.5wt% of hemp fibre to a maximum value of 11.81MPa at 3wt% of hemp fibre whereby it decreased to a value of 9.92MPa at the maximum fibre weight of 5wt%. The flexural modulus, shown in Figure 9 displayed a similar trend to the peak flexural stress whereby an increase is observed from a minimum value of 100MPa at 0.5wt% of hemp fibre through to a maximum value of 145MPa at 3wt% of hemp fibre. The flexural modulus then begins to decrease to a value of 126MPa at the maximum 5wt%. This decrease in flexural properties after 3wt% of hemp fibre is attributed to fibre-matrix interactions, whereby the wettability of the fibre is being compromised leading to the formation of voids at the fibre-matrix interface and ultimately a more porous composite with lower mechanical properties.
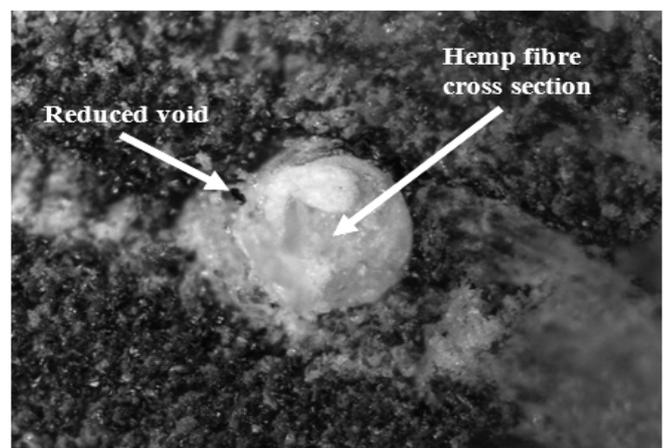
Figure 7. Micrograph of 15% NaOH treated hemp fibre/epoxy composite sample (×100).
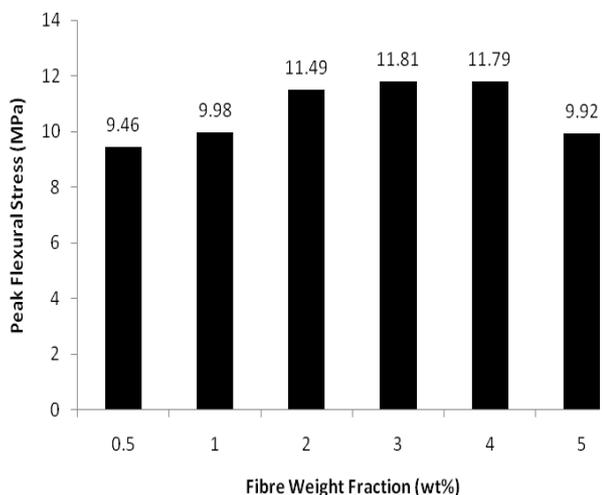
Figure 8. Peak flexural stress of hemp fibre/ EHO 20% composite versus fibre weight fraction.
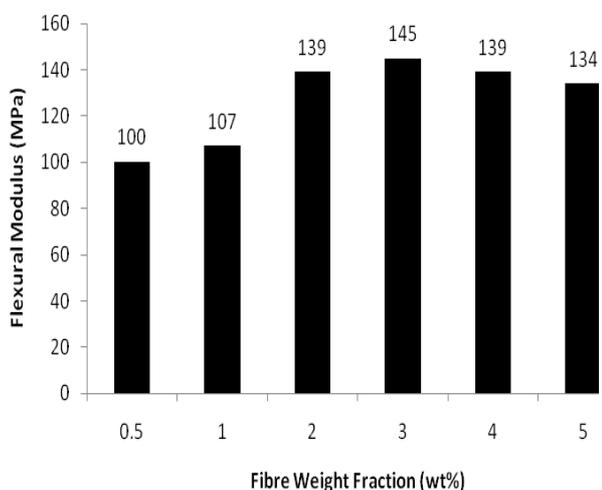
Figure 9. Flexural modulus of hemp fibre/ EHO 20% versus fibre weight fraction.

4 CONCLUSIONS

Due to the plasticising effect of EVO addition a decrease in flexural stress and flexural modulus corresponding with an increase in EVO concentration was observed. Samples using EHO displayed values that were consistently higher than samples using ELO. DMA showed that samples made using EHO exhibited a higher glass transition temperature and both storage and loss modulus than samples with ELO suggesting a higher degree of curing due to more pronounced crosslinking.

It was found that alkali treatment had a positive effect on the mechanical properties of the composite. Peak flexural stress and flexural modulus were found to increase with an increase in NaOH concentration up to 10-15% concentration. Microscopic analysis showed that alkali treatment resulted in a marked reduction in void size and frequency thereby enhancing fibre-matrix adhesion and ultimately improving the mechanical properties of the composite.

From flexural testing the optimum fibre weight fraction was determined as 3wt%. A trend was observed for both peak flexural stress and flexural modulus whereby the properties increased to maximum values at 3wt% upon then decreasing due to compromised wettability of the fibres.

This study has demonstrated the ability of natural fibres and EVO resins as viable materials from which to construct fibre composites. Improvements were also realised through the use of alkali treatment of the fibres. In terms of cost and specific material properties, natural composites represent an alternative to traditional synthetic fibre composites in certain applications. This study has confirmed that natural fibres and EVO based resins are feasible resources from which to manufacture fibre composites.

5 ACKNOWLEDGEMENTS

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