Surface Energetics Effects on Mechanical Strength of Fibre Reinforced Polymer Matrix

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Abstract-
Surface energetics effects on the mechanical strength of fibre reinforced polymer matrix been studied employed the manual scraper mechanism in extracting fibre from plantain pseudo-stem and was treated with nine different treatments. Cylindrical shape mould was prepared for mechanical test samples with continuous and unidirectional aligned fibres. Two probe liquids; water and glycerol were used in contact angle measurement for all the treated and untreated samples. The contact angle data was used for the interfacial energetics computations using Neumann and Fowkes models and the mathematical analysis were carried out using Matlab software tools. van der Waals notion of particle-particle interaction was employed to explain the physiochemical properties such as the surface interfacial energies. The average value for the interfacial free energy of adhesion for fibre-water and fibre-glycerol are -10mJ/m² and -16MJ/m² respectively signifying attractive van der Waal forces. The tensile test results unveil that the average value for treated fibres is greater than the average value of 171.29N/mm² for untreated fibre except for potassium permanganate and phosphoric acid. These results reveal that an increase in tensile strength leads to an increase in the interfacial surface energy of adhesion. The treated fibres show a significant increase in interfacial surface energy and change in free energy of adhesion which suggests a better bonding mechanism of interaction between the fibre and matrix except for phosphoric acid which reveals otherwise, it may be as a result of the chemical chopped off the fibre during the treatment. The average strain rate of about 0.003 per seconds, 0.002 per seconds and 0.005 per seconds were deduced from the treated Mercerization, Acetone and MEKP respectively which reveals the lower strain rate as compared to the untreated fibre of 0.008 per seconds. The negative strain rate for the potassium permanganate and phosphoric acid was found to be -0.002 and -0.001 respectively reveals that the treatments will debond faster than other treated fibres.

Key words: Surface energetic, Adhesion, Fibre, polymer, Interfacial energy, Strain rate, tensile strength.

1. Introduction
Composite materials have been the dominant materials over the last three decades. Engineers chose composite materials for engineering products for diverse reasons, such as high stiffness, low thermal expansion, lightweight, corrosion resistance, high strength, and long fatigue life [1]. The development of composite materials in terms of the volume and number of applications has steadily incisive and conquering new markets insistently [2]. The composites consist of high strength fibres (reinforcement) entrenched in polymeric matrices are fibre reinforced polymer materials. The load-carrying elements are the fibres in these materials and it provides rigidity and strength [3], while the position and orientation of the fibres are sustained by the polymer
matrices which shield them against the environment and possible damage [4]. However, the poor resistance to moisture absorption and the lack of good interfacial adhesion leads to debonding with age, which makes the use of natural fibre reinforced composite less attractive. The cellulose fibres are naturally hydrophilic and are usually incompatible with hydrophobic hydrocarbon polymers [5-6]. The composite interface controlled the physical properties of the composite. Fibre surface modification can be used to modify the interfacial interactions by chemical or physical methods.

Conventionally, the interface is where the bond between fibre and matrix occurs. The interfacial bond is considered to have a thickness in the molecular range and results from the interaction between the matrix material and the fibre surface. This interface between the matrix and the fibre plays an important role and, in numerous cases, turn out to be a limiting factor in improving mechanical properties (toughness and strength) of the composites [7]. Bonding between the matrix and the reinforcing fibre has an important effect on the composite properties since load distribution efficiency and stress transfer at the interface is determined by the degree of adhesion between the components. However, the hydrophilic nature of natural fibres reduces their potential as reinforcing agents due to low interfacial interactions with certain important hydrophobic thermoplastic matrices, such as polypropylene and polyethylene, leading to poor interfacial strength [8-9].

The high surface energy of both matrix and fibre contributes to a high adhesion work, while the matching of surface energy components results in good fibre-matrix interfacial compatibility [10-11]. These interactions are mainly controlled by the functional groups on the surface of the matrix and the fibre at the interfacial contact area. The effect of physical adhesion on the mechanical properties of a composite structure not only affects the composite strength [12], but it is also important for moisture resistance and impact behaviour (high adhesion typically leads to lower penetration impact energy, but it is favourable for damage tolerance) [13].

The wettability and compatibility of the fibre and matrix can be assessed by analysis of their surface energies [14]. This can be done by measuring the contact angle, which is a quantitative measure of solid-liquid molecular interactions and thus provides information on the surface energy of solids. Therefore, the aim of this paper is to determine the fibre-matrix interfacial energies of adhesion, the strain rate constant and the correlation between the surface energy and tensile strength.

2. Materials and Methods
2.1. Materials
The basic raw materials are Plantain pseudo stem fibres sourced from Patani, Delta State, Nigeria; unsaturated polymer resin with a density of 1.967g/cm³.

2.2. Methods
The fibres were extracted from Plantain pseudo-stem fibres using the manual scraper method [2,15]. The fibres were washed in water and sun-dried for about three days. The fibres preparation was done with the aim of moulding cylindrical mechanical test samples with unidirectional and continuous aligned fibres. The fibres were cut to the same length of 50cm and measured. The fibres were bundled together in each case until the required weight of the
bundle was accomplished. The mould internal diameter is about 6 mm. The weight of fibre used is 0.109 g. Each 0.109 g bundle of fibre was fused together at the ends by means of hot plastic glue. For each fibre treatment category, two sets of fibre bundles were weighed including an untreated control category of fibres. The fibres bundles were set aside for treatment after labelling. Acetone [16], Acetylation [17-18], Alkaline [19, Hydrogen peroxide, Methanol, Phosphoric acid, and Potassium permanganate treatments [18] were carried out to render fibre surfaces hydrophobic. Measurements of the contact angle were carried out by means of a special microscope (HD colour CMOS sensor, high-speed DSP) using glycerol and water as probe liquid.

2.3. Mechanical Tests

**Tensile Strength Measurements:** The test was measured according to ASTM (D638) standard.

**Density**: The densities were determined according to the ASTM guidelines;

\[
\rho_f = \frac{\text{mass of fibres, } M_f}{\text{volume of density bottle, } V_c}
\]

The volume fraction of plantain fibre was accomplished as shown in table 1 using Eq. (2-7):

\[
M_c = M_f + M_R
\]

\[
V_f = \frac{M_f}{\rho_f}
\]

\[
V_R = \frac{M_R}{\rho_R}
\]

\[
V_c = V_f + V_R
\]

\[
\frac{V_f r}{V_c} = \frac{V_f}{V_f + V_R}
\]

\[
V_f r = \frac{V_f}{V_c} \left(1 - \frac{V_f r}{V_c}\right)
\]

Where: density of fibre = 1.360 g/cm$^3$, mass of composite $M_c$ = 6.561 g; mass of fibre $M_f$ = 0.242 g; mass of resin $M_R$ = 16.007 g; density of composite, $\rho_c$ = 1.591 g/cm$^3$; density of resin, $\rho_R$ = 1.967 g/cm$^3$; volume of composite = $V_c$ (cm$^3$); volume fraction of fibre $V_f r$ = 0.2; volume of resin = $V_R$ (cm$^3$); volume of fibre = $V_f$ (cm$^3$).

2.4. Theoretical Considerations

1. **Interaction Energies:** Young’s equation was employed in the evaluation of Interfacial free energies using contact angle measurement;

\[
\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos \theta
\]

Where; $\gamma_{sv}$, $\gamma_{sl}$ and $\gamma_{lv}$ are the interfacial energies of the liquid-vapour, solid-vapour and solid-liquid interfaces.

To calculate the surface free energies, Fowkes proposed that;

\[
\gamma_{sv} = 0.25 \gamma_{lv} (1 + \cos \theta)^2
\]

Neumann et al 1983, derived the equation of state is;

\[
\gamma_{sl} = \frac{[(\gamma_{sv})^{0.5} - (\gamma_{lv})^{0.5}]}{[1 - 0.0015(\gamma_{sv} \gamma_{lv})^{0.5}]}\]

Then the adhesion energy of fibre (f) to the matrix (m) gives Eq. (11):

\[
\Delta \gamma^{\text{adh}} = \gamma_{mf} - \gamma_{mv} - \gamma_{fv}
\]

Where; f = fibre, v = vapour (air), and m = matrix

The Hamaker Coefficient which is the interaction energy is;

\[
\Delta \gamma^{\text{adh}} = -\frac{A_{ijk}}{12\pi d_0^4}
\]
Where; \( \delta_0 = 1.82 \, \text{Å} \)
Since the fibre is cylindrical, the surface area of fibre is;
\[
A = 2\pi rl
\]
The total surface area in \( n \) fibres is;
\[
A_T = 2\pi rl n
\]  
(13)
Therefore, the total energy of adhesion is;
\[
F^{\text{adh}} = 2\pi rl n (\gamma_{mf} - \gamma_{mv} - \gamma_{fv})
\]  
(14)

II. Strain Rate: In this paper, however, a different approach that considers the relationship of stress to fibre adhesive energy with the matrix will be considered, in the determination of strain rate. The ratio of work of adhesion to the stress on the composite has been defined as the strain rate of the deformation of the composite:
\[
\text{Strain rate} = \frac{\text{Work of Adhesion}}{\text{Tensile Strength}}
\]  
(16)
Dimensionally, equation (3) gives the unit of strain rate: Strain rate \( \equiv \frac{\text{mJ}/\text{m}^2}{\text{N}/\text{mm}^2} \equiv 10^{-9} \text{s}^{-1} \)
Thus, to determine the strain rate, the work of adhesion (\( \Delta F^{\text{adh}} \) in mJ/m\(^2\)) between the fibre (f) and the matrix (m) should be determined using the expression:
\[
\Delta F^{\text{adh}} = \gamma_{mf} - \gamma_{mv} - \gamma_{fv}
\]  
(17)
Where \( \gamma \) is the interfacial surface energy in mJ/m\(^2\) and the tensile strength \( \sigma \) is in N/mm\(^2\).

3. Result and Discussions
3.1. Change in Free Energy of Adhesion
The results of the change in free energy of adhesion are presented in table 1.

| Samples                  | \( \Delta F^{\text{adh}} \) (mJ/m\(^2\)) |
|--------------------------|-----------------------------------------|
| Untreated                | -40.3752                                 |
| Acetone                  | -42.3604                                 |
| Acetylation              | -44.1663                                 |
| Glycerol                 | -41.24065                                |
| Hydrogen Peroxide       | -42.3791                                 |
| MEKP                     | -45.8592                                 |
| Mercerization (NaOH)     | -46.1778                                 |
| Methanol                 | -42.7380                                 |
| Potassium Permanganate  | -42.0328                                 |
| Phosphoric Acid          | -37.8042                                 |

From table 1, the change in free energies of adhesion showed negative values which imply attractive net van der Waals forces and provides the strong relationship between fibre bonding to the matrix. The treated fibres give higher energy of adhesion than the untreated fibres showing that the fibre is hydrophobic which increases the fibre-matrix bonding and the composite strength. MEKP and NaOH treated fibre gives the highest bonding effectiveness while phosphoric acid treated fibre gives the lowest bonding effect. The decrease in lignocelluloses and hemicelluloses properties of the fibres was as a result of fibre treatments. Increasing the treatment of fibre minimized the surface area of the phase boundary as a result of attractive van der Waals forces. At the surface, the treatment liquid molecules reduce the free
energy at the adjacent phase as a result of the interaction with the composite particles and hence, the surface energy decreases.

3.2. Hamaker Coefficient
The energies of interaction can be expressed in terms of the Hamaker coefficient. They are obtained from the values of surface energies and changes in free energies of adhesion obtained from the contact angle data.

Table 2: Average Hamaker Coefficient, A_{131}

| Samples                  | A_{131} (x10^{-17}mJ/m^2) |
|--------------------------|----------------------------|
| Untreated                | 3.8966E-17                 |
| Acetone                  | 4.0882E-17                 |
| Acetylation              | 4.2809E-17                 |
| Glycerol                 | 3.9802E-17                 |
| Hydrogen Peroxide        | 4.0900E-17                 |
| MEKP                     | 4.4259E-17                 |
| Mercerization (NaOH)     | 4.4566E-17                 |
| Methanol                 | 4.1247E-17                 |
| Potassium Permanganate   | 4.0566E-17                 |
| Phosphoric Acid          | 3.6485E-17                 |

From table 2, the Hamaker coefficients are all positive signifying that the van der Waals forces are attractive. Neumann model treated fibre have higher Hamaker coefficient than Fowkes model treated fibre. Neumann model indicated highest Hamaker coefficient (4.6502x10^{-17}mJ/m^2) and lowest attraction (3.7913x10^{-17}mJ/m^2). Mercerization (NaOH), MEKP and Acetylation treated fibre has the highest attraction for both Neumann and Fowkes models (4.6502x10^{-17}mJ/m^2, 4.6051mJ/m^2 and 4.4368x10^{-17}mJ/m^2 respectively)–Neumann and (4.2630x10^{-17}mJ/m^2, 4.2466mJ/m^2 and 4.1249x10^{-17}mJ/m^2 respectively)–Fowkes. Neumann model untreated fibre indicated a decrease of about 11.8% from the highest treated fibre (NaOH). While Fowkes model untreated fibre, indicated a decrease of about 13.4% from the highest treated fibre (Mercerization). The untreated fibres have lower Hamaker coefficients than the treated fibre. The results shown indicate that the values of the Hamaker coefficients are within the range of x10^{-16}mJ/m^2 - x10^{-19}mJ/m^2.

3.3. Strength Analysis
The tensile strength of fibres was determined and the average values are presented as shown in table 3.

Table 3: Average Tensile Strength of untreated, Treated fibre and Unreinforced Polyester
Tensile Strength (N/mm$^2$)

| Samples                  | $\Delta F_{adh}$ (mJ/m$^2$) | $\sigma$ - UTS (N/mm$^2$) | Strain rate $\dot{\varepsilon}$ ($10^{-9}$ s$^{-1}$) |
|--------------------------|-----------------------------|---------------------------|-----------------------------------------------|
| Unreinforced Polyester   | 148.18                      |                           |                                               |
| Unreinforced Polyester   | -40.3752                    | 171.98                    | 0.2348                                        |
| Treated                  |                             |                           |                                               |
| Acetone                  | -42.3604                    | 190.41                    | 0.2225                                        |
| Acetylation              | -44.1663                    | 186.63                    | 0.2367                                        |
| Glycerol                 | -41.2407                    | 177.07                    | 0.2329                                        |
| Hydrogen Peroxide        | -42.3791                    | 185.25                    | 0.2288                                        |
| MEKP                     | -45.8592                    | 194.43                    | 0.2359                                        |
| Mercerization (NaOH)     | -46.1778                    | 198.49                    | 0.2326                                        |
| Methanol                 | -42.7380                    | 179.29                    | 0.2384                                        |
| Potassium Permanganate   | -42.0328                    | 165.51                    | 0.2540                                        |
| Phosphoric Acid          | -37.8042                    | 148.84                    | 0.2540                                        |

Table (3) represents the effect of different treated fibre and untreated fibre on the ultimate tensile strength of matrix composite reinforced with plantain fibre. Table (3) shows that the fibre sample treated with MEKP and NaOH both have the maximum ultimate strength. This reveals that the ultimate tensile strength of the developed composite increases with reinforcement.

Equation (16) gives a link between the work of adhesion, strength and strain-rate. Strain rate was calculated using equation (16) together with the relevant data and listed in the table (4).

From figure (4), the strain rate varies from $0.2225 \times 10^{-9}$ s$^{-1}$ for Acetone treatment to $0.2540 \times 10^{-9}$ s$^{-1}$ for Potassium Permanganate and Phosphoric Acid treatments. These values measure the rate at which the distances of adjacent parcels of the material change with time in the neighbourhood of that fibre. Polymer materials exhibit this time-dependent behaviour in a load-bearing material. The low values of strain rates ($\sim 10^{3}$s$^{-1}$) show that relative movements between the fibre and matrix, and also within the composite, are very low and that Potassium Permanganate and Phosphoric Acid treated systems are most probable to fail than the Acetone treated samples. The strain rate for untreated fibre is of the same order of magnitude. This raises the question as to the contribution of strain rate to fibre/matrix integrity. However, relative movements of fibres in the matrix are important. The strain rate for the fibre reinforced polymer matrix was of the order of $10^{-9}$/sec while that reported in the literature for polypropylene was of the order of $10^{-4}$/sec. This result may suggest that the fibre sliding against the polymer matrix...
to which it was bonded was infinitesimally low and would not cause a noticeable change in their bonding.

4. Conclusion
The contact angle, surface energetic and mechanical tests were analyzed on the composite material which showed that interfacial energy enhanced considerably with the plantain fibre reinforced polyester composite. Interfacial energy and Hamaker coefficient were determined with their correlation using Neumann and Fowkes models. Adhesive-tensile stress model was used to calculate the strain rate and strain-rate sensitivity index. The low values of the strain rate suggest that the fibre sliding against the polymer matrix to which it was bonded was infinitesimally low and would not cause a noticeable change in their bonding. In this study, the strain rate sensitivity index, m, is less than 0.30, it can be surmised that the reinforced plastic is relaxed and so would not be adversely subjected to stress build up at the interface between the fibre and the matrix. The Fowkes model shows a higher change in free energy of adhesion for treated and untreated fibre reinforced composite when compared with Neumann model indicated lowest attraction (low change in free energy of adhesion) indicated by the degree of negative signs. Since the low energy has noted for the hydrophobic surface. It suggests that Neumann model (equation of states) would give a better approximation between empirical formulations and contact angle data. This work also shows that the use of adhesive energy concept to determine the strain rate is valid since the values of strain rate indices calculated are comparable with values reported in the literature.

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