

# MECHANICAL PROPERTIES OF EPOXIDIZED HEMP OIL BASED BIOCOMPOSITES: PRELIMINARY RESULTS

MANTHEY, N.W. \*†, CARDONA, F. \*, & ARAVINTHAN, T. \*

pp. 100-105

\* Centre of Excellence in Engineered Fibre Composites (CEEFC), Faculty of Engineering and Surveying,  
University of Southern Queensland, Toowoomba, Australia

† E-mail: [nathan.manthey@usq.edu.au](mailto:nathan.manthey@usq.edu.au)

**Abstract:** Vegetable oils or plant-oils are a sustainable, renewable resource able to be used for the production of bioresins. Oils with high levels of unsaturated fatty acids are used in the production of bio-based epoxy resins for use in biocomposite applications. A novel hemp oil based bioresin, epoxidized hemp oil (EHO) was synthesised at the Centre of Excellence in Engineered Fibre Composites (CEEFC). Biocomposite samples were manufactured from EHO and commercial epoxidized soybean oil (ESO) (for comparison purposes) blended with an amine cured synthetic epoxy resin. Untreated jute matting was used as the fibre reinforcement. Tensile, flexural and impact properties were compared for EHO/epoxy and commercial ESO/epoxy, jute biocomposites. Both EHO and ESO functioned as tougheners to the commercial synthetic epoxy resin. Biocomposite samples containing EHO displayed superior mechanical properties than samples containing ESO. It was found that ESO quantities up until 10-20% and EHO quantities up until 30% compared favourably with the commercial synthetic epoxy resin. This comparable performance is attributed to enhanced fibre-matrix adhesion of EHO/ESO and the jute fibres. Overall the results of this preliminary research demonstrate that EHO is an excellent bioresin for use in biocomposite applications, with mechanical properties being comparable to commercial synthetic epoxy (up to 30% EHO content) and superior to commercial ESO across the data range.

**Key words:** Biocomposite, bioresin, epoxidized hemp oil, mechanical properties, sustainable.

## 1 INTRODUCTION

Throughout the world increasing levels of environmental awareness are driving the development of sustainable 'green' materials. Fibre composites generally use petro-chemical based resins such as epoxy, polyester and vinylester because of their advantageous material properties such as high stiffness and strength. However these resins also have serious drawbacks in terms of biodegradability, initial processing cost, energy consumption, and health hazards. Consequently there is a requirement to develop novel bioresins from renewable feedstocks for use in fibre composites and biocomposites.

Biocomposites embody a new class of materials which offer enormous potential as a substitute for timber and glass fibre composites in various civil engineering applications. However the majority of biocomposites research focuses on using natural fibres in petro-chemical derived matrices. Although a step in the right direction in terms of sustainability, these biocomposites are only partially based on renewable constituents. The production of 100% sustainable biocomposites requires the synthesis and characterisation of sustainable bioresins such as vegetable oil based resins.

Extensive research has been performed throughout the world on the development and commercialisation of bioresins and biocomposites based on soybean oil and to a lesser extent on linseed oil and canola oil. However these particular vegetable oil feedstocks are also used in food production thereby representing a conflict of interest. A potential solution is to focus on using fast growing, non-food oil crops for use as bioresin feedstocks. Due to the numerous diverse fatty acid profiles of different types of non-food vegetable oils a multitude of different oil options exists. One such identified type of oil is hemp oil.

The objective of this paper is to determine whether epoxidized hemp oil (EHO) can be used as a bioresin applied to biocomposites by comparing the mechanical properties of EHO and commercial epoxidized soybean oil (ESO) based jute biocomposites.

## 2 TECHNICAL BACKGROUND

### 2.1 Industrial hemp oil

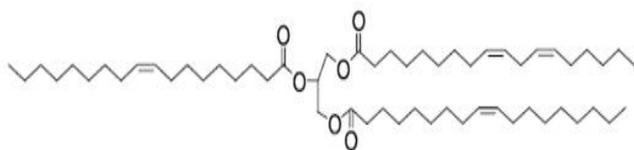
Industrial hemp (*Cannabis sativa* L.) is a rapidly growing plant that is one of the oldest crops known and used by humans. In addition to fibre, oil is also produced from the industrial hemp plant. The majority of industrial applications and research has focused on using the fibre with hempseed oil being viewed essentially as a by-product of fibre production. For every tonne of hemp yarn produced there is the potential to produce 1-1.2 tonnes of hemp oil (Hu & Lim, 2007). Currently hempseed oil is used throughout the world as livestock food oil and in pharmaceutical applications.

The unique fatty acid structure of hempseed oil makes it a suitable candidate as a bioresin feedstock. Vegetable oils that are high in unsaturated fatty acids are favoured due to a higher number of reaction sites therefore resulting in a superior polymer. According to Ecofibre Industries Ltd. (2010) the hempseed oil used in this research has a fatty acid profile of; palmitic acid (C16:0, 6%), stearic acid (C18:0, 2%), oleic acid (C18:1, 12%), linoleic acid (C18:2, 57%), and linolenic acid (C18:3, 19%) and gamma-linolenic acid (C18:3, 1.7%).

### 2.2 Vegetable oil chemistry

Vegetable oils are lipids derived from plants and are differentiated from fats in that they are liquid form at room temperature. The majority of vegetable oils are extracted from oil seeds (e.g. sunflower, hemp and linseed) although some oils may be extracted from different plant sources such as pulp (e.g. palm, avocado and olive). Chemically, vegetable oils consist of triglyceride molecules which can be categorised as comprising of a glycerol molecule attached to three fatty acid chains. The glycerol molecule (C<sub>3</sub>H<sub>5</sub>OH<sub>3</sub>) consists of a chain of three carbon atoms that are connected to three hydroxyl groups (-OH). A triglyceride molecule can be seen in Fig. 01 overleaf.

A fatty acid is a carboxylic acid attached to a long unbranched aliphatic carbon chain. Although variations in length do occur, the majority of common fatty acids found in vegetable oils are usually between 14-22 carbons atoms in length (Wool & Sun, 2005).



**FIGURE 01: Triglyceride molecule**

Fatty acids can be characterised as being saturated fatty acids (SFA), monounsaturated fatty acids (MUFA) and polyunsaturated fatty acids (PUFA).

A multitude of different types of SFA and USFA exists. Although vegetable oil based triglycerides contain both SFA and USFA they are predominately comprised of the following USFA; oleic acid, linoleic acid and linolenic acid. Different vegetable oils show variations in both the quantity and the type of fatty acids and subsequently variations in both the quantity and the type triglycerides. Tab. 01 below shows the fatty acid compositions of some common vegetable oils.

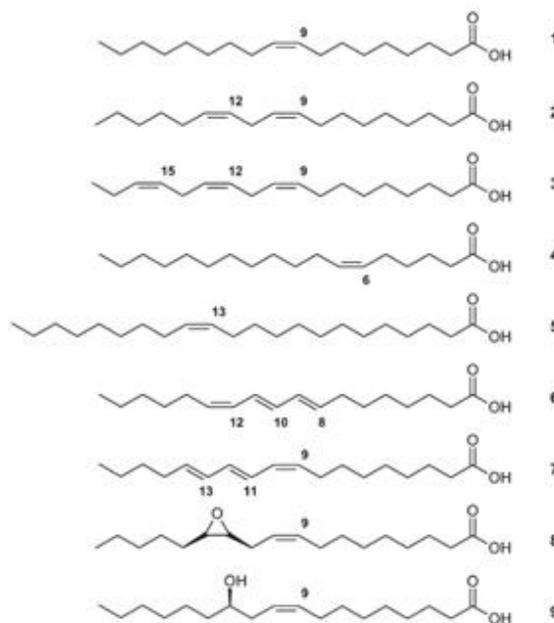
**TABLE 01: Fatty acid compositions of common plant oils. (Callaway, 2004; Ecofibre Industries Ltd., 2010; Wool & Sun, 2005)**

Fatty acid	#C:DB	Canola	Linseed	Soybean	Hemp
Myristic	14:0	0.1	0.0	0.1	<b>0.0</b>
Palmitic	16:0	4.1	5.5	11.0	<b>6.0</b>
Palmitoleic	16:1	0.3	0.0	0.1	<b>0.0</b>
Margaric	17:0	0.1	0.0	0.0	<b>0.0</b>
Stearic	18:0	1.8	3.5	4.0	<b>2.0</b>
Oleic	18:1	60.9	19.1	23.4	<b>12.0</b>
Linoleic	18:2	21.0	15.3	53.2	<b>57.0</b>
Linolenic	18:3	8.8	56.6	7.8	<b>21.7</b>
Arachidic	20:0	0.7	0.0	0.3	<b>0.0</b>
Gadoleic	20:1	1.0	0.0	0.0	<b>0.0</b>
Behenic	22:0	0.3	0.0	0.1	<b>0.0</b>
Eurcic	22:1	0.7	0.0	0.0	<b>0.0</b>
Lignoceric	24:0	0.2	0.0	0.0	<b>0.0</b>
<b>Avg. # DB/TAG</b>		<b>3.9</b>	<b>6.6</b>	<b>4.6</b>	<b>5.6</b>

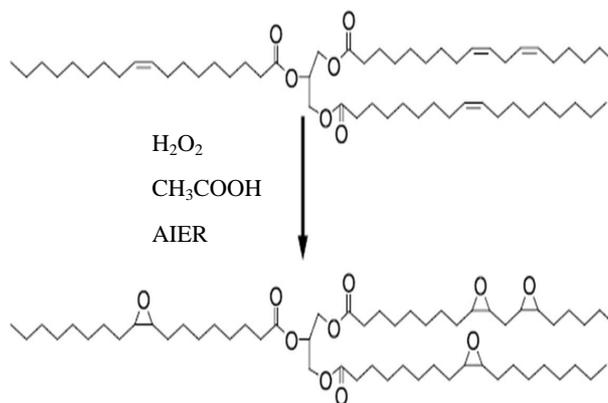
An overview of the structures of some types of unsaturated fatty acids is shown in Fig. 02 adjacent. C=C are represented as parallel lines, for example in Fig. 02 it can be observed that oleic acid has C=C between the ninth and tenth carbon atoms. The C=C that are present in UFA are used as the primary reaction sites in the formation of epoxides, which are used in crosslinking.

### 2.3 Epoxidation of plant-oil

Epoxidation of a plant-oil or triglyceride, entails breaking the C=C and adding an oxygen atom. This creates an epoxide, also known as an oxirane (C-O-C). Epoxidation is an important reaction because the formed epoxides are intermediates that are able to be converted into numerous products. Epoxidation is achieved through the reaction of acetic acid (CH<sub>3</sub>COOH) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) on the surface of an Acidic Ion Exchange Resin (AIER) to produce peroxyacetic acid (CH<sub>3</sub>CO<sub>3</sub>H) and water (H<sub>2</sub>O). The peroxyacetic acid reacts with the C=C in the oil to produce epoxides. This reaction can be seen in Fig. 03 adjacent.



**FIGURE 02: Structures of unsaturated fatty acids: (1) oleic (2) linoleic (3) linolenic (4) petroselinic (5) erucic (6) calendic (7) α-eleostearic (8) vernolic (9) ricinoleic (Meier, Metzger, & Schubert, 2007)**



**FIGURE 03: Epoxidation of plant-oil triglyceride**

### 2.4 Mechanical properties of EVO based bioresins and biocomposites

Measurement of the mechanical behaviour of EVO based biocomposites under tension, flexure and impact provides a powerful way of assessing the performance of the studied biocomposites. By characterising mechanical properties comparisons to other building materials such as timber and composites can be made.

Different types of biocomposites have been manufactured using natural or synthetic fibres with blends of EVO based bioresins with synthetic epoxies. Numerous studies have been performed pertaining to the characterisation of the thermal and mechanical properties of the aforementioned biocomposites.

Miyagawa, Mohanty, Misra, and Drzal (2004) evaluated the thermo-physical and impact properties of an epoxidized linseed oil (ELO)/epoxy amine cured system. ELO content varied between 10% to 27.5% wt. Izod impact strength was found to increase with an increase in ELO content to a maximum value of approximately 90J/m at 27.5% wt of ELO.

Miyagawa, Misra, Drzal, and Mohanty (2005) performed a similar study using anhydride cured ELO and epoxidized soybean oil (ESO) epoxy systems. ELO content used was 30 and 50% wt and ESO used was 30% wt. Fracture toughness and Izod impact strength performance were greatly improved with addition of ESO due to a result of the formation of a rubbery second phase of ESO particles. ELO (30 and 50% wt) exhibited similar behaviour to the neat synthetic epoxy.

Chandrashekhara, Sundararaman, Flanigan, and Kapila (2005) characterised the mechanical properties of composites containing 10% to 30% of soy-based resin. Mechanical tests showed that the pultruded glass fibre soy-based composites possessed characteristics such as flexural strength, modulus and impact resistance comparable to the synthetic resin based composite.

Zhu, Chandrashekhara, Flanigan, and Kapila (2004) studied the mechanical properties and curing of soy/epoxy based resin systems containing soy-based resin at levels of 10% to 30% wt. Flexural modulus, flexural strength and tensile modulus decreased with an increase in ESO content although ESO 10% wt samples displayed higher values than the neat epoxy resin.

Espinoza-Perez, Wiesenborn, Ulven, Haagenon, and Brudvik (2009) evaluated blends of ESO and epoxidized canola oil (ECO) with commercial synthetic epoxy resins as the matrix in composites reinforcement by glass fibers. The flexural strength of the biocomposites showed a reduction ranging from 15% to 86% in comparison with the synthetic epoxy. Flexural modulus of the biocomposites also showed a reduction ranging from 13% to 65% when compared with the control. Reduced interlaminar shear strength (ILSS) was displayed, indicating a low fibre-matrix adhesion. Impact toughness increased with increased ESO/ECO due to the fatty acid chains imparting flexibility to the matrix.

Morye and Wool (2005) performed tensile, compression and flexural tests on acrylated epoxidized soybean oil (AESO) glass/flax hybrid biocomposites with varying ratios of glass and flax fibre. Tensile strength ranged from 31.8MPa for 100% flax to 128.8MPa 100% glass specimens. Compressive strength ranged from 18.5MPa for 80% flax to 89.8MPa 100% glass specimens. Flexural modulus ranged from 3.8GPa for 100% flax to 9.0GPa 100% glass specimens.

### 3 EXPERIMENTAL

#### 3.1 Materials

Jute matting (90°/0°) in 4 layers was used with a wt % of approximately 20 %. The mats were cut to size, washed with water to remove any dust particles and other such contaminants and were oven dried for 4 h at 80 °C. No chemical treatments were performed. Kinetix R246TX epoxy resin (EEW≈195), Isophorone diamine (IPD) (EEW≈42.6) supplied from ATL composites and triethylenetetramine (TETA) (AHEW≈24) from Huntsman was used as supplied. ESO, oxirane oxygen content 6.8 % was used as supplied from Hallstar. Cold pressed raw industrial hemp oil was used as supplied by Ecofibre. EHO, oxirane oxygen content approximately 8.2 % was synthesised at Centre of Excellence in Engineered Fibre Composites (CEEFC). Acetic acid (99.7 %) and hydrogen peroxide (30 %) were used as supplied from Biolab. Amberlite IR-120 hydrogen form was used as supplied from Fluka.

#### 3.2 *In situ* epoxidation of hemp oil

EHO was produced by the epoxidation of cold pressed raw industrial hemp oil (HO) by peroxyacetic acid, formed *in situ* by the reaction of hydrogen peroxide and acetic acid in the presence of an acidic ion exchange resin (Amberlite IR-120 hydrogen form) as the catalyst. Fig. 04 adjacent shows the *in situ* epoxidation reaction.

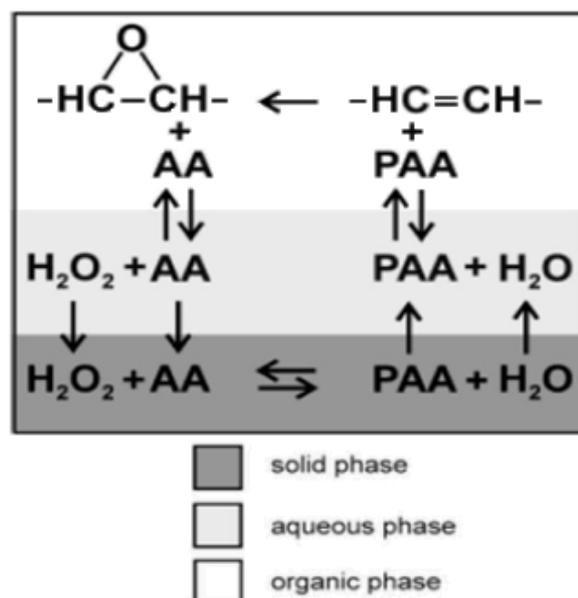


FIGURE 04: Two phase model of *In situ* epoxidation using acidic ion exchange resin (Benaniba, Belhaneche-Bensemra, & Gelbard, 2008)

A solution of hemp oil (156.25 g, 1 mol), acetic acid (40.04 g, 0.67 mol) and Amberlite IR-120 (23.44 g) were added to a four-necked reaction vessel equipped with a mechanical stirrer and thermometer, Fig. 05 below. The reactor contents were mixed for five minutes prior to dropwise addition of hydrogen peroxide (30 %, 113.4 g, 1 mol) for one hour. The reaction was then performed over a period of seven hours at 110 rpm and 75 °C. On completion of the reaction the solution was washed with water three times (cool, hot, cool) to remove the residual peroxyacetic acid and then filtered to remove the catalyst.

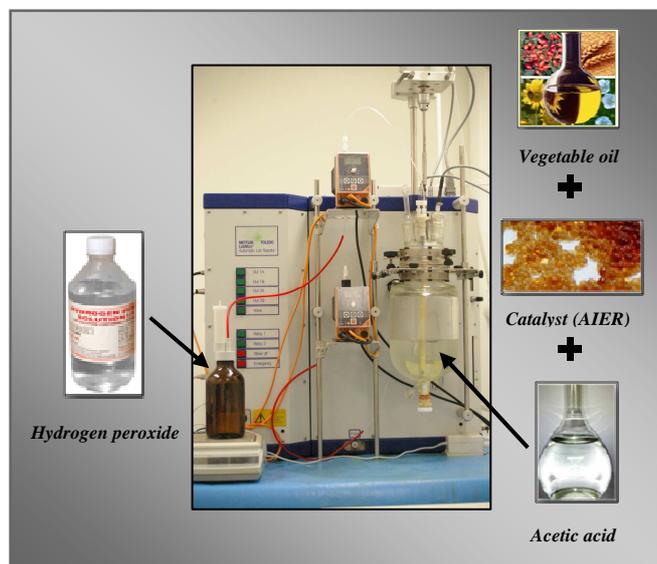


FIGURE 05: Mettler Toledo LabMax reactor as used for epoxidation of hemp oil at CEEFC

The resin was dried using a centrifuge and also by aeration. To remove any remaining water, the resin was further dried with anhydrous sodium sulphate (1:0.15) in an oven at 70 °C for 12 h. The water content after drying using a Sartorius MA-50 moisture analyser was found to be less than 0.3 %. Percentage relative conversion to oxirane and iodine was measured at approximately 88 % and 84 % respectively. FT-IR spectroscopy determined approximately 99 % consumption of C=C.

### 3.3 Specimen preparation

Samples were prepared in an open metal mould using the hand lay-up process. Layers of jute fibre were placed in the mould one on top of another after wetting each layer with resin. A cross section of a sample displaying the jute fibre and resin layers is shown in Fig. 06 below. Resin was distributed by hand over the jute layers. Pressure was then applied in the form of a roller to ensure even resin distribution throughout the four layers of jute fibres.



**FIGURE 06:** Cross section of test specimen showing layers of jute fibre and resin

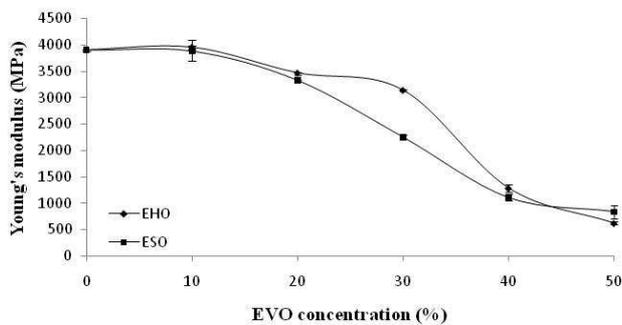
Initial curing at room temperature was performed for a period of 4 hours. The samples were then post cured at 120°C for 4 hours. The moulds were removed and samples for testing were cut using a wet saw and polished using a rotating sander to the required dimensions. Samples were then dried at 80°C for 4 hours.

This entire process was repeated using blends of synthetic epoxy with EHO and ESO ranging from 0-50% EVO content.

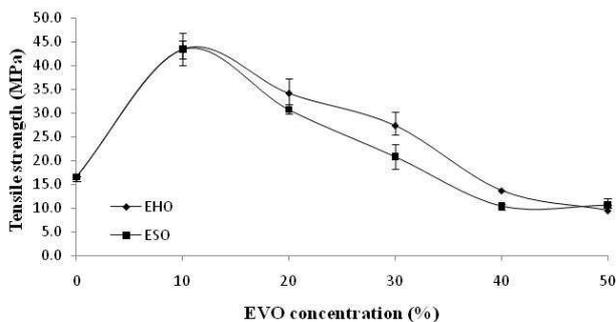
## 4 RESULTS & DISCUSSION

### 4.1 Tensile properties

Tensile tests were conducted to determine the ability of the specimens to withstand uniaxial tensile forces. Young’s modulus and tensile strength were obtained from the tests. Tests were conducted using a MTS Insight 100kN machine with a cross-head speed of 2mm/min in accordance with ISO-527. Specimen dimensions were 250 × 25 × 5 mm. Results are presented in Fig. 07 & 08 below.



**FIGURE 07:** Comparison of Young’s modulus for EHO/epoxy and ESO/epoxy based jute biocomposites



**FIGURE 08:** Comparison of tensile strength for EHO/epoxy and ESO/epoxy based jute biocomposites

The outcome from the tensile testing suggests that both EHO and ESO act as tougheners. EHO and ESO samples displayed similar tensile behaviour up to a concentration of 10%. Samples containing EHO exhibited higher tensile properties than ESO samples throughout the intermediate data range.

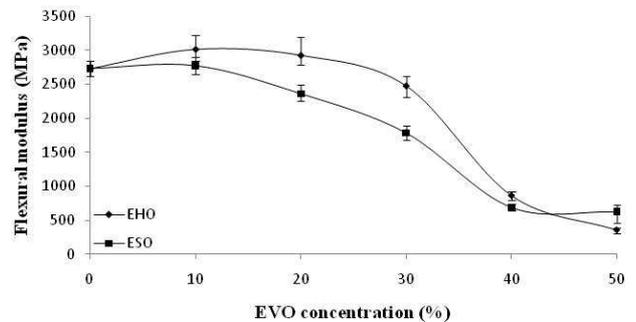
Both EHO and ESO samples showed higher Young’s modulus at a concentration of 10% than the synthetic epoxy resin. Tensile strength for EHO and ESO samples up to a concentration of 30% was greater than the synthetic epoxy. This increase in tensile performance is attributed to enhanced fibre-matrix adhesion due to interactions associated with EHO/ESO and jute fibre. Further investigation into fibre-matrix adhesion to confirm this is required.

Overall EHO outperforms ESO in tensile properties due to its unique fatty acid profile which consists of a higher PUFA content compared to ESO.

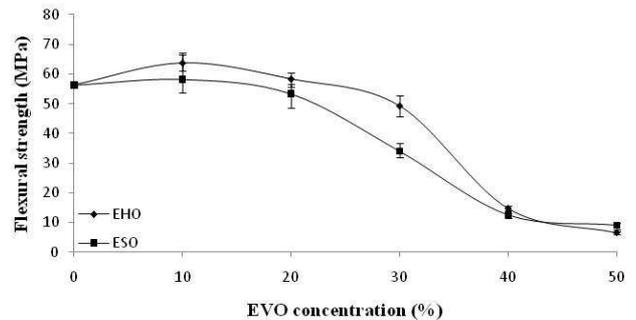
### 4.2 Flexural properties

Flexural testing was conducted to measure the behaviour of biocomposite specimens subjected to 3-point simple beam loading. The matrix has a greater influence on the flexural properties than tensile due to the fibres not being in the direction of the applied force. Therefore it is an important test when characterising the mechanical properties of resins and bioresins.

Flexural properties were measured using a MTS Alliance RT/10 machine in accordance with ISO 14125:1998(E) with a cross head speed of 2mm/min and a span depth ratio of 16:1. Results are presented in Fig. 09 & 10 below.



**FIGURE 09:** Comparison of flexural modulus for EHO/epoxy and ESO/epoxy based jute biocomposites



**FIGURE 10:** Comparison of flexural strength for EHO/epoxy and ESO/epoxy based jute biocomposites

Flexural strength ( $\sigma_f$ ) and flexural modulus ( $E_f$ ) were calculated from (1) and (2) respectively:

$$\sigma_f = \frac{3PL}{2wt^2} \quad (1)$$

$$E_f = \frac{PL^3}{4wt^3y} \quad (2)$$

Where P is the applied load, L is the support span length, w and t are the width and thickness of the test specimen respectively and y is the deflection located at the centre of the specimen.

EHO shows a greater flexural modulus than synthetic epoxy up until a concentration of 30%. In comparison ESO shows a higher flexural modulus than synthetic epoxy up until a concentration of 10%. A similar trend is observed for flexural strength. As for the tensile data the reason for this behaviour is attributed to enhanced fibre-matrix adhesion due to interactions associated with EHO/ESO and jute fibre.

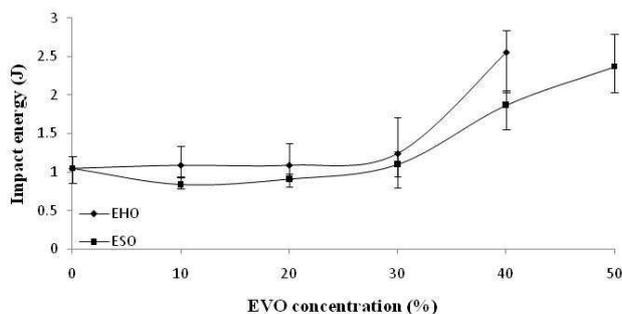
These results can be attributed to the higher crosslink density of EHO in comparison with ESO. The higher levels of PUFA in EHO compared with ESO provide more active sites for crosslinking thereby resulting in superior mechanical performance.

#### 4.3 Impact properties

Charpy impact properties of laminates were determined using ISO 179-1 test method with a falling weight of 3.91kg on an Instron Dynatup M14-15162. Results are presented in Fig. 11 below.

The results indicate that impact energy increased for both EHO and ESO samples over the synthetic epoxy resin. This behaviour is attributed to the EVO containing long fatty acid chains which tend to add flexibility to the matrix thereby increasing the energy required to break the biocomposite samples.

Although impact behaviour was similar, EHO samples displayed higher absorbed impact energy compared to ESO samples. This phenomenon is unexpected as EHO should theoretically have lower impact strength than ESO because of its higher crosslink density. Observing Fig. 11 it is conceivable to conclude that the high scatter throughout the testing data may have compromised the outcomes. As this is a preliminary study this will be re-examined in due course.



**FIGURE 11: Comparison of impact strength for EHO/epoxy and ESO/epoxy based jute biocomposites**

## 5 CONCLUSIONS

EHO was produced through *in situ* epoxidation and was applied in the manufacture of jute fibre reinforced biocomposites. Comparisons of EHO with commercial ESO based biocomposites was performed in terms of tensile, flexural and impact properties. Increasing the EHO and ESO content above 10% in the epoxy blend matrix resulted in a reduction of mechanical performance.

When compared with the synthetic biocomposite samples EHO based samples up to a concentration of 30% EHO and ESO samples up to a concentration of 10-20% ESO performed comparably. This comparable mechanical behaviour is attributed to enhanced fibre-matrix adhesion of EHO/ESO and the jute fibres. However further investigation into the fibre-matrix adhesion through scanning electron microscopy (SEM) and interlaminar shear testing is required for confirmation of this phenomena.

Overall the results of this preliminary research indicate that EHO is an excellent bioresin candidate for use in biocomposites, with mechanical properties being comparable to commercial synthetic epoxy resin (up to 30% EHO content) and superior to commercial ESO across the data range. The higher crosslink density of EHO due to higher levels of PUFA compared with ESO provides more active sites for crosslinking thereby resulting in overall superior mechanical performance.

## 6 ACKNOWLEDGEMENTS

The authors acknowledge the assistance provided by Ms. Karola Lorenz in the manufacturing of samples and Mr. Martin Geach for the procurement of the required resources. The first author would like to thank the Queensland State Government for providing a Smart Futures PhD Scholarship to make this research possible.

## 7 REFERENCES

- Benaniba, M.T., Belhaneche-Bensemra, N. & Gelbard, G. (2008). Epoxidation of sunflower oil with peroxyacetic acid in presence of ion exchange resin by various processes. *Energy Education Science and Technology*, 21(2), 71-82.
- Callaway, J. (2004). Hempseed as a nutritional resource: An overview. *Euphytica*, 140(1), 65-72.
- Chandrashekhara, K., Sundaraman, S., Flanigan, V., & Kapila, S. (2005). Affordable composites using renewable materials. *Materials Science and Engineering: A*, 412(1-2), 2-6.
- Ecofibre Industries Ltd. (2010). *Hemp Seed Oil*. Retrieved February 19, 2010, from <http://www.ecofibre.com.au/hemp-seed-oil>
- Espinoza-Pérez, J., Wiesenborn, D., Ulven, C., Haagenon, D., & Brudvik, R. (2009). Epoxy resins from high-oleic oils applied to composites. In *Proceedings of the 2009 ASABE Annual International Meeting*. Reno, Nevada: American Society of Agricultural and Biological Engineers.
- Hu, R., & Lim, J.-K. (2007). Fabrication and mechanical properties of completely biodegradable hemp fiber reinforced polylactic acid composites. *Journal of Composite Materials*, 41(13), 1655-1669.
- International Organization for Standardization. (2010) *Plastics – Determination of Charpy impact properties – Part 1: Non-instrumented impact test (ISO 179-1)*. Geneva: Switzerland: International Organization for Standardization.
- International Organization for Standardization. (2009) *Plastics – Determination of tensile properties (ISO 527:2009)*. Geneva: Switzerland: International Organization for Standardization.

- International Organization for Standardization. (1998) *Fibre-reinforced plastic composites – Determination of flexural properties* (ISO 14125:1998). Geneva: Switzerland: International Organization for Standardization.
- Meier, M., Metzger, J., & Schubert, U. (2007). Plant oil renewable resources as green alternatives in polymer science. *Chemical Society Reviews*, 36, 1788-1802.
- Miyagawa, H., Mohanty, A., Misra, M., & Drzal, L. (2004). Thermo-physical and impact properties of epoxy containing epoxidized linseed oil - Amine-cured epoxy, *Macromolecular Materials and Engineering*, 289(7), 636-641.
- Miyagawa, H., Misra, M., Drzal, L., & Mohanty, A. (2005). Fracture toughness and impact strength of anhydride-cured biobased epoxy. *Polymer Engineering & Science*, 45(4), 487-495.
- Morye, S., & Wool, R. (2005). Mechanical properties of glass/flax hybrid composites based on a novel modified soybean oil matrix material. *Polymer Composites*, 26(4), 407-416.
- Wool, R., & Sun, X. (2005). *Bio-based polymers and composites* (1st ed.). Oxford, U.K.: Academic.
- Zhu, J., Chandrashekhara, K., Flanigan, V., & Kapila, S. (2004). Manufacturing and mechanical properties of soy-based composites using pultrusion. *Composites Part A: Applied Science and Manufacturing*, 35(1), 95-101.