Mechanical properties of bio-epoxy resins and synthetic epoxy resins blends

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Abstract. This paper studies the mechanical properties of bio-epoxy resins blended with synthetic epoxy resins (epoxamite). The bio-epoxy resins were derived from Jatropha methyl esters through epoxidation method. They were formulated with epoxamite and hardener at different compositions and then cured at different temperature and time settings. The cured blends were subjected to tensile and flexural tests using Instron machine. Tensile and flexural strength of the mixtures were compared with the 100% epoxamite in order to evaluate the suitability of bio-epoxy resins as an alternative to synthetic epoxy resins with respect to mechanical properties. Tensile strength of 100% epoxamite is 38.32 MPa and flexural strength is 63.32 MPa. The mixtures of bio-resins and epoxamite demonstrated very low mechanical strengths compared to the 100% epoxamite. Therefore, they are not suitable to be used as an alternative to synthetic epoxy resins in industrial applications. However, they may find other usage due to high reactivity of the bio-epoxy resins.

1. Introduction

In recent years, the formulation of polymers from bio-based materials and sustainable resources has gained attention due to polymers such as epoxy resins are used extensively in engineering and composite materials. However, these resins are synthesized using raw materials derived from non-renewable resources such as petroleum. Various issues associated with these resources in the context of depletion of the reserves and environmental problems have urged the need of an alternative or replacement [1,2].

Bio-epoxy resins derived from plant materials have been synthesized and their properties have been studied to evaluate the suitability for various engineering applications including paints, coating, adhesives, and biomedicine [3]. However, they have a tendency to form aggregates during processing and demonstrates a low resistance to moisture absorption which reduces the compatibility between matrix-fibre compatibility resulted in poor performance of composite material. Alkali treatment was introduced to enhance the compatibility of the composite materials by modifying the structure and the surface properties of the composite materials. Good adhesiveness, rigidity, specific resistance, dimensional stability, chemical resistance and high fluidity prior to curing which allows for an easy processing are some of the properties of epoxy ring that enabled them to be used in mechanical applications [4,5,6]. Matrix components reinforced with fibres formed a composite material. The selection of the material’s composition depends on the desired composite material properties. It is
important that the combined material’s properties have improved compared to matrix or fibre materials alone [7].

Abundant researches have been conducted using synthetic epoxy resins in the formulation of composite materials [8,9,10]. However, with regards to the previous mentioned depletion of non-renewable resources and environmental issues, this research used epoxy resins prepared from fatty acid methyl esters (FAMEs) derived from Jatropha oil which is an interesting natural resource alternative as FAMEs are biodegradable, non-toxic, non-depletable, non-volatile, low cost and available in abundant [11,12]. The utilization of renewable resources is growing rapidly worldwide, and becoming a popular choice for alternatives. This includes Malaysia which is looking forward to achieve 50% utilization of renewable resources such as palm oil by 2025 [13] since palm oil is a major crop in Malaysia. However, it is still regarded as major source of vegetable oil all over the world rather than a fuel. Therefore, utilizing Jatropha oil will not become any issue since it is inedible and toxic for both human and animal consumption [1].

Few studies and experiments have been conducted utilizing epoxidized Jatropha oil in various applications including coating, adhesives, tribology, and polymers [14,15,16]. However, research about FAME or biodiesel in production of bio-epoxy resins is scarce. FAMEs or biodiesels have been used mainly in the automobile industry. The availability of its structure to undergo for chemical modifications has reopened new dimension to oleochemical synthesis, which primarily transforms the double bonds into oxirane ring that produces the bio-epoxy resins. The mechanical properties of bio-epoxy resins which are often evaluated are the tensile and flexural strength. Tensile strength is the ability of a material to resist a force that tends to pull it apart, while flexural strength means the maximum stress in a material just before it yields in a bending test.

This project is relevant to this aim in the exploration of finding alternative and improve awareness on the importance of renewable resources in this country. Previous studies have been done to synthesize epoxy bio-resins from Jatropha oil and evaluate its physical and chemical properties. However, in this study, bio-epoxy resins are synthesized from Jatropha methyl esters (JME). There is limited research on their mechanical properties. Therefore, this research is essential to evaluate their mechanical properties in order to observe their suitability as an alternative to synthetic epoxy resins.

2. Materials and methods

![Figure 1. Process flow diagram](image-url)
The process flow diagram for the production of bio-epoxy resins from Jatropha oil is shown in figure 1. Jatropha seed oil used in this work was purchased from BATC Development Berhad (Bionas) without further purification. Production of Jatropha methyl ester was prepared through transesterification, conducted in a 1000 ml tree-necked flask completed with mechanical stirrer, reflux condenser, and thermometer under atmospheric pressure. Bio-epoxy resins was synthesized using epoxidation method with peroxyacetic acid generated in-situ [17,18].

For the polymerization process, commercial synthetic epoxy resins (epoxamite) and hardener were used. For sample preparation, homogenous mixtures of bio-epoxy resins from this study and epoxamite were prepared in different compositions [19]. A mechanical stirrer was used to mix the composition and stirred about 10 min continuously. Then, the mixture was poured into steel mould plates (230 × 230 × 10 mm) and treated according to the curing conditions set based on the composition’s percentage. Those resins blends were prepared to investigate the properties of the blends and also to evaluate their mechanical properties. The thickness of sample was 5–6 mm to ensure the compatibility with tensile and flexural machine for analysis. After curing was completed, all samples were cut using a vertical cutting machine (Metabo Bas 260 Swift, Germany) equipped with a three-roller guide; therefore, the saw blade is guided optimally and renders high precision cutting results for subsequent analysis.

2.1 Mechanical test
The mechanical properties of sample which are tensile and flexural strength were conducted using universal testing machine.

2.1.1 Tensile. Tensile tests were carried out following ASTM D3039-08 using universal test machine, Instron model 3382 with a load cell of 100 kN and a crosshead rate of 8 mm/min. This simple but reliable machine is originated from North America, and is ideal for tension and/or compression applications. Cured synthetic epoxy resins and bio-epoxy resins were cut in the dimensions of 250 × 25 × 5 mm before being tested using Instron machine. Four specimens of each sample type were used in each test. The dimensions of samples were programmed into the machine’s computer and then, the sample was positioned vertically and the grip was tightened at the top before being lowered down slowly. Subsequently, the lower grip was tightened firmly to prevent any slippage. The value of crosshead was entered and load was applied to the sample. The testing of the sample was prolonged until the sample broke. The procedure was repeated for other samples as well. The values of tensile strength and modulus were obtained and analysed accordingly.

2.1.2 Flexural. With regards to flexural tests, a universal test machine, Instron model 30 K with a load cell of 500 N was used as suggested by ASTM D790-10. A span:depth ratio of 16:1 were used with specimen dimensions 220 × 20 × 5 mm. The sample was mounted on two supports and loaded with crosshead speed of 8 mm/min. The test was prolonged until the sample broke. The procedure was repeated for other samples as well, and the values of flexural strength were obtained and analysed accordingly.

3. Results and discussion
In order to investigate the mechanical properties of bio-epoxy resins/synthetic epoxy resins (epoxamite) blends, five samples were prepared in different blend compositions as shown in figure 2, with curing temperature and time for each composition shown in table 1. Increasing the percentage of synthetic epoxy resins will require the increase of curing temperature and time. Bio-epoxy resins are expected to have lower performance compared to synthetic epoxy resins. The polymerization of bio-epoxy resins with hardener is slower, hence requiring higher temperature and longer curing time [19].
Figure 2. Percentage compositions five samples of bio-epoxy resins/epoxamite blends

The mechanical strength of epoxamite blended with bio-epoxy resins was investigated by the measurement of tensile and flexural strength. Data for Samples 4 (75–25% bio-epoxy resins/epoxamite) and 5 (100% bio-epoxy resins) were unable to be obtained because the blends failed to crosslink and polymerization attempt resulted in high viscosity of liquid, even after curing. This could be due to the non-reacted hardener with the epoxides in the composition [19]. In order to undergo the tensile and flexural tests, the sample must be in solid form. Hence, Samples 4 and 5 were unable to be tested. As demonstrated in table 1, only data for Samples 1, 2, and 3 were obtained and discussed in further sections. [20] stated that tensile strength is taken as the stress value at the maximum of the nominal stress–strain curve. The ductility is expressed as percentage of total elongation at fracture. The average values for tensile strength and tensile modulus measurements are reported in table 2. The value obtained is in MPa.

Table 1. Curing temperature and time of bio-epoxy resins and synthetic resins blends

| Samples  | Curing conditions |
|----------|-------------------|
| Sample 1 | 24hr RT + 3hr (60 °C) + 3hr (80 °C) |
| Sample 2 | 24hr RT + 3hr (60 °C) + 3hr (80 °C) |
| Sample 3 | 24hr RT + 4hr (80 °C) + 4hr (120 °C) |
| Sample 4 | 24hr RT + 4hr (80 °C) + 8hr (120 °C) |
| Sample 5 | 24hr RT + 4hr (80 °C) + 12hr (120 °C) |

3.1 Tensile

Tensile strength and modulus of blends for Samples 1, 2, and 3 are shown in table 2. Clearly, at 100% epoxamite composition (Sample 1), it had the highest values for tensile strength and tensile modulus with 38.32±3.16 MPa and 751.00±96.45 MPa, respectively. These values correlated with the strain-stress curve depicted in figure 3. An object or medium under stress becomes deformed and the quantity that describes this deformation is called strain. Strain is given as a fractional change in either length of the sample. Hence, it is a dimensionless number. The relationship of stress and strain is proportional as can be seen in the figure below; the greater the stress, the higher the strain.
From figure 3, it can be seen that Sample 1 has the lowest strain of 6% which indicated that the molecules in the cured resins are high in the interatomic bonding that is due to the formation of three-dimensional network and the strong chains making the material hard and tough [19]. Thus, it led to the difficulty of the sample to absorb stress which resulting a high value of tensile strength and tensile modulus. These results also explained the physical state of Sample 1 which was rigid and hard to bend by hand. These findings also conformed with the previous study which mentioned that rigid structure or the highly crosslinking density contributed to the high mechanical strength of [21]. Sample 2 (25–75% bio-epoxy resins/epoxamite) had tensile strength and tensile modulus of 2.42±1.2 MPa and 6.00±1.5 MPa, respectively, and the failure strain of Sample 2 was at 80% as depicted in figure 4.

Table 2. Tensile strength and tensile modulus

| Sample | Bio-epoxy resins/epoxamite (%) | Tensile strength (MPa) | Tensile modulus (MPa) |
|--------|--------------------------------|------------------------|-----------------------|
| 1      | 0/100                          | 38.32±3.16             | 751.00±96.45          |
| 2      | 25/75                          | 2.42±1.2               | 6.00±1.5              |
| 3      | 50/50                          | 0.49±0.24              | 0.75±0.34             |

**Figure 3.** Tensile stress-strain curve of Sample 1(0–100% bio-epoxy resins/epoxamite)
Sample 3 (50–50% bio-epoxy resins/epoxamite) had the lowest tensile strength and tensile modules with the values of 0.49±0.24 MPa and 0.75±0.34MPa, respectively. The lowest values of tensile strength and tensile modulus of Sample 3 can be related to the stress-strain curve (figure 5) which illustrated the strain of 150%. High failure of strain in Sample 3 showed that the molecules allowed to withstand more stress when subjected to stress. These results also explained the physical state of Sample 3 which was more ductile compared to Sample 2.

Therefore, it can be concluded that the addition of bio-epoxy resins in the blend of the cured resins led to a low value of tensile strength and tensile modulus, which resulted into a high value amount of failure strain. Thus, it can be seen that the tensile strength and tensile modulus decreased as the amount of epoxamite composition decreased. A similar trend was observed in the studies of epoxidized hemp oils/jute fibre composites [4,7,22].
3.2 Flexural

Conducting flexural test generally helps to determine the degree of brittleness of the material. The brittle materials tend to break abruptly without any specific warning. However, symptoms of breakage are usually visible before the fracture point [23]. Flexural properties of biopolymers composites are strongly affected by the quality of the interface between the materials, including the static adhesion strength and the interfacial stiffness [24]. Flexural strength and flex modulus for tested samples are summarized in table 3. As can be seen, Sample 1 with 100% epoxamite had the highest value of flexural and flex modulus which were 63.32±7.52 MPa and 2260.82±86.32 MPa, respectively. The addition of bio-epoxy resins reduced values of flexural strength and flex modulus tremendously.

Table 3. Flexural strength and flex modulus

| Sample | Bio-epoxy resins/epoxamite (%) | Flexural strength (MPa) | Flex Modulus (MPa) |
|--------|---------------------------------|-------------------------|--------------------|
| 1      | 0/100                           | 63.32±7.52              | 2260.82±86.32      |
| 2      | 25/75                           | 0.63±0.2                | 11.90±3.12         |
| 3      | 50/50                           | 0.055±0.013             | 1.20±0.54          |

Graph of flexural stress-strain can be used to evaluate the changes in the properties of pure synthetic epoxy with addition of bio-epoxy resins. Figure 6 illustrated the graph of flexural stress-strain pure synthetic epoxy. At the highest flexural strength, the strain value was very low, 6%. Flexural stress and modulus were clearly reduced with the increment of bio-epoxy resins composition from 25% to 50%. Figure 7 depicted that as the composition of bio-epoxy resins was increased to 25%, the flexure stress and modulus of the sample reduced to 0.63±0.2 MPa and 11.90±3.12 MPa, respectively. It was observed that increasing the amount of bio-epoxy resins contributed to the higher formation of epoxy groups which leads to the brittleness of the materials through the reaction with the hydroxyl groups. As the sample easily bends and breaks during the tests, it indicated the weak linkages between the hardener and the bio-epoxy resins [19].

Figure 6. Flexural stress-strain curve of Sample 1 (0–100% bio-epoxy resins /Epoxamite)
There is limited literature that discussed about bio-epoxy resins and epoxamite resins blends. In general, it is reported that the tensile strength and flexural strength of synthetic epoxy resins (epoxamite) are higher compared to the mixture of bio-epoxy resins and epoxamite blend [23]. This effect was due to the fact that the bio-epoxy resins is formed from monoglycerides which may contain unsaturated double bonds in the molecular structure. The absence of the double bonds in some of the transesterified methyl esters was the reason for the mechanical properties (tensile and flexural) of the bio-epoxy resins. A research conducted by [25] reported a similar trend, and stated that higher content of bio-epoxy resins decreases crosslinking network of epoxy by partially unreacted epoxidized methyl esters and fatty acid chains. In addition, the internal oxirane rings of bio-epoxy resins are less reactive than petroleum-based epoxies. Therefore, the mechanical performances of bio-based resins are low compared to a petroleum-based epoxy resins.

4. Conclusion
Synthetic epoxy resins and bio-epoxy resins blends were successfully prepared, and were subjected to mechanical tests. Based on the obtained results, the modulus of elasticity of blend materials is significantly lower than the 100% synthetic epoxy resins. Blends with higher percentage of bio-epoxy resins in the composition had lower mechanical because excess amount of epoxy groups leads to the formation of the ether groups and the copolymerization, making the material weak and easy to be compressed. The performance of bio-epoxy resins in the aspect of mechanical strength were still incomparable to the synthetic epoxy resins, hence are unsuitable to be used as an alternative for engineering purposes. However, since the content of the oxirane ring in the bio-epoxy resins makes it highly reactive, bio-epoxy resins synthesized from Jatropha methyl esters may find applications as biolubricants or reactive diluents. All in all, findings of this research are very important to provide another pathway for the production of high-quality materials using safe and economical techniques.

The following recommendations are suggested for future works:
- Evaluation of other properties of synthetic epoxy resins and bio epoxy resins blends for other applications such as lubricants, reactive diluents plasticizers, toughening agents and etc. These properties are included dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), drying time, scratch hardness, chemical resistance, rheology analysis and etc.
- The study of curing kinetics because time and temperature are essential to produce bio-epoxy resins-based polymers for specific purposes.

Figure 7. Flexural stress-strain curve of Sample 2 (25–75% bio-epoxy resins/epoxamite)
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