

Interpenetrating Polymer Network (IPN) with Epoxidized and Acrylated Bioresins and their Composites with Glass and Jute Fibres

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Epoxidized (EHO) and acrylated (AEHO) bio-resins from hemp oil were synthesized, and their interpenetrating networks (IPNs) were investigated in reinforced bio-composites with natural jute fibres and glass fibres. The mechanical properties (tensile, flexural, Charpy impact, and inter-laminar shear) and viscoelastic properties (glass transition temperature, storage modulus, and crosslink density) of the bio-resins and their hybrid IPNs EHO/AEHO system were investigated as a function of the level of bio-resin hybridization. The hybrid bio-resins exhibited interpenetrating network (IPN) behaviour. Composites prepared with the synthetic vinyl ester (VE) and epoxy resins showed superior mechanical and viscoelastic properties compared with their bio-resins and IPNs-based counterparts. With glass fibre (GF) reinforcement, increases in the EHO content of the IPNs resulted in increased stiffness of the composites, while the strength, inter-laminar shear strength (ILSS), and impact resistance decreased. However, in the jute fibre reinforced bio-composites, increases in AEHO content generated increased tensile modulus, ILSS, and mechanical strength of the bio-materials. Crosslink density and glass transition temperature (T_g) were also higher for the synthetic resins than for the bio-resins. Increased AEHO content of the IPNs resulted in improved viscoelastic properties.

Keywords: Bio-resins; Epoxy; Vinyl ester; EHO; AEHO; IPN; Impact strength; DMA; FTIR

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INTRODUCTION

Increasing environmental awareness is driving the research and development of environmentally friendly materials, specifically bio-resins and bio-composites based on renewable natural resources. Interpenetrating polymer networks (IPNs) simultaneously or sequentially combine two or more intertwined polymer chains *via* independent curing reactions of the blend constituents (Sperling 1981). The proper combination and interpenetration of polymer networks enhances mechanical properties that are difficult to achieve solely by the individual polymer components. IPNs exhibit varying degrees of phase separation, depending on the compatibility of the component polymers (Sperling *et al.* 1972; Frisch *et al.* 1975; Xiao *et al.* 1984), but the mechanical properties of the IPN blends can be much better than the constituent polymers (Sperling *et al.* 1969; Klempner *et al.* 1970).

Bio-resins synthesized from vegetable oils are alternatives to synthetic petro-chemical resins (Morye and Wool 2005; Wool and Sun 2015). The synthesis, characterisation, and industrial applications of epoxidized vegetable oil-based bio-resins (EVO) have been investigated (Khot *et al.* 2001; O'Donnell *et al.* 2004; Park *et al.* 2004; Hong and Wool 2005; Czub 2006; Dweib *et al.* 2006). Most research has focused on soybean and canola oils, which are traditionally used in food production and also linseed oil, which is used as drying oil. Because there is a fundamental conflict between their traditional applications of those oils and the new application as industrial bio-resins, bio-resins must be developed from other fast growing, non-food oil crops. There are numerous diverse fatty acid profiles from non-food vegetable oils, for example, hemp oils, which are promising feedstocks for bio-resin production. Hemp oil is a by-product of hemp fibre production, and its main uses are in livestock food and pharmaceutical applications. Its unique fatty acid profile is high in both linoleic and linolenic acid.

Fibre-reinforced polymer composites have extensive applications in the automotive, aerospace, and wind energy industries because of their high specific strength, high modulus, and their relative light weight compared with metals (Li *et al.* 2000). Recently, the composite industry has developed environmentally friendly bio-composites that use natural fibers as reinforcements. The increasing cost of glass, carbon, and aramid fibres, as well as their lack of biodegradability and the generally negative environmental impact of synthetic fibers, have driven this change. Natural fibres have additional advantages over synthetic fibers including good acoustic properties, low density, non-abrasiveness, and lower processing cost (Joshi *et al.* 2004).

In recent years it has been recognized that the formation of an interpenetrating polymer network (IPN) in thermosets results in improved properties, particularly in toughness. Identified conditions for IPN formation with thermoset resins are that the curing reactions of their components do not interfere with each other and that their relative amount is proportionally balanced with a phase ratio close or equal to 1:1. IPN-structured thermosets with Epoxy (EP) resins have been synthesized by the simultaneous reaction with *in-situ* formed polyurethanes (PU) (Harani *et al.* 1998; Chern *et al.* 1999; Park and Jin 2001; Hsieh *et al.* 2001); unsaturated polyester (UP) resins and PU (Meyer and Mehrenberger 1977 and Chen and Chen 2006); aliphatic acrylates (Vabrik *et al.* 1998; Chakrabarty *et al.* 1998; Hua and Hu 1999; Sands *et al.* 2001), and with vinyl ester (VE) (Lin *et al.* 1999; Dean *et al.* 2001b,c; Ivankovic *et al.* 2002). Most of the cited studies were focused on improving viscoelastic and mechanical properties.

As a result of the formation of compatible chemical networks between the components the thermosetting IPN resins may exhibit outstanding durability. Styrene cross-linkable vinyl ester (VE) and amine cross-linkable epoxy (EP) resins have mechanical and rheological properties that can be tailored to a broad range of applications (Ahn *et al.* 1999; Dean *et al.* 2001a,b). To achieve optimum toughness, the aromatic backbone (bis-GMA type) of VE should be combined with aliphatic or cycloaliphatic EPs (Kalachandra *et al.* 1993; Feilzer and Dauvillier 2003). Epoxy resins are widely used as matrix materials in thermoset composites (Lubin 1982), and even epoxy-sized fibres (GF and CF) are popular products. In contrast, VE resins have fibre-matrix adhesion problems that limit their use (Czigany *et al.* 2005). Therefore, VE/epoxy resin blends are advantageous and effective in improving the interfacial matrix-fibre adhesion properties of composites. Atomic force microscopy (AFM) demonstrated that VE/epoxy hybrid resins form IPNs (Karger-Kocsis *et al.* 2003; Gryshchuk *et al.* 2004).

Hemp (*Cannabis sativa* L.) is an annual herbaceous plant that is grown agriculturally for its fibre and oil. Hempseed, in addition to its nutritional value, has demonstrated positive health benefits, including the lowering of cholesterol and high blood pressure (Jones 1995). It has been consumed in food and folk medicinal preparations, or employed as a feed. The highly polyunsaturated oil of hempseed has been used for printer's ink, wood preservative, and also for detergents and soaps. Hempseed oil has been suggested to be perfectly balanced in regards to the ratio (3:1) of the two essential polyunsaturated fatty acids (linoleic and linolenic acids) for human nutrition. In recent years we have investigated the utilization of hemp oil as bio-source for the synthesis of thermoset bio-resins in the form of epoxidized hemp oil (EHO) (Manthey *et al.* 2011; Manthey *et al.* 2013; Francucci *et al.* 2013) and acrylated epoxidized hemp oil (AEHO) (Cardona *et al.* 2013; Francucci *et al.* 2014). However, those pioneering research works on hemp oil-based bio-resins were carried out on each individual bio-resin. In this study thermosetting hemp oil-based bio-resins of epoxidized hemp oil (EHO) and acrylated epoxidized hemp oil (AEHO) were synthesised and used in the preparation of IPNs with different EHO/AEHO ratios and in glass and jute fibre-reinforced bio-composites. The controls were composite panels with synthetic VE and epoxy resin as the matrix and with the GF and jute fibre reinforcements, which were manufactured by the hand lay-up technique. Similar hand lay-up procedures were used in for reinforced panels with EHO, AEHO, and the hybrid IPN bio-resins. Mechanical properties of the bio-composites (tensile, flexural, Charpy impact, and inter-laminar shear strength) and their visco-elastic properties (glass transition temperature, storage modulus, and crosslink density) were investigated. To the best of our knowledge, no previous research has been reported on the investigation of IPNs obtained from hemp oil-based bio-resins and their related composites with synthetic and natural fibres.

EXPERIMENTAL

Materials

Industrial raw hemp oil with a fatty acid profile consisting of palmitic (6.0%), stearic (2.0%), oleic (12.0%), linoleic (57.0%), and linolenic acids (21.0%) was obtained from Ecofibre Ltd. (Toowoomba, Australia). The iodine number of the virgin hemp oil was 165 (g I/100 g oil), and the saponification value was 193.

Analytical grade glacial acetic acid (C₂H₄O₂) and hydrogen peroxide (H₂O₂; 30% in water) were obtained from Sigma-Aldrich (Kuala Lumpur, Malaysia). Amberlite IR-120 of the ionic H⁺ form was obtained from Sigma-Aldrich and was. A heating mantle reactor with a 2.0-L four-necked round-bottom flask, equipped with a mechanical 'anchor' stirrer and thermometer, was used for the epoxidation procedure.

Woven jute fibre (90°/0°, 550 g/m²) was used as the natural fibre reinforcement. The fibre was cut to the mould size, washed with warm water to remove dust, and dried for 12 h at 110 °C. No chemical treatments were performed. E-glass fibre mats (plain weave, 450 g/m²) were obtained from Brazen Composites Sdn. Bhd. (Melaka, Malaysia). Alchemix EP 504 epoxy resin (Alchemie Ltd., Warwick, UK) had an EEW of approximately 195. The epoxy hardeners were isophorone diamine (IPD), AHEW (42.6), triethyl-ethylene-tetramine (TETA), and AHEW (24), from ATL-composites (Shenzhen Lianhai Coatings Ltd., China). The IPD and TETA hardeners were mixed by weight (25%/75%); the curing time at room temperature was approximately 45 min.

Epoxidation of Hemp Oil

EHO was synthesised via *in situ* epoxidation as previously reported (Fig. 1; Petrovic *et al.* 2002; Goud *et al.* 2006, 2007; Cai *et al.* 2008; Dinda *et al.* 2008; Mungroo *et al.* 2008; Goud *et al.* 2010; Manthey *et al.* 2011; Carbonell-Verdu *et al.* 2015). Hemp oil (156 g, 1 mol), acetic acid (40 g, 0.67 mol), and Amberlite IR-120 (23.4 g, 15% by weight of hemp oil) were mixed thoroughly for 30 min from room temperature to 40 °C. Once the temperature reached 40 °C, hydrogen peroxide (113.4 g, 1 mol) was slowly added over 1 h. The stirring speed and temperature were increased to 120 rpm and 70 °C, respectively, and maintained for 8 h. After the epoxidation reaction, the solution was washed with water three times (cool, hot, and cool) to remove residual peroxy-acetic acid and then filtered to remove the Amberlite IR-120 catalyst. The oxirane oxygen content was determined by titration as 8.1%. EHO bio-resin viscosity was measured at room temperature (25 °C) using a DV-II+ viscometer (Brookfield, Harlow, UK). Its viscosity was 840 cP, and the viscosity of the synthetic Alchemix EP 504 epoxy was 1050 cP.

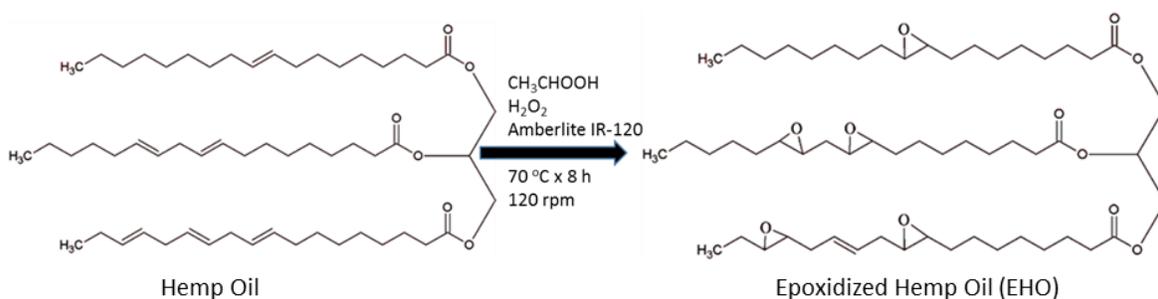


Fig. 1. *In situ* epoxidation of hemp oil

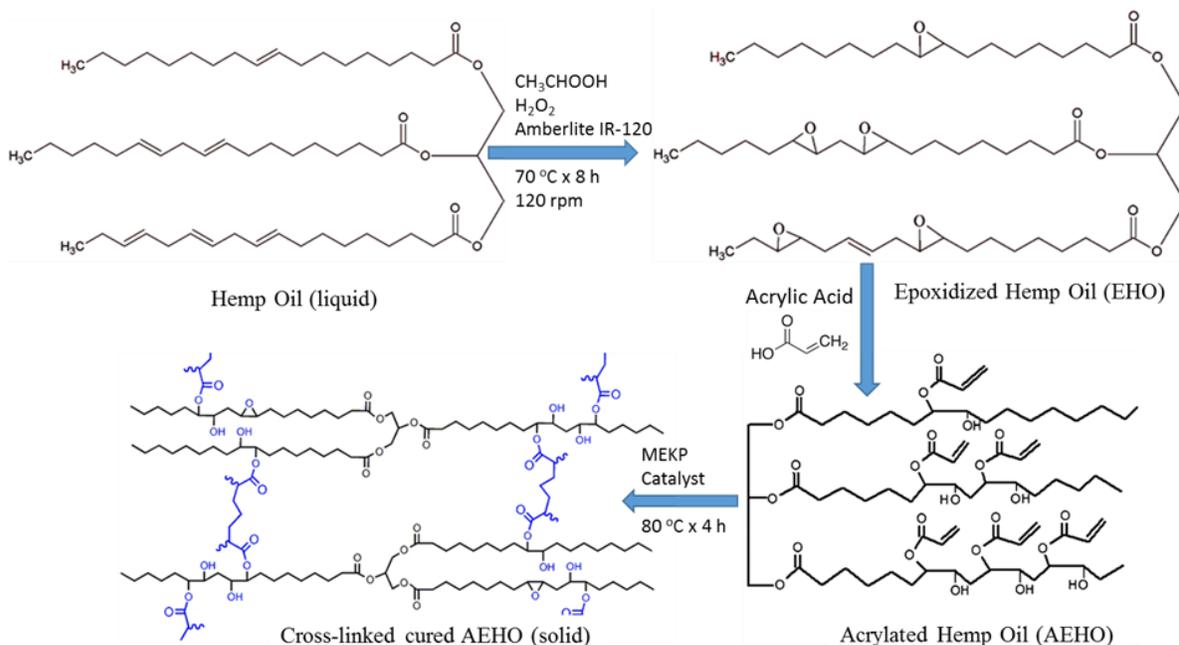


Fig. 2. Acrylation of hemp oil (AEHO)

Acrylation of EHO Bio-resin

AEHO bio-resin was synthesised from EHO bio-resin as previously reported (Fig. 2; Cardona *et al.* 2013; Francucci *et al.* 2014); it contained 4.0 acrylate and hydroxyl groups per triglyceride unit. Vinyl ester resin Atlac-580 (CFS Fibreglass Ltd, Cornwall, UK) was used for the control samples. For the AEHO bio-resin, the styrene co-monomer was supplied by Fischer Scientific (Loughborough, UK), and the Promoter N2-51P was sourced from Axon Nobel Ltd. (Oxfordshire, UK). A 40% Methyl ethyl Ketone Peroxide (MEKP) catalyst was used for curing (CFS Fibreglass Ltd, Cornwall, UK). The styrene co-monomer, promoter, and catalyst were all used as received. Styrene monomer (33 wt.%) was added to the AEHO bio-resin to decrease viscosity and normalize the styrene content to the synthetic VE resin. Blends of AEHO and synthetic VE (50/50 % by weight) were prepared, and AEHO/VE and VE resin bio-composites were manufactured with bidirectional woven jute fabric (90°/0°, 550 g/m²) and GF, following the same procedure as the EHO epoxy bio-resin. The promoter was added (0.25 wt.%) to VE/AEHO blends and thoroughly mixed. Subsequently, the MEKP catalyst was added (3.0 wt.%) and stirred continuously for 5 min. The blended resins were degassed under a vacuum. Both the VE and the 50/50 by weight VE/AEHO were cured following a similar procedure. However, for the neat Atlac-580 VE resin, no styrene monomers were added, as the synthetic resin already contained 33 wt.% styrene. The promoter was added (0.25%), and only 2.0% of the MEKP catalyst was used for curing. Testing samples of the acrylated bio-resin and the synthetic VE resin were produced in a waxed glass mould.

Specimen Preparation

The IPNs were prepared by blending EHO/EP and AEHO/VE resins (50/50 by weight) at different ratios also by weight (25/75 of EHO-EP/AEHO-VE: IPN-I; 50/50: IPN-II and 75/25: IPN-III). Therefore, EHO bio-resin was mixed with synthetic Alchemix EP 504 epoxy resin in a 1:1 ratio by weight. The blended resin was mixed with the hardener, degassed, poured into a waxed mould, cured as outlined below, and finally cut to size for the mechanical tests in accordance with the corresponding standards. Two sets of laminate panels were manufactured from the EHO/EP blends, one with four layers of jute fibre mats and the second with the glass fibre reinforcement using the hand lay-up process. Control composite samples were prepared using the synthetic epoxy, Alchemix EP 504 resin, and the glass and jute fibre reinforcements. Manufactured panels were 300 × 300 mm with a thickness of approximately 5 mm, and the fibre weight percentages in the laminates were approximately 25% and 55% for jute and glass fibre samples, respectively. Initial curing for both the synthetic composites and bio-composite samples was performed at room temperature for 24 h, followed by post curing at 120 °C for 4 h. The samples were removed from the mould, cut to size, dried at 80 °C for 4 h to remove moisture, and placed in a desiccator. A similar procedure was followed for the preparation of the AEHO-based composites with GF and the bio-composites with jute fibre fabrics. The composites and bio-composite panels were manufactured using the hand lay-up process using 4 layers of bidirectional E-glass fibre and woven jute mat reinforcement. No chemical treatments were performed on the GF or on the natural fibres. The manufacture of the composite panels was performed immediately upon removing the fibre from the oven to prevent atmospheric moisture absorption, which could affect the final mechanical properties. For each of the epoxy and the VE-based systems, three different sets of composite (with GF) samples and bio-composites (with jute fibre) were prepared; in the particular case of epoxy and jute fibre: first, EP + jute fibre, secondly 50/50 (EP/EHO) +

jute fibre, and third, EHO + jute fibre-reinforced panels. Manufactured panels were $300 \times 300 \times 5$ mm, with a jute fibre weight percentage of approximately 25%. A flat metal plate was placed on top of the composite sample to improve the surface finish and to ensure a consistent thickness. Two sets of IPNs samples, IPN-I to IPN-III, with the EHO and AEHO bio-resins and with GF and jute fibre reinforcement, were prepared following a similar procedure. Initial curing for both neat bio-resins and bio-composite samples was performed at room temperature (25 °C) for 24 h, followed by a 4 h post-curing stage at 80 °C for the synthetic resins and at 120 °C for the bio-resin composites. The samples were removed from the moulds, cut to size, dried at 80 °C for 4 h to ensure the removal of any induced moisture, and then cooled in a desiccator ready for testing.

Mechanical Testing

Tensile tests were conducted on EHO/EP and jute fibre/GF bio-composite samples in accordance with the ISO 527-1 standard (2012). Tests were performed with a cross-head speed of 2 mm/min using an Insight 100 kN machine (MTS, Petaling Jaya, Malaysia). Specimen dimensions were 250×25 mm, with a thickness of around 5 mm.

Flexural testing was conducted to determine the behaviour of the bio-resin and bio-composite samples subjected to 3-point simple beam loading. Bio-resin flexural properties were obtained through 3-point bending tests conducted per the ISO 178 testing standard (2010) using an Alliance RT/10 machine (MTS, Petaling Jaya, Malaysia). A cross head speed of 2 mm/min and a span/depth ratio of 16:1 were used with specimen dimensions of $80 \times 10 \times 4$ mm. Bio-composite flexural properties were measured in accordance with the ISO 14125 standard (1998).

The impact properties of the bio-resins and their IPNs in this study were determined using the ISO 179-1 standard (2010) on an IT-30 Impact Tester from Fuel Instruments Ltd (Kolhapur, India). Charpy impact strength (kJ/m^2) was calculated from Eq. 1,

$$a_{cU} = (W_B / bh) \times 10^3 \quad (1)$$

where a_{cU} , h , b , and W_B are the Charpy impact strength (kJ/m^2), thickness (m), width (m), and the energy at break (J), respectively.

Inter-laminar shear strength (ILSS) examined the effects of the bio-resins on the fibre-matrix interfacial shear strength. Testing was performed per the ISO 14130 testing standard (year) on an MTS Alliance RT/10 10 kN machine (Petaling Jaya, Malaysia) with a crosshead speed of 1.0 mm/min. Five specimens of each sample type were used in each mechanical test, and the results are presented as mean values and the standard deviation.

Dynamic Mechanical Analysis (DMA)

Rectangular specimens ($60 \times 10 \times 4$ mm) were tested in dual cantilever mode on a calibrated TA Instruments Q800 DMA apparatus (New Castle, DE, USA) at a temperature ramp of 3 °C/min over a temperature range of 25 to 180 °C. A frequency of 1.0 Hz with an oscillating displacement of ± 10 μm was used. Storage modulus (E') and $\tan \delta$ were plotted as a function of temperature using Universal Analysis 2000 version 3.9A software (TA Instruments, New Castle, DE, USA). Glass transition temperature (T_g) was calculated as the peak of the $\tan \delta$ curve, and the experimental crosslink density (v_e) was calculated from the modulus of elasticity of rubbers (Eq. 2). The rubber elasticity theory shows that the molecular weight between cross-links (M_c) and cross-link density (V_e) are related to the modulus of elasticity (MOE) of rubbers (Flory 1953; Palmese and McCullough 1992),

$$E = 3RT\rho / M_c = 3RTv_e \quad (2)$$

where E , v_e , R , ρ , and T are the storage modulus in the rubbery plateau region ($T_g + 50$ °C), crosslink density (mol/m^3), gas constant ($8.314 \text{ J}\cdot(\text{K}\cdot\text{mol})^{-1}$), polymer density (g/cc) and the absolute temperature in K, respectively.

Fourier Transform Infrared (FTIR) Analysis

FT-IR spectra were recorded with 4 cm^{-1} resolution and 64 scans on a Nicolet 6700 spectrometer (Thermo Fisher Scientific, Waltham, USA) and OMNIC Series Suite software (Thermo Fisher Scientific), as previously reported (Yoke *et al.* 1994).

Scanning Electron Microscopy (SEM)

Cross-section morphologies of the bio-composite samples were investigated using a JSM 6460 LV microscope (JEOL, Hsin-Chu, Taiwan). The exposed surfaces were coated with gold, and the samples were scanned at room temperature with an accelerating voltage of 15 kV.

RESULTS AND DISCUSSION

Mechanical Properties

Mechanical testing of the synthetic resin-based and the bio-resin-based composite samples showed that laminates with glass fibres (Figs. 3-5, “a” panels) had greater values than bio-composites with jute fibre reinforcements (“b” panels). This effect was attributed to the superior mechanical properties of the synthetic E-glass fibres (see Table 1). The tensile and flexural strength and modulus of the laminates manufactured with the EP and VE neat resins were superior to EHO- and AEHO-based bio-resins and IPNs systems, which confirms the superior mechanical and physical properties of the synthetic resins (Cardona *et al.* 2013; Francucci *et al.* 2013). Specifically, neat EP and VE resin samples exhibited approximately 2.0 to 2.5 times the flexural strength of EHO- and AEHO-based samples.

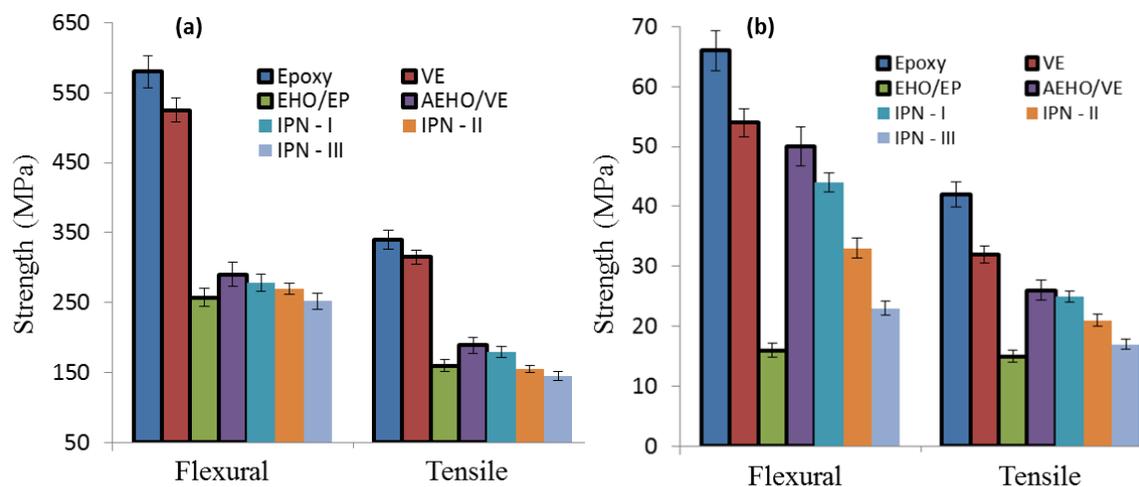


Fig. 3. Flexural and tensile strength of composites with neat synthetic resins, bio-resins, and IPNs with glass fibre (a) and jute fibre reinforcements (b)

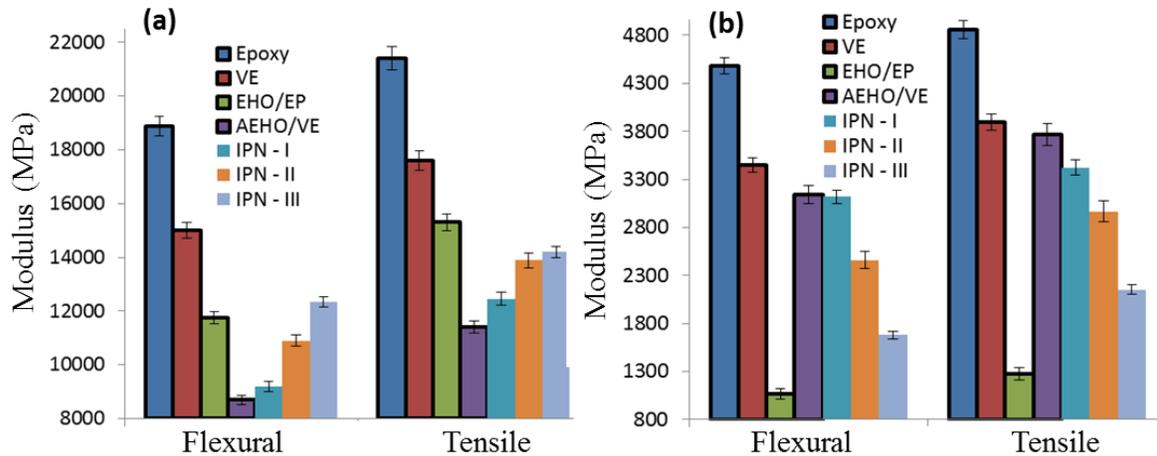


Fig. 4. Flexural and tensile modulus of composites with neat synthetic resins, bio-resins, and IPNs with glass fibre (a) and jute fibre reinforcements (b)

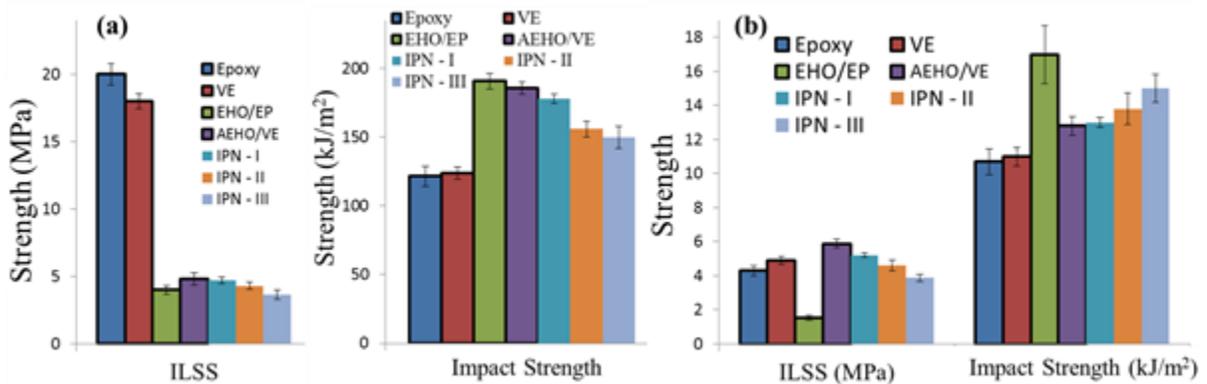


Fig. 5. Inter-laminar shear strength (ILSS) and impact strength of composites with neat synthetic resins, bio-resins, and IPNs with glass fibre (a) and jute fibre reinforcements (b)

The greater strength was attributed to the long fatty acid chains of the EHO and AEHO bio-resins, which decrease the crosslink density and induce high flexibility in the matrix. Additionally, bio-composites with the IPN hybrid bio-resins and jute fibre reinforcement achieved higher impact strength with increasing bio-acrylated content (AEHO), as shown in Fig. 5(b). The synthetic VE and EP resins displayed higher ILSS than the EHO and AEHO bio-resins and associated IPNs for the laminates with glass fibre reinforcement. For the bio-composites with jute fibre, the opposite behaviour was observed, with the bio-resins EHO, AEHO, and IPNs having higher ILSS values than the samples with the synthetic EP and VE resins. Bio-resins and IPNs enhanced the impact resistance of the composites (with GF) and bio-composite panels compared with panels manufactured with the synthetic EP and VE resins (Fig. 5). These results indicated better inter-laminar shear and impact strength for the bio-resin-based materials, which was confirmed by SEM analysis; the EHO- and AEHO-based samples exhibited improved fibre-matrix interfacial adhesion (Figs. 6 and 7). The enhanced fibre-matrix adhesion in the acrylated-based bio-composites can be attributed to better surface chemical compatibility between the natural fibres and the acrylated bio-resin, specifically the greater quantity of hydroxyl groups present in the AEHO bio-resin compared with VE.

Jute fibre increased the flexural strength and flexural modulus for the AEHO-based laminates compared with the EHO bio-resin samples. This effect was attributed to the best

curing performance and the highest crosslink density of AEHO, which contained 30% styrene monomers; EHO was found to be unreactive and contained mid-chain epoxy groups in the aliphatic chains that were not accessible for crosslinking with the epoxy amine hardeners. In the bio-composite laminates the volume fraction of the jute reinforcing fibre was lower than the critical quantity, and therefore the composites strength could not have been significantly improved by the addition of more fibres (Fu *et al.* 2009). This effect is associated with the poor ability of stress transfer between the matrix and the fibres, in the presence of low fibre volume fraction within the composites (Fu *et al.* 2009). The reduction of tensile strength and modulus has been previously observed in banana fibre-reinforced polyester composites, which lost up to 10% of the fibre weight content compared to those with neat resin (Pothan *et al.* 1997). In addition, Elbadry and colleagues (2012) found that the tensile strength of jute/UPE resin composites was lower than that of the neat resin for fibre weight contents of only 14%; increasing the fibre content over 22% increased the tensile strength and Young's modulus.

In previous investigations, acrylated soybean oils (AESO) were blended with VE in different proportions, and the properties of the hybrid system were examined (Grishchuk and Karger-Kocsis 2010). The neat VE displayed a flexural modulus and strength of 3210 and 123 MPa, respectively. Reductions in flexural properties were observed with increased AESO concentration, in a similar fashion to the results obtained in this study for the IPNs with jute fibre reinforcement. In this study, styrene was not added to AESO. A USA patent awarded to Wool and colleagues (2000) indicated a flexural modulus of AESO prepared in the ratio 100:45:5 (AESO: styrene: divinyl benzene) equal to 723 MPa. In comparison, the AEHO bio-resin reported in a previous study by other researchers exhibited a flexural modulus of 744 MPa (Cardona *et al.* 2013). An acrylated bio-resin based on linseed oil (AELO) has a reported flexural modulus and strength of 2.31 GPa and 78.73 MPa, respectively (Lu *et al.* 2006). The high level of epoxides per triglyceride in the linseed oil (6.2), resulted in a high number of acrylate groups per triglyceride, approximately 5.7-5.8, thereby resulting in a highly cross-linked network of the cured AELO bio-resin. The results obtained in this study for the jute fibre-reinforced AEHO/VE compared favourably with the mechanical properties reported for the AESO/flax fibre bio-composites system (Williams and Wool 2000). Through the addition of natural fibre reinforcement, in this study the AEHO-based laminates exhibited superior fibre-matrix adhesion compared with the neat synthetic VE resin, as shown in Fig. 5.

Charpy Impact Testing

Both types of bio-resins and their hybrid IPNs increased the impact strength of the bio-composites compared with the synthetic counterparts (Fig. 5). This result reflected the decreased stiffness and better fibre-matrix interface adhesion of the bio-resins. Long fatty acid chains in the vegetable oil triglycerides imparted flexibility to the matrix, thereby increasing the energy required to break the bio-composite laminates. SEM micrographs confirmed the better fibre-matrix adhesion in the bio-resin-based laminates.

Glass fibre (Fig. 5a) displayed similar properties to jute fibres with regard to superior impact strength of the bio-resins in comparison to the synthetic EP- and VE-based laminates (Fig. 5b). The main difference between the two systems was that the impact strength decreased with increasing EHO in GF-reinforced samples, while the opposite occurred in jute fibre-reinforced bio-composites, which resulted in the higher value of the IPN-based jute reinforced samples for IPN-III (25/75 of AEHO/EHO bio-resins).

Inter-Laminar Shear Testing (ILSS)

The laminate samples prepared with the synthetic EP and VE and the GF reinforcement showed higher ILSS values than their EHO, AEHO, and IPN-based counterparts (Fig. 5a). However, the opposite behaviour was observed in jute fibre-reinforced bio-composites. The samples manufactured with synthetic resins had lower ILSS than their bio-resin-based laminate counterparts. These results are similar to previous reports for ESO and epoxidized canola oil (ECO) glass fibre-reinforced composites (Sharma and Kundu 2006; Espinoza-Perez *et al.* 2009). Thus, increasing the bio-resin content above 20% has negative effects on the ILSS of GF-reinforced composites. Notably, for panels with jute fibre, the ILSS was higher for the acrylated bio-resin (AEHO) than for the epoxy-type bio-resin (EHO), with the ILSS value decreasing with increased epoxidized hemp oil content (Fig. 5b).

Fibre-matrix adhesion and interaction were lower for the bio-resin IPN systems than for the synthetic resin-based samples. Composite properties depend on the properties of the reinforcement, matrix, and the matrix/reinforcement interface. Usually, stronger interfaces lead to higher tensile and flexural strength but reduced impact strength because energy-consuming mechanisms during composite fracture, such as fibre pull-out, are inhibited. In this study, IPNs exhibited higher impact strength for both GF- and jute fibre-reinforced composites than for the equivalent synthetic VE and EP resin-based samples (Fig. 5). Therefore, the low ILSS values of the IPN composites were not due to a poor fibre-matrix interface adhesion but were rather a product of the lower strength and modulus of the bio-resins and the jute fibres (Table 1).

Table 1. Mechanical Properties of Jute, E-glass, and Carbon Fibres

| Fibre | Specific Gravity | Young's Modulus (GPa) | Tensile Strength (MPa) | Specific Strength (MPa) | Specific Modulus (GPa) |
|---------|------------------|-----------------------|------------------------|-------------------------|------------------------|
| Jute | 1.46 | 600-1000 | 10-30 | 410-750 | 7-21 |
| E-glass | 2.60 | 2000-3400 | 75 | 1310 | 29 |
| Carbon | 1.40 | 4000 | 235 | 2850 | 168 |

Note: These values were summarized from Shah *et al.* 1981 and Gassan and Bledzki *et al.* 1999.

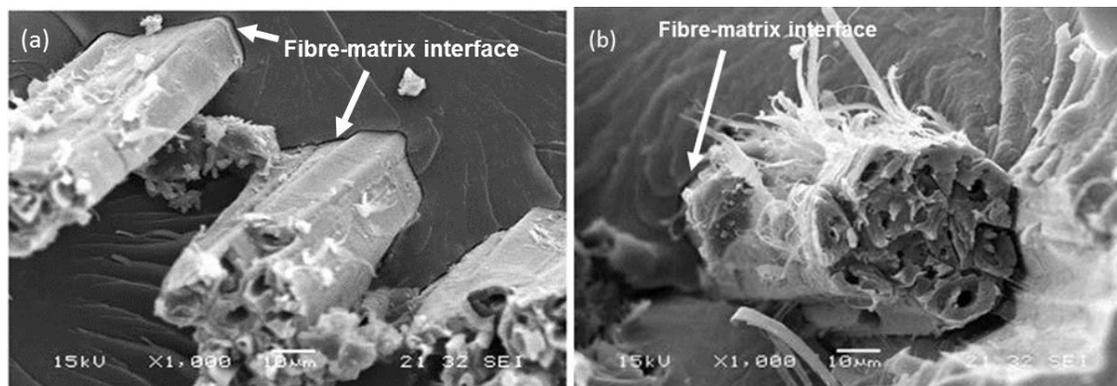


Fig. 6. SEM of jute fibre-reinforced bio-composites with (a) synthetic epoxy resin and (b) 50/50 EHO/EP resins

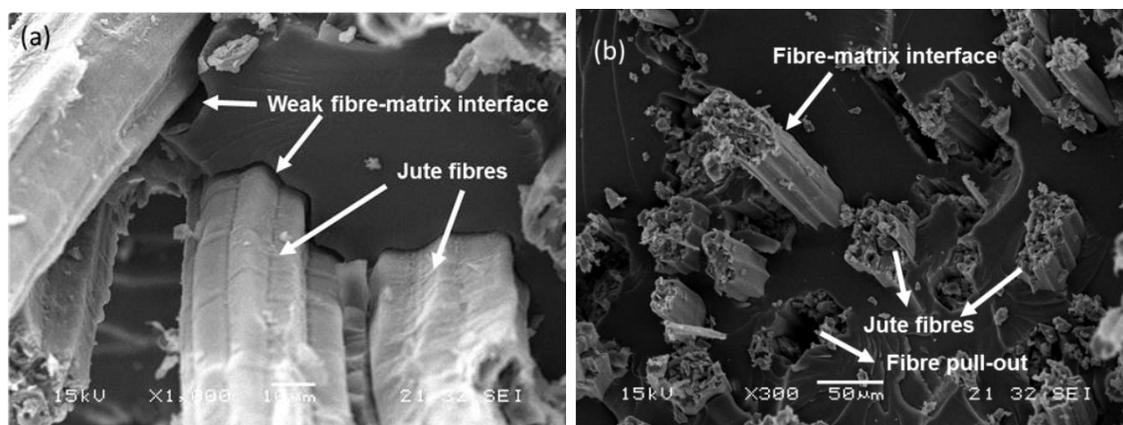


Fig. 7. SEM of jute fibre-reinforced bio-composites with (a) synthetic VE resin and (b) 50/50 AEHO/VE resins

SEM Analysis

The fracture surfaces of the synthetic epoxy, VE, EHO, and the AEHO bio-resin-based jute fibre-reinforced samples were examined by SEM (Figs. 6 and 7). Different magnifications (300X and 1000X) were used to closely examine the fibre-matrix topography at the interface. Fibre pull-out was observed for all samples, and this effect was visible at 300 \times magnification (Fig. 7b). There were gaps in the fibre-matrix interface; this condition was somewhat anticipated because the jute fibre was not chemically treated. The micrograph of the synthetic epoxy and of the EHO/epoxy (50/50) jute-reinforced bio-composite samples (Fig. 6) shows that the jute fibre-matrix interfacial adhesion was relatively poor, but the adhesion was notably improved for the EHO bio-resin sample. Similar fiber-matrix interface characteristics were observed from a synthetic vinyl ester and the AEHO bio-resin-based samples (Fig. 7). Hence, bio-composites with bio-resins matrices demonstrated enhanced fibre-matrix interfacial adhesion.

Table 2. Mechanical Properties of the EHO, AEHO, and IPN Hybrid Bio-Resins

| Composite Material | Storage Modulus at 30 °C (MPa) | T_g (°C) | Crosslink Density (mol/m ³) |
|--------------------|--------------------------------|------------|---|
| Epoxy | 1880 | 106.5 | 3820 |
| VE | 1830 | 102.0 | 6650 |
| EHO/EP (50/50) | 1140 | 76.4 | 1450 |
| AEHO/VE (50/50) | 1310 | 81.2 | 6130 |
| EHO | 320 | 57.0 | 660 |
| AEHO | 560 | 68.0 | 4420 |
| IPN-I | 380 | 78.6 | 4130 |
| IPN-II | 440 | 72.4 | 2850 |
| IPN-III | 385 | 70.8 | 1540 |

Dynamic Mechanical Properties

The viscoelastic behaviour of the AEHO-based bio-resins and bio-composites with jute fibre reinforcement (JF) were examined in terms of the DMA storage modulus and $\tan \delta$ as a function of temperature (Fig. 8). For all of the bio-composite systems, the storage modulus, T_g , and crosslink density decreased with the addition of EHO and AEHO (Table 2). The VE resin-based system displayed the highest viscoelastic properties. Jute fibre

reinforcement improved the storage modulus, ranging from 560 MPa for the AEHO neat bio-resin sample to a maximum of 1830 MPa for the VE synthetic resin sample. This behaviour agreed with the tensile and flexural properties of the bio-composites and IPNs compared with the neat synthetic resins. Within the bio-resin and IPN samples, the AEHO resin displayed the highest flexural and tensile strength, which was attributed to its better viscoelastic properties.

The synthetic epoxy showed the highest T_g value, which was reduced in the EHO-, AEHO-, and IPN-based systems. Fibre reinforcement resulted in a marginal increase in T_g from 102 to 106 °C for the VE system. The EHO- and AEHO-based bio-composites with JF realised an increase in T_g of 25% and 28% from the neat bio-resin samples, respectively. This behaviour reflects the higher storage moduli of the bio-composites compared with the neat bio-resins. Notably, jute fibre-reinforced bio-composites displayed similar crosslink densities, with a data spread of less than 10%. Given the similarity of crosslink densities for the bio-composites, the greater quantity of hydroxyl groups in the AEHO bio-resin compared with the VE contributed to crosslinking. Consequently, there was a greater improvement in crosslink density for the AEHO-based samples compared with the VE samples. In comparison to the crosslink densities found in this research work, Lu and Wool (2006) determined the crosslink density for AELO to be 5030 mol/m³, which is higher than the values for the EHO and AEHO determined in this study. Indeed it is expected that the synthesized AEHO would have a lower crosslink density than AELO because it has less acrylates per triglyceride unit. It has been observed that the crosslink density of AESO resins was influenced by the styrene content (Campanella *et al.* 2009). Moreover, it was observed that the crosslink densities ranged from 3700 to 2100 mol/m³ for AESO samples containing no styrene through to 35 wt.%. In a study to determine the properties of AESO-based material intended to be used in the PCB industry, Zhan and Wool (2010) determined the crosslink density of AESO polymers containing 30 wt.% styrene and 0 to 15 wt.% of divinyl-benzene (DB). This study found that the crosslink densities increase with DB content from 1830 to a maximum of 7130 mol/m³ at 15 wt.% DB. This study showed that the $\tan \delta$ peaks of the EHO- and AEHO-based samples became broader in comparison with the VE and epoxy synthetic resin samples. Similar results were found for the AESO/VE resin systems, as studied by Grishchuk and Karger-Kocsis (2010), who also found that the glass transition temperature (T_g) value of the resin blends decreased with increasing AESO bio-resin content.

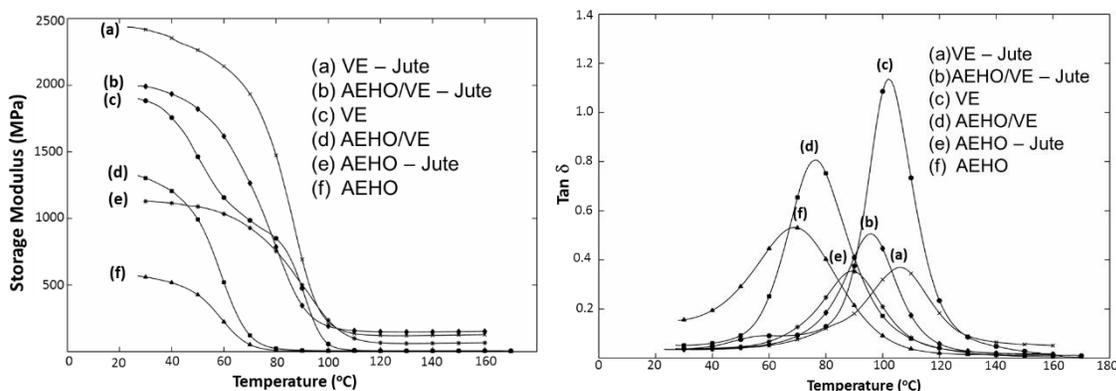


Fig. 8. Storage modulus and $\tan \delta$ values vs. temperature for the acrylated resins, bio-resins, and bio-composites. (a) VE+JF, (b) 50/50 AEHO/VE+JF, (c) VE, (d) AEHO/VE 50/50, (e) AEHO+JF, and (f) AEHO

In this study, no peak doubling was found to occur in the $\tan \delta$ of the DMA analysis of the IPN bio-resin samples or in the EHO/epoxy and AEHO/VE blends, indicating full compatibility between the bio-resins and their synthetic counterpart resins. In comparison, the storage modulus of the neat AEHO sample (Khot *et al.* 2001; Lu and Wool 2006) and the storage moduli of AESO, with 40 wt.% styrene and AELO with 33 wt.% styrene monomer, were determined to be in the order of 1.3 GPa and approximately 2.0 GPa, respectively. Additionally they also reported T_g values of 79 °C for the AESO bio-resin and 105 °C for the AELO neat resin samples, which are higher than the value recorded in this study for the AEHO (68 °C), which is associated with the comparatively better properties of the linseed oil-based bio-resins over the hemp oil based bio-resins.

FTIR Spectroscopy

FTIR spectroscopy has been used to quantify epoxy groups and the percentage consumption of C=C groups in EVO during the epoxidation reaction (Khot *et al.* 2001; Espinoza-Pérez *et al.* 2009). In this study, FTIR was used to identify chemical structures in hemp oil before and after epoxidation and acrylation (Fig. 9).

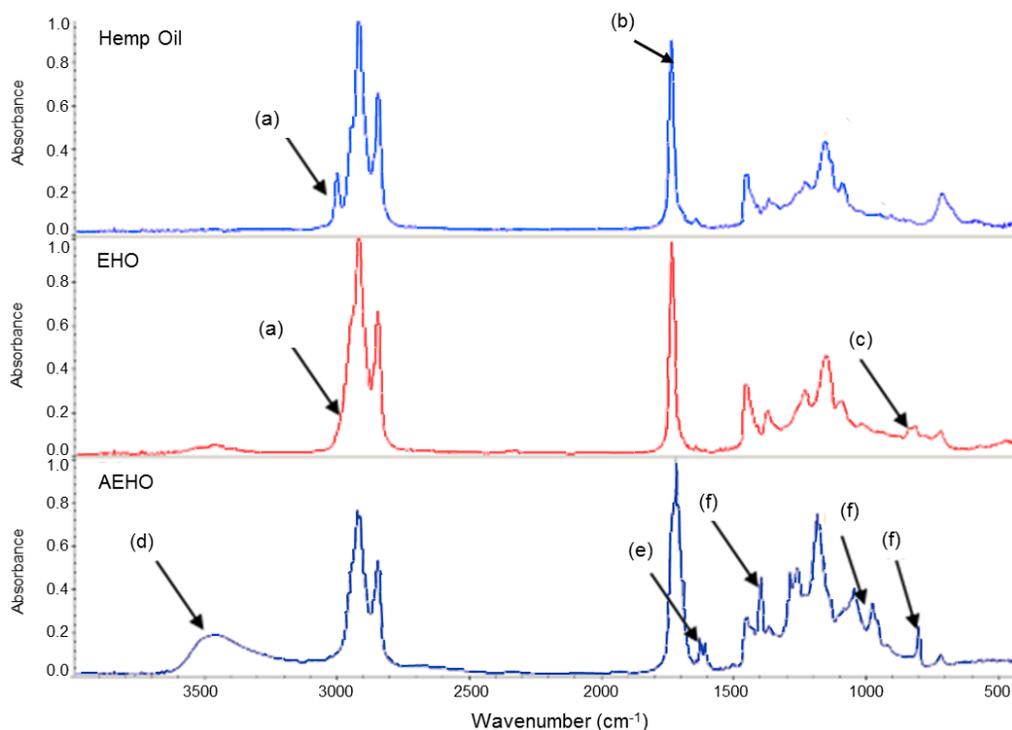


Fig. 9. Infrared spectra of untreated hemp oil (top), epoxidized (middle), and acrylated epoxidized hemp oil (bottom)

In the spectra from hemp oil and the bio-resins, the band at 1741 cm^{-1} signifies C=O stretching of carboxylic group of fatty acids (peak *b*). Peak *a* at wavenumber 3009 cm^{-1} corresponded to the stretching of C=C double bonds, which are consumed during epoxidation and acrylation (Chen *et al.* 2002; Mungroo *et al.* 2008; Espinoza-Pérez *et al.* 2009). Peak *c* at 823 cm^{-1} in the EHO spectrum corresponded to C-O-C stretching in the epoxide ring (Vlcek and Petrovic 2006; Espinoza-Pérez *et al.* 2009; Mustata *et al.* 2011). Together with the disappearance of the peak at 3009 cm^{-1} , this result shows that the hemp oil epoxidation reaction went to completion. The three bands at 1247 , 1196 , and 1169 cm^{-1} signified fatty acid methyl esters, as previously noted in linseed oil-based

epoxidized methyl ester (Martini *et al.* 2009). In the AEHO spectrum, the peak at 3400 to 3800 cm^{-1} (peak *d*) was attributed to the hydroxyl groups formed by the acrylic acid reaction and cleavage of the epoxide groups (La Scala *et al.* 2004; Kahraman *et al.* 2006). Furthermore, the peak visible at 1630 cm^{-1} (peak *e*) represented stretching vibrations of the C=C groups in acrylic acid. In the AEHO spectrum, peaks at 1400, 985, and 810 cm^{-1} (peaks *f*) were associated with the acrylation of EHO and signified the acrylic functional group (Fu *et al.* 2010).

Overall, both EHO and AEHO bio-resin-based composites have lower mechanical and viscoelastic properties than their synthetic resin-based counterparts, which indicates that the bio-resins and their IPN systems are best suited to a plasticizing role rather than complete neat bio-resin matrices, although it was demonstrated that EHO- and AEHO-based samples have higher ILSS and impact strengths than the synthetic epoxy and VE resin-based composites.

CONCLUSIONS

1. EHO and AEHO bio-resins were synthesized from hemp oil, and IPNs were prepared by blending the bio-resins and their synthetic counterparts. Their composition and mechanical properties were investigated.
2. Jute and glass fibres were used as reinforcements in biocomposites using the bio-resins as polymeric matrices. Their thermo-mechanical and viscoelastic properties were determined.
3. Synthetic epoxy and vinyl ester resins and their composites displayed superior thermo-mechanical properties than the bio-resin and IPNs -based samples.
4. Glass fibre reinforcements imparted better mechanical and viscoelastic properties than their jute fibres for both the synthetic and bio-resin-based matrices, including the IPNs bio-resins. Composites with glass fibers and synthetic epoxy resin exhibited the best mechanical and thermal properties of all the samples.
5. In the IPN composites, flexural and tensile strength increased with the AEHO bio-resin content. In glass fibre composites, the flexural and tensile modulus decreased with the AEHO content, while for the bio-composites with jute fibre reinforcement the value of the mechanical modulus decreased with the EHO content in the IPNs.
6. The ILSS was found to increase in the IPN-based materials with increasing AEHO bio-resin content for both, the jute and glass fibre reinforced panels indicating that the jute and glass fibre-matrix interfacial adhesion is stronger for the AEHO-based samples compared with the epoxidized bio-resin-based samples. Also, the ILSS and the impact strength values were higher for the bio-resins and the IPN-based samples than for the synthetic resins. The SEM micrographs confirmed those results by showing a comparative better fibre-matrix interfacial adhesion in the bio-composites with the bio-resins matrices than in the synthetic resin-based composite samples.
7. The VE and epoxy synthetic resins showed higher viscoelastic properties than their bio-resin-based counterparts. VE-based samples were found to have higher T_g , storage modulus and crosslink density values than AEHO-based samples, while the synthetic epoxy resin samples have higher viscoelastic properties than their EHO bio-resin

counterparts. For the bio-resins, the storage modulus, the T_g , and the crosslink density were found to be higher for the AEHO than for the EHO bio-resin. Accordingly, the viscoelastic properties of the IPNs increased with the AEHO bio-resin content.

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