

Influence of Fiber Surface Energy on Mechanical Properties of Sisal Fiber - Bio Based Epoxy Composites

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ABSTRACT

The main objective of this study is to correlate the surface energy and mechanical properties of bio-based composites and also to establish the relationship between surface energy and composite performance. The surfaces of sisal fibers are treated by NaOH and isocyanate reagents to improve the surface properties. The surface energy of the untreated and treated fibers were estimated from contact angle measurements by using the theoretical approach. The adsorption between fibers and matrix was also examined. Modified fiber surface showed better adsorption performance as compared to untreated fiber and thus indicated good wetting behaviour of the treated fibers. Fibers with higher surface energy yielded higher tensile strength of composites. A qualitative agreement between the surface energy of the sisal fibers and mechanical strength of treated fibers was observed. Differential Thermo Gravimetric Analysis (DTG) was carried out to study the thermal stability of treated fibers. SEM studies support the results derived from the evaluation of mechanical properties by understanding the fiber/matrix adhesion.

KEY WORDS : *Composites, Contact angle, Surface tension, Wettability, Mechanical testing, Infusion, Surface treatments.*

1. INTRODUCTION

A detailed understanding of the correlation between the surface characteristics and

properties of composite would be beneficial for future development to improve overall performance of composites. In general, strong

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adhesion between fiber and polymer matrix provides better load transfer capacity from fiber to matrix. It is well known fact that good adhesion is achieved through chemical bonding, favorable wettability, and mechanical interlocking. The chemical modification of fiber can improve the adhesion through increasing the surface energy of the fiber^[1]. Gacitua et al. observed that the natural fiber lumens filled polymer matrix allows better adhesion and mechanical properties than collapsed lumens^[2]. Migneault et al. found that there is a positive correlation between atomic oxygen-to-carbon(O/C) ratios and mechanical properties of composite^[3]. Bouafif et al. also found very close correlation between O/C ratio and tensile/flexural strength of composite. Added to this, it was noticed that higher lignin surface contain lower O/C ratio and lower mechanical strength^[4].

Stark et al. examined the effects of particle size on the mechanical properties of composite and concluded that the flexural and tensile strength increase with increasing particle size^[5]. The increasing fiber size improves tensile strength and stiffness, but reduces elongation and energy to break^[4]. Fiber aspect ratio and size play an important role in the strength development of natural fiber-reinforced composites^[6]. Migneault et al. observed that the stress transfer capacity increases with increasing fiber aspect ratio. It attains the highest value when fibers are aligned along the direction of applied load. Further they observed that the mechanical properties generally increase with increasing density^[7].

The processing conditions such as temperature, pressure, residence time, cooling rate, and shear rate also affect the properties

of final composites^[8]. Migneault et al. suggests that fiber orientation is one of the key factors to improve the tensile properties of the composites. Besides above they also found that the fiber/matrix stress transfer capacity is increases with increasing fiber aspect ratio^[9]. In another discussion, Migneault et al. highlighted that the variation between the physical and mechanical properties of the wood based composites from different sources is mainly due to their cellulose content, while the fiber aspect ratio is not an important factor^[10]. Soucy et al. emphasized that the chemical composition of the paper mill sludge provides the variation in wood based composite mechanical properties. It is observed that the cellulose and ash compounds lead to improve composite strength and the presence of gas voids or amine/amide groups reduce composite toughness^[11]. Fu et al. highlighted that the composite strength is strongly affected by fiber/matrix adhesion and fiber loading^[12]. The surface treatment changes the surface chemistry of the fiber, thereby providing good bonding that creates better adhesion and increase in surface energy that lead to increase in work of adhesion provides better mechanical properties^[13].

Although many studies reported the significant effects of natural fiber on mechanical strength of bio composites, there are some contradiction as reported in literature. Thus, the objective of the present study is to characterize the surface energy of fibers and to investigate the relationships between fiber surface chemical characteristics and natural fiber strength. The surface energy varies with surface treatments, and the variations of properties of composites according to fiber modification can be explained by the surface energy of fibers.

2. EXPERIMENTAL

2.1 Material

The diglycidyl ether of bisphenol A (DGEBA) was used as a base component of epoxy resin. 30% epoxidized soybean oil (ESO) with 6.5 wt% oxirane content and specific gravity of 0.987 was added to the resin base. The woven unidirectional sisal fiber mat with an areal density of 575 g/m² was used as reinforcement.

2.2 Natural fiber surface modification

Natural fibers do not efficiently adhere to non - polar resins due to difference in surface energy. This difficulty can be overcome by chemical modification of fibers.

NaOH treatment: The sisal fiber mats were immersed in 2 wt % sodium hydroxide (NaOH) solution for 1 h at room temperature. The mats were further washed with distilled water until pH of the water reaches a steady value to remove the excess of NaOH present on the fiber surface. After that, the fiber mat was dried in a vacuum oven at 80°C for 12 h^[14]. The isocyanate treatment is done by placing sisal fiber mat in 6wt% of Methylene diphenyl diisocyanate (MDI) solution in toluene^[15]. The fiber mat was then heated to 50 °C as for about 30 min. After that the mat was removed and dried in an oven at 70 °C for 2 h.

2.3 Composites manufacturing

The vacuum infusion process was applied with woven fabrics. A gel coat was given to infusion mould inner surface to improve the resin impregnation and surface finishing of final product. The natural fiber fabric was first cut as per the mold shape and then placed over the die. The peel ply was {normally only partial cover} placed over the fiber fabrics and flow media (green mesh)/core layer was applied over the peel ply, to accelerate the resin flow. The mould was then vacuum-bagged. The vacuum bag creates compaction during process and the flow behavior has to include local deformations of the porous medium. The vacuum of around 27 inch of Hg was applied to bag which resulting in a compaction pressure of 90 kPa. The resin is allowed to infuse into the fabric smoothly and slowly for wet out, assisted by the vacuum. After completing the resin

infusion, the natural fiber composites were left to cure under vacuum for 24 h at ambient temperature.

The fiber volume fraction was determined from the following equation.

$$v_f = v_{f_0} \cdot P_{comp}^B \quad (1)$$

where the P_{comp} (90 kPa) is the compaction pressure and the coefficients v_{f_0} (0.236) and B (0.067) are experimental fitting parameters adopted from compaction master curve^[16]. The fiber volume fraction value was found to be 32%.

2.4 Estimation of Surface energy or Surface tension

The surface free energy of fiber mat infused with SO resin was estimated using Young's equations as given below.

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \quad (2)$$

where γ is the surface free energy (or surface tension) and the subscripts sl, sv, and lv refer to the solid-liquid, solid-vapor, and liquid-vapor interfaces, respectively.

Generally, it is accepted that the $\gamma_{lv} \equiv \gamma_l$. The surface tension of the liquid was estimated using pendant drop technique.

Free energy of sisal mat is unknown. Therefore, there are two unknown (γ_{sv}) and (γ_{sl}) parameters in the equation 2 and only one known datum (θ). In this study, the contact angle is measured by a goniometer. To solve the equation 2 Good et al introduce an equation^[17].

$$\gamma_{sl} = \gamma_s + \gamma_l - \sqrt{2\phi (\gamma_s \gamma_l)} \quad (3)$$

Where ϕ is the constant characteristic of the system and is expressed as

$$\phi = \frac{4 (V_s V_l)^{1/3}}{(V_s^{1/3} + V_l^{1/3})^2} \quad (4)$$

Where the V 's are molar volume. To evaluate the surface free energy of fiber mat, equations (4) and (3) to equation (2). To calculate the surface energy

$$\gamma_s = \gamma_l \left(\frac{(1 + \cos \theta)^2}{4\phi^2} \right) \quad (5)$$

2.5 Adsorption Measurements

A 20 mm x 50 mm fiber mat is held underneath a high precision balance by a metallic wire, and then the balance is tared. The fiber mat was then brought into contact with resin by carefully adjusting the level of a measuring jar containing resin. The change in the mass of fiber samples is continuously observed as a function of time.

2.6 Mechanical characterization

Tensile testing was performed according to ASTM D3039 using a universal testing machine. Rectangular test specimens of 25 mm x 255 mm as specified by the standard, were tested for tensile properties at a crosshead speed of 2 mm/min. For statistical significance, 5 samples were tested for each case for different tests. The tensiles labs were fabricated by vacuum infusion process. The flexural strength was determined by applying bending load on rectangular specimen of size 60 mm x 10 mm x 4 mm as per ASTM D 790. The Izod impact strength were measured as per ASTM D256 (2010) using an impact pendulum tester (Tiniusolsen USA, model 104).

2.7 Thermo Gravimetric analysis (TGA)

TGA was conducted to evaluate the thermal stability of the fibers using a NETZSCH STA 409PC/PG. The mass of the samples is between 5 and 6 mg. TGA was carried out in a temperature range of 30–650 °C at a heating rate of 10 °C/min.

2.8 SEM characterization

The fracture surface of the composite specimens were examined using Scanning Electron Microscope (SEM) model Carl Zeiss, EVO15 operating in the high vacuum mode at accelerating voltage of 10–15 kV.

3. RESULTS AND DISCUSSION

3.1 Surface energy of sisal fiber

In order to get good bonding, the surface energy of a fiber should be higher than that of the resin which facilitates good wetting between fiber and resin during composite fabrication. Moreover, the surface energies will play an important role in wetting^[18]. A proper match of the surface properties of resins to those of reinforcement's fiber is one of the key concerns in achieving successful wetting during infusion molding. Measurements of surface energies can lead to a prediction of the compatibility of the reinforcement fibers and the resin matrix.

Figure 1 shows the effects of the surface modification on the surface energy of natural sisal fiber with the ESO resin. The surface energy (or tension) of the ESO resin as calculated from pendant drop technique is = 28 mN/m. The increase in surface energy for NaOH treated fibers correspond is attributed to that the extraction of lignin, hemicellulose, other derivatives and reduces the polar group on the surface of the fiber. The similar trend is observed for isocyanate treated fibers while impregnated with ESO resin. The common explanation is that the surface treatments increase the surface energy through decrease in the value of contact angle of natural fiber with ESO resin. This is attributed to the fact that the surface treatment alters the surface chemistry of fiber by introducing polarity. The key focus of this work is to correlate the surface energy with properties of the fiber and not on chemistry aspects of the fiber.

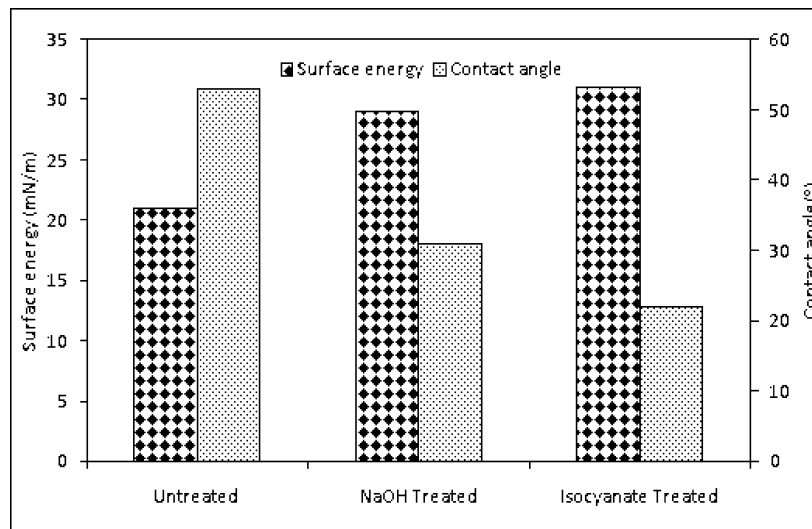


Fig. 1. Effect of fiber treatments on contact angles and surface energy of natural sisal fibers

3.2 Wetting (or adsorption) analysis

The Washburn theory proposes that if any porous solid medium is brought into contact with a resin matrix, there will be a flow of resin into the pores of the solid medium induced by capillary forces^[19]. These form of measurements allowed us to assess the effect of natural fiber reinforcements in resin on the wetting.

The treated and untreated natural fibers are immersed in ESO resin to measure an adsorption mass as a function of time. The results indicated that the registered sorption mass initially fluctuated owing to the movement of wetting line on the rough surface of the natural fibers. Besides, this fluctuation may be attributed to the “edge” effects. After that, it typically attained a stable value after approximately 25 s (Figure 2); Figure 2 indicates that the rate of resin impregnation in treated fiber is higher as compared to untreated fiber mat.

Increase in the impregnation rate of treated fiber is attributed to higher surface energy promoted by favorable contact angle. Higher surface energy promotes good wetting characteristics. The negative weight gain readings observed at the initial part of the wicking curves are due to the buoyancy effect such that a negative force is applied to the mats as it penetrates the resin interface.

3.3 Mechanical characterization

3.3.1 Tensile strength

It is clear that in all cases of treatments an improvement in tensile properties is observed (Figure 3). The main purpose of the NaOH treatment on natural fibers is to dissolve part of the impurities and waxes present on the fibers surface. It also helps in removing lignin from surface. This leads to the fibers surface become coarser and provide more wetting surface area, and better interaction with

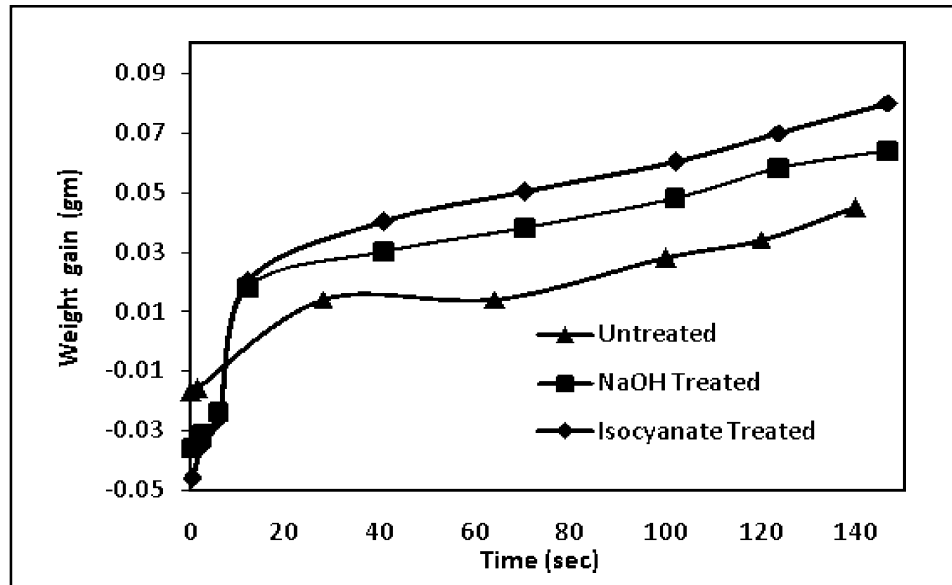


Fig. 2. Adsorption of bio based epoxy into the unidirectional sisal fiber mat during the wicking experiments

the resin. During isocyanate treatment, the isocyanate functional group ($-N=C=O$) reacts with the hydroxyl groups of the fibers i.e cellulose, and consequently, a urethane linkage is formed. This chemical linkage provides strong covalent bonds between the fiber/resin and provides enhancement in bonding with the matrix. Typically, a low resin surface tension and higher surface energy is necessary for good and fast fiber impregnation. It is evident that good wetting is a critical condition for obtaining good adhesion properties between the matrix and reinforcement systems during processing.

In natural fiber reinforced composite, the interfacial properties of fiber/matrix play a significant role in the concluding mechanical performance. The interactions between fiber and matrix at the interface is generally depends

on physical adhesion, and chemical bonding. In addition to that the mechanical properties depend on the polarity of the matrix.

An excellent physical adhesion is controlled by wetting between fiber/matrix, which is strongly relying on the surface energies of the materials. The results clearly indicated that the higher surface energy provides good interaction between fiber and matrix by increasing the compatibility. This fact leads to good tensile properties of the composite. The tensile strength of the fabricated composites are correlated well ($R^2 = 0.82$) with the surface energy as shown in above Figure 4. The high correlation coefficient between tensile strength and surface energy suggests that the higher surface energy, higher permeability, good wetting characteristics and formation of strong bonds have to be assured for higher tensile strength.

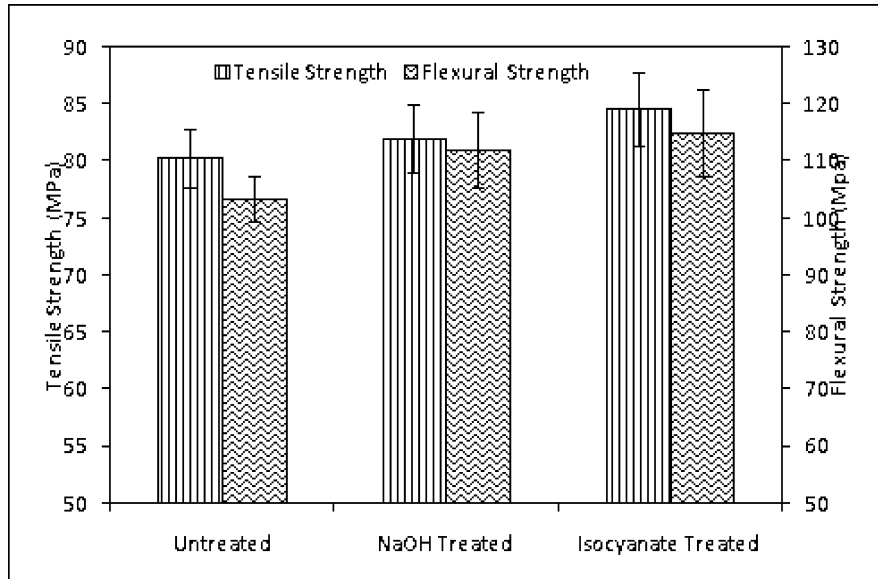


Fig. 3. Tensile and Flexural strengths of treated and untreated sisal/bio based epoxy composites.

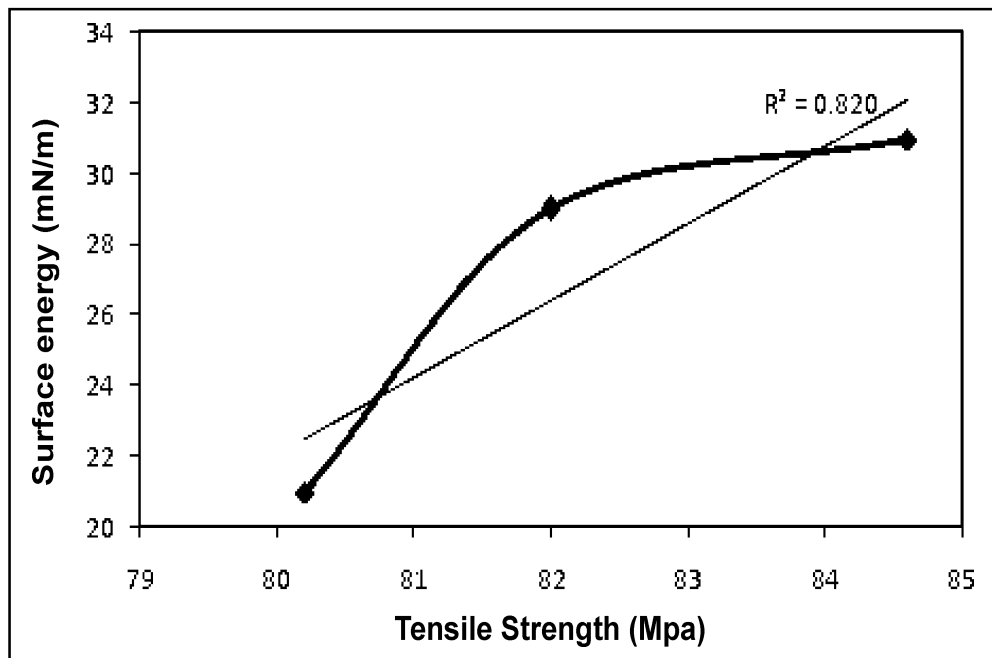


Fig. 4. Correlation between tensile strength and surface energy of the investigated materials.

3.3.2 Flexural strength

All types of surface modifications result in a flexural strength increase as compared to the untreated fiber samples (Figure 3). The flexural properties of composites are governed by the resistance to inter laminar failure. The explanation for these results is the same as for tensile strength increases because the flexural strength is mainly influenced by the fiber/matrix interface interaction. Therefore, the higher flexural strength treated fiber composites owing to the better interfacial adhesions in the composite. The influence of surface modifications on mechanical properties is similar to that on the tensile strength and flexural strength and extensibility increases with increase of interaction in terms of surface energy.

3.3.3 Impact strength

It is clear that the impact strength decreases slightly with NaOH and isocyanate treatments. The NaOH treatment breaks the structure of natural fibers partially and the blended epoxy resin is filled the gaps between the fibrillations, thus the impact energy absorbed by them is lower. Due to the surface treatment with highly reactive reagents such as isocyanate lead to strong chemical bonds with the natural fiber. The higher surface energy of treated fibers possess lesser impact strength as compared to untreated fiber. This may be attributed that the modified surface can further bond with epoxy system and initiates a good bonding. When there is good bonding/adhesion at the interface, the contribution of this work is lesser, resulting in a reduced impact strength.

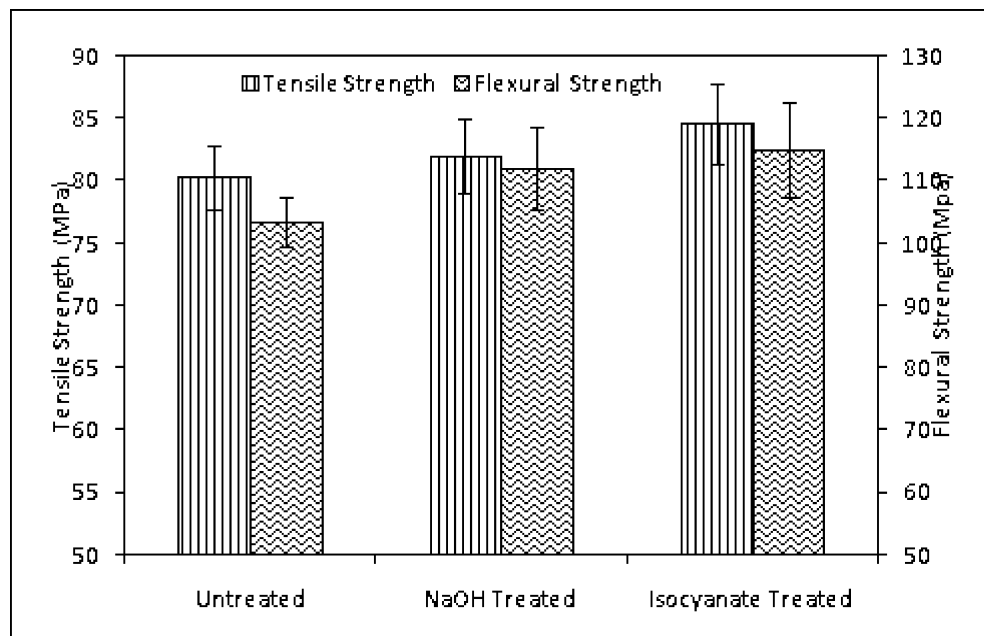


Fig. 5. Impact strength of the treated and untreated sisal/bio based composites

3.3.4 Thermogravimetric Analysis (TGA)

It also evidently proves the shifting of the DTG maxima towards the higher temperatures for the treated fiber, as this can be seen on Figure 6. In fact, the temperature at which the rate of degradation (thermal stability) increases with the treatments as compared untreated fiber. It is the fact attributed to NaOH treatments could remove portions of hemicelluloses and lignin elements from the fiber. Due to this, the decomposition process mainly occurred on the cellulose which in turn increases the overall degradation temperature of the treated fibers. The slightly higher thermal stability of isocyanate treated fiber may be due to the formation of covalent bond between the cyanate group and functional group of fiber.

Besides, the increasing surface energy is also contributing to higher thermal stability of the treated fiber.

3.3.5 SEM characterization

SEM characterization of untreated fiber composites shows the brittle nature of the fracture at a macroscopic level with presence of fibrillation. Several hollow portions after the fracture can be seen in the SEM image (Figure 7), representing that the phenomenon of fiber 'pull-out' occurred to a large magnitude. The decrease in tensile strength of untreated composite is maybe due to following reason fiber pull out, more amount of voids present and large gap between the fiber and the matrix which can be seen in Figure 7, which indicates the poor bonding between the fiber and matrix.

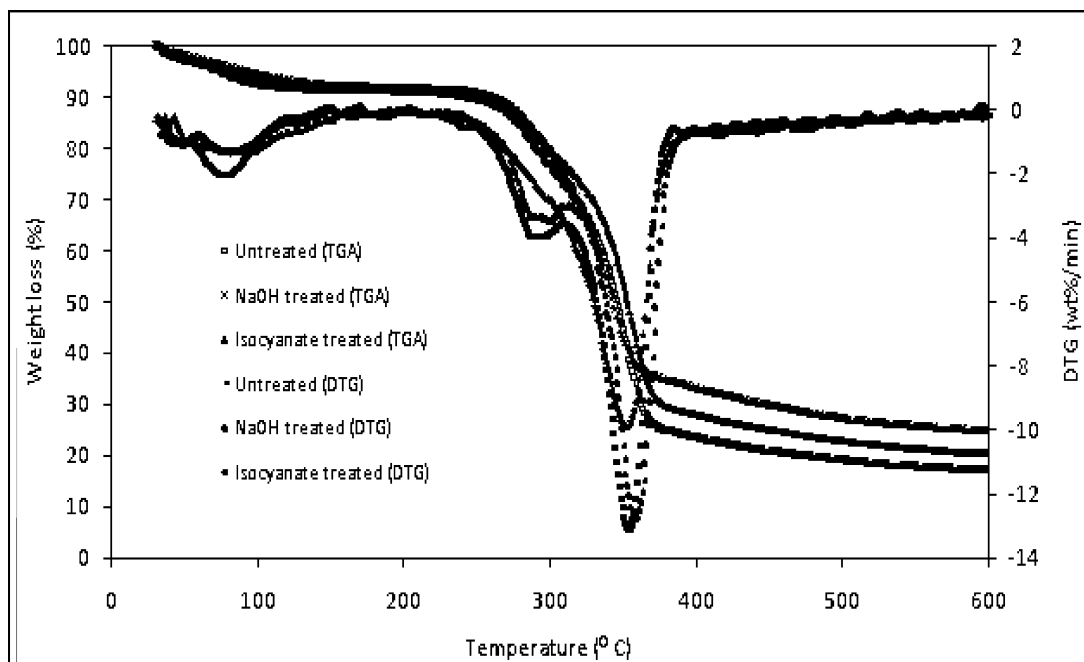


Fig. 6. TGA analysis curve for thermal analysis.

Subsequently NaOH treated composites shows that the gap between the fiber and epoxy is closer than in the untreated fiber composite due to fact that the matrix will easily infuse (due to surface energy effect) into the

gaps of fibrillation and subsequently strongly joint the fibers together. However, the voids are present over the fracture surfaces due to fiber pull out. However, the voids are lesser compare to untreated composites.

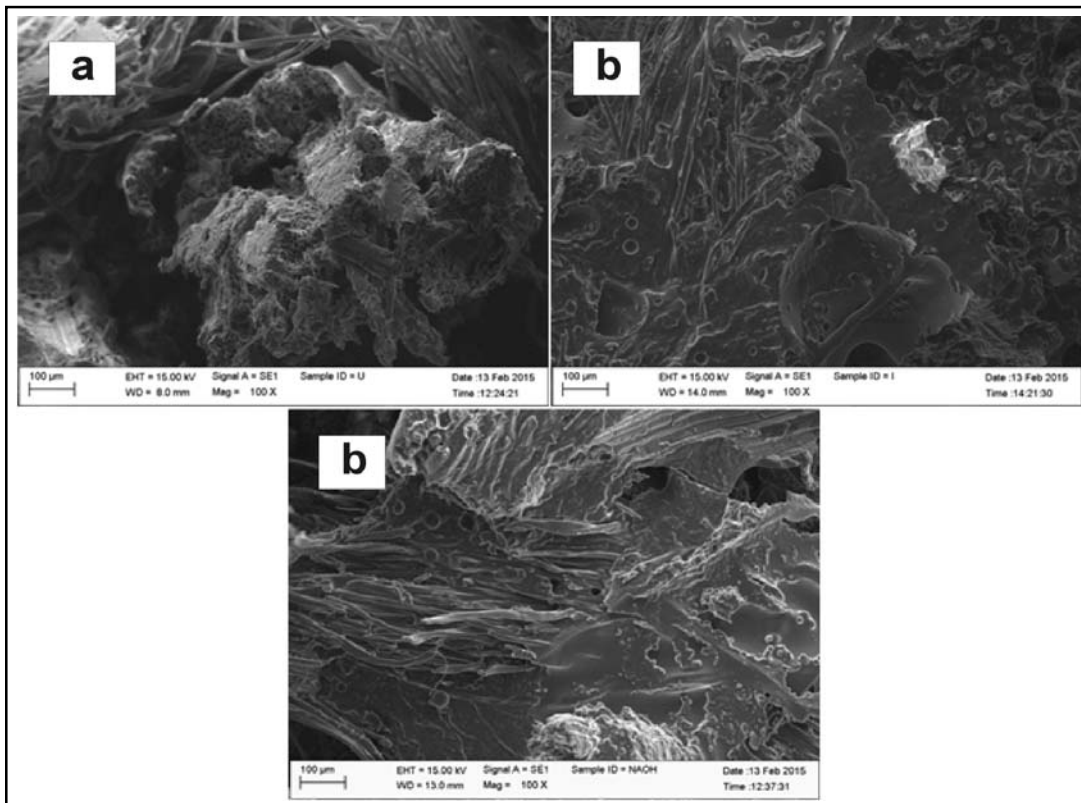


Fig. 7. SEM micrographs of sisal fiber composite a) Untreated (b) NaOH treated (c) Isocyanate treated composites

A good link between the isocyanate treated fibers and the matrix could be seen from SEM image. This is attributed to present lesser voids and closed packing between the fiber and matrix then previous untreated composites. From the SEM images, the results clearly indicates that the treated composites shows higher strength

compared to untreated composite is may be due to surface energy effects.

4. CONCLUSION

Surface energy and mechanical properties of developed bio based epoxy – natural fiber composites were determined. An increment in

the surface energy of the treated fibers was observed by contact angle measurements. An improvement in the adsorption performance of treated fibers was also observed. This result indicated that the increase in the surface energy of the treated fibers enhancing the overall wetting behaviour of the system. The treated fiber composites showed a higher tensile strength and flexural strength than the untreated fiber due to the high surface energy of the fiber. The key explanation for this improvement in the properties in bio based composites is the strong interaction between fiber and matrix due to high surface energy. SEM images of treated composites confirmed there is an enhanced bonding between the fiber and matrix. The significant correlation is found between surface energy and mechanical properties (excepted impact strength) of developed bio based composites.

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