The Effects of Chemical Treatment on the Structural and Thermal, Physical, and Mechanical and Morphological Properties of Roselle Fiber-Reinforced Vinyl Ester Composites

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Roselle fiber is a type of natural fiber that can potentially be used as a reinforcement material in polymer composites for different applications. This study investigated the chemical, physical, thermal, mechanical, and morphological characteristics of roselle fiber-reinforced vinyl ester subjected to different fiber treatments. The roselle fiber was treated with alkalization and a silane coupling agent, and samples were prepared using the hand lay-up method. Treated roselle fiber significantly enhanced most of the properties of vinyl ester biocomposites compared with an untreated biocomposite. The results revealed that alkalization and silane treatment of the fiber changed its chemical properties. The treated fiber improved water repellence behavior of the roselle fiber-reinforced vinyl ester compared with the untreated fiber. Use of a silane coupling agent was determined as the best chemical treatment for the water absorption effect. Thermogravimetric analysis (TGA) demonstrated that alkalization-treated fiber had improved thermal stability; however, the opposite result was obtained with the silane-treated fiber. The morphological examination of treated and untreated roselle fiber-reinforced vinyl esters showed a good fiber adhesion between the treated fiber and the matrix, and less fiber pull-out from the matrix was observed. This observation provides good indication of the interfacial interlocking between the fiber and the matrix, which improved the tensile properties of the composites. In contrast, the impact results revealed that the treated fiber had a decreased impact energy compared with the untreated fiber. POLYM. COMPOS., 00:000–000, 2016. © 2016 Society of Plastics Engineers

INTRODUCTION

Natural fibers, such as hemp, kenaf, jute, sisal, banana, flax, and oil palm, have been in considerable demand in recent years due to their ecofriendly and renewable nature [1]. Recently, in line with increasing environmental concerns, scientists and researchers have been replacing synthetic fibers with natural fibers as the primary component in composites [2–8]. The advantages of natural fibers include low cost, good mechanical properties, abundant availability, material renewability, biodegradability, nonabrasive nature, and ease of recycling compared with synthetic fibers [9, 10]. These advantages have encouraged material engineers to use natural fibers as reinforcing fillers in polymer composites to reduce the use of timber or forest resources and to explore under-used natural fibers.

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FIG. 1. Water retting process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Natural fibers are widely used in automotive [11] and construction engineering [12]. Natural fibers can be found in southeast Asian countries, such as Malaysia, Indonesia, and Thailand [9].

Natural fibers, such as roselle, are found abundantly in nature and are cultivated in Borneo, Guyana, Malaysia, Sri Lanka, Togo, Indonesia, and Tanzania. Roselle is one of the plants that has been found suitable for use in the production of natural fibers. The scientific name for roselle is *Hibiscus sabdariffa* L., and it belongs to the Malvaceae family. Roselle belongs to the hibiscus genera and is found abundantly in tropical areas. These plants are commonly used as an infusion and to produce bast fiber. There are various uses of roselle. The fruit is commonly used in the medical [13, 14] and food industries [15, 16], while the fiber is used as a textile [17] and as a reinforcement material for polymer composites [18]. However, limited studies have been performed on the application of roselle fibers and its composites [19]. The roselle stem is red in color during the water retting process, as illustrated in Fig. 1. In Malaysia, after a year, the roselle plant is cut and becomes a waste product because the quality of roselle fruit is no longer optimal. To efficiently use this plant, the fiber can be employed as a reinforcement material for polymer composites.

Although roselle fibers have some advantages over synthetic fibers, especially in terms of material cost, they present certain disadvantages regarding the fiber matrix interface. Crucial issues in using natural fibers include poor adhesion between fiber and matrix as well as high water absorption and high moisture content, which leads to fiber instability that can cause microcracking of the composite and degradation of the mechanical properties. The performance and quality of the composite product highly depend on fiber matrix adhesion because it influences the stress transfer from the matrix to the fiber. Researchers have reported modifications of the roselle fiber to improve the fiber/matrix interfacial bonding for fabrication of polymer composites for different applications [20–23]. In addition, review papers covering the chemical and mechanical properties of roselle fibers in polymer composites have been published [18].

Alkalization is a common surface treatment for natural fibers. Many studies examining the effect of transformed into a more hydrophobic nature by the alkali treatment [24]. The alkali treatment also reduces the fiber diameter, thus increasing the aspect ratio. The increase in aspect ratio roughens the surface, which further improves the mechanical properties of the fiber, resulting in better bonding between the fiber and matrix [25]. After treatment, the roselle fiber clearly developed a rough surface, and the impurities were removed, which leads to an improvement of the mechanical properties of the composites, as shown in Fig. 2. Physically, the presence of a rough surface provides a mechanical locking between the fiber surface and the matrix, which may enhance their interfacial bonding [26]. Alkali treatment of natural fiber is illustrated in Scheme 1 [27].

An additional effective chemical treatment of natural fibers involves immersion in a silane coupling agent. Many studies have been performed using this method, and an extensive review was performed by [28]. Before immersion into this chemical, pretreatment with NaOH is required to enable a more effective reaction with the chemical. Finally, this treatment improves the interface and bonding between the fiber/matrix surface [27]. Generally, there have four steps of chemical reaction between silane coupling agent and natural fibers which are hydrolysis, self-condensation, hydrogen bonding, and finally surface grafting [28]. Figure 3 shows the reaction of natural fibers with silane chemical. In this study, alkalization and a silane coupling agent treatment were used due to the low cost and efficiency of these methods. Different percentages of NaOH (3%, 6%, 9%) and a silane coupling agent treatment were used to study their effects on the chemical [Fourier transform infrared spectrometry (FTIR)], physical (water absorption), and mechanical (tensile and impact tests) properties as well as the morphology (scanning electron microscopy) of the fiber.

METHODOLOGY

Materials

Vinyl ester (VE) obtained from Polymer Technology Pte. (Singapore) was used in this study. The density, heat distortion temperature (HDT), viscosity and glass transition temperature of VE are 1.6 g/cc, 120°C, 400 cps, and 104.44–143.33°C, respectively. Methyl ethyl ketone peroxide (MEKP) was used as a hardener. Roselle plants were collected from Selangor, Malaysia. Roselle fibers were extracted using a water retting process for 14 days. The retted stem of the roselle plant was washed in running water, and the fibers were removed manually. Next, the fibers were cleaned and dried in the sunlight. Finally, the fibers were ground and segregated using a sieve

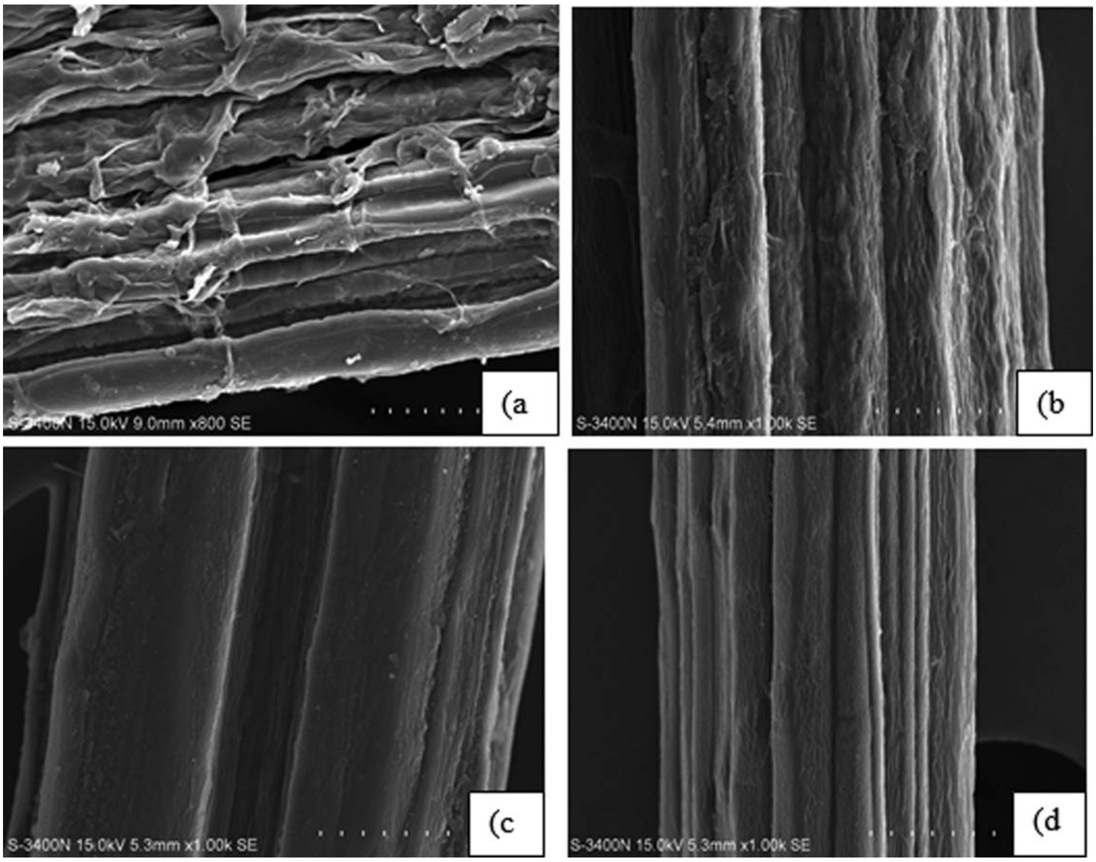

FIG. 2. SEM micrograph of (a) untreated roselle fiber, (b) 3% NaOH-treated roselle fiber, (c) 6% NaOH-treated roselle fiber, (d) 9% NaOH-treated roselle fiber (Nadlene et al. 2015).

machine (100–425 μm) to create the composite samples. The water retting process, fiber preparation, and composite fabrication are illustrated in Fig. 4.

Chemical Treatment

In this study, the fibers were prepared via 4 different treatments. Roselle fibers were immersed into three concentrations of NaOH (3%, 6%, 9%) for 2 h at room temperature in a basin. For the silane coupling agent treatment, the 6% NaOH-treated fibers were further immersed in silane solutions for 24 h. After the chemical treatment of the roselle fiber, the fibers were thoroughly washed with running water and dried in oven at 104°C for 48 h to eliminate the moisture effect of the fibers [29].

Composites Samples

The wet hand lay-up process was used for sample preparation of roselle fiber-reinforced vinyl ester composites. A rectangular mold constructed of an aluminum sheet with a certain dimension was used for the composite samples. The composite sample was prepared by mixing 5 wt% of roselle fiber and 92.5 wt% of VE. First, the roselle fiber was gradually added to the VE composite and stirred using a mechanical stirrer at 100–250 rpm until the mixture was uniformly distributed. Then, 2.5 wt% of MEKP was added to the composite mixture for curing. Finally, the mixture of the roselle fiber and VE resin was poured into the aluminum mold and cured for 24 h at room temperature. The samples were cut from the cured composites into certain dimensions according to the ASTM for the tensile test and impact test.

Water Absorption Test

In this study, the water absorption percentages for roselle fiber were determined using ASTM D570-98 [30]. The test was conducted by immersing the composite samples into distilled water for 10 days. The weight difference can be used to determine the water absorption rate. In this study, the rate of percentage weight increase was recorded for 10 days at different time intervals (2, 8, 24, 240 h). Prior to the test, the moisture content in the composite specimens was removed by placing them in the oven at 80°C until no mass change could be measured. The samples were then immersed and removed from water, and then all of the water on the sample was removed with a cloth or tissue paper. The water absorption percentage was determined using *Eq. 1*. Three

$$Fiber - OH + NaOH \rightarrow Fiber - O - Na + H_2O$$

SCH. 1. Alkali treatment of natural fiber [27].

samples were prepared, and the average water absorption percentage was calculated. The samples were weighed as M_0 prior to immersion in fresh water. After immersion, the samples were then weighed again as M_1.

$$\text{Water absorption } (\%) = \frac{M_1 - M_0}{M_0} \times 100 \qquad (1)$$

Fourier Transform Infrared Spectrometry

To examine the effects of the roselle fiber treatments on its chemical composition, FTIR was performed. IR spectra of the fibers were recorded using a Jasco FT-IR 615 cc spectrometer over a frequency range of 400–5,000 cm^{-1}, operating in attenuated total reflectance (ATR) mode.

Thermogravimetric Analysis

Thermal characterization of treated and untreated roselle fibers was performed using a Q series thermal analysis machine from TA Instruments. ASTM D3850 was used in this analysis. Thermogravimetric analysis (TGA) measures the weight changes in a material as a function of temperature (or time) under a controlled atmosphere. It is important to determine the degradation of the natural fiber at a high temperature before using it in a polymer composite. Approximately 4.8 mg of roselle fiber was placed in the chamber. Analysis was performed in a nitrogen atmosphere over a temperature range of 50–600°C and with a heating rate of 10°C/min.

Mechanical Testing

To evaluate the effect of the fiber surface treatment on its mechanical properties, tensile and impact tests were performed. The goal was to analyze the interfacial bonding between fiber and matrix from the failure samples. The tensile test is a simple method that reveals the mechanical properties of composite materials. Several significant mechanical properties can be obtained from tensile tests, such as Young's modulus, tensile stress, maximum elongation, tensile strain and yield stress. The samples were cut into 150 × 15 × 3 mm strips using a band saw. The tensile properties of roselle fiber-reinforced vinyl ester composites were determined using a Universal Testing Machine (model Instron 5556) according to ASTM D5083. The gauge length of the samples was 100 mm, and the cross-head speed was 50 mm/min with a 5 kN load cell. Five samples were prepared to perform a tensile test for each group of the different fiber treatments. The Izod impact test was performed according to ASTM D256 at room temperature. The impact test was performed using a digital INSTRON CEAST 9050 pendulum impact tester. The samples were cut into 64 × 12.7 × 3 mm strips for testing. At least five samples were examined for each test. Impact strength was calculated by dividing the impact energy by the cross-section area of the specimen, as shown in *Eq. 2*.

$$\text{Impact strength} = \text{Impact energy (J)} / \text{area} \left(\text{mm}^2\right) \qquad (2)$$

Morphological Analysis

Morphological studies were performed in detail on the fractured surface of impact test samples using a scanning electron microscope (SEM), model Hitachi S-3400N, at an accelerating voltage of 15 kV. The samples were gold coated to provide electrical conductivity, which did not significantly affect the resolution, thus obtaining good quality results.

RESULTS AND DISCUSSION

Water Absorption Behavior

Natural fibers have many advantages for use as a reinforcement material, that is, they are environmentally friendly and possess similar properties to synthetic fibers; however, flaws remain in natural fibers. The hydrophilic behavior of natural fibers causes difficulty in attaining a good adhesion between fiber/matrix and contributes to high water absorption of the natural fiber, which weakens the composite product in applications [31]. However, this problem can be overcome with surface treatment of the natural fiber. In this study, the untreated and treated roselle fiber was investigated to evaluate the effect of the treatment on reducing the water uptake of the roselle fiber-reinforced vinyl ester. From the literature, it can be concluded that water absorption on the natural fiber-reinforced composites is a crucial limitation for the product application because natural fiber absorbs more water compared with synthetic fiber [30]. The effect of this absorbed water content is to degrade the mechanical properties [32, 33]. Figure 5 shows the water absorption percentages of roselle fiber-reinforced vinyl ester with the different chemical treatments of 3%, 6%, and 9% NaOH and a silane coupling agent.

Water in natural fiber-reinforced composites can be transported through several natural plant mechanism. Microcracks in the polymer matrix can enable the water molecules to penetrate, while microgaps between polymer molecular chains may allow the inward diffusion of water molecules. In addition, the capillary effect may transport water through the fiber/matrix interface. These phenomena cause unwanted deformation or changes in the mechanical properties, such as swelling, plasticizing and even

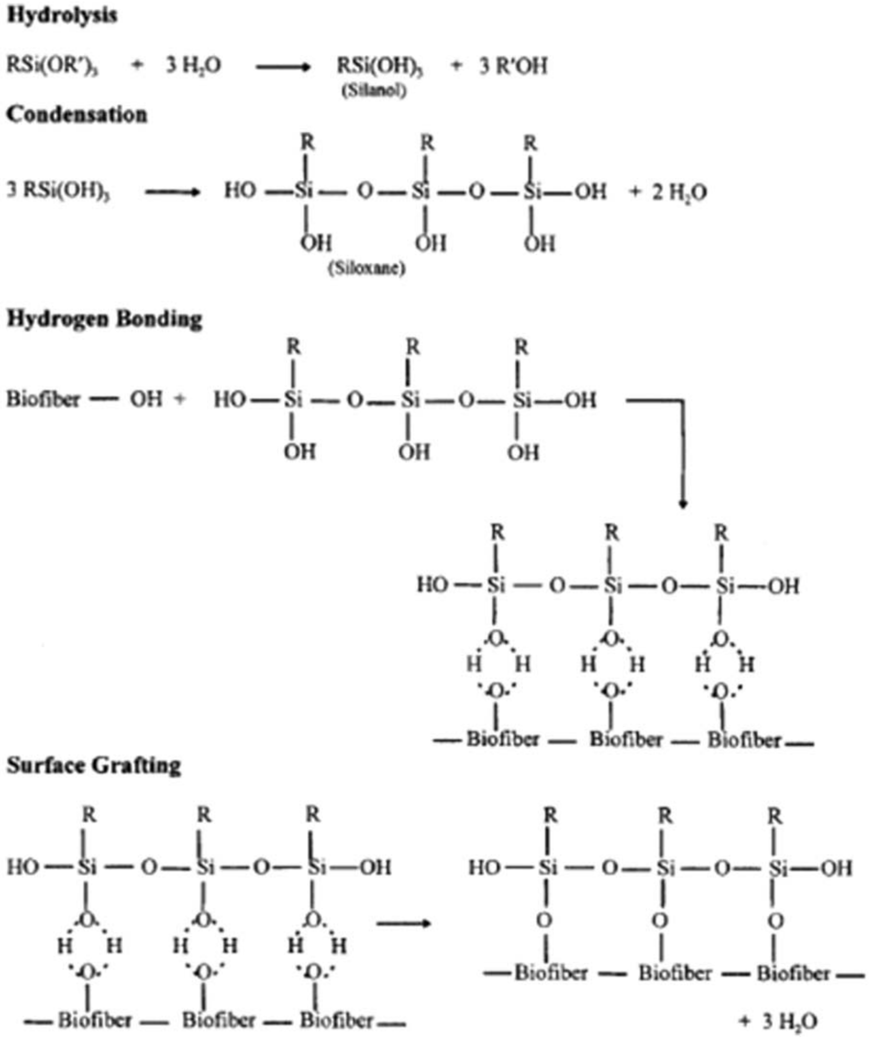

FIG. 3. Chemical reaction of silane coupling agent with natural fibers.

degradation. Flaws such as micro-voids caused by incompatibility of the hydrophobic resin and the hydrophilic roselle fibers may further cause water retention [34].

Generally, the treated fiber has been shown to reduce the water absorption percentage of the composite samples and this finding is in good agreement with other research paper [35]. All samples show that the water absorption occasionally increases, which is most likely due to the hydrophilic behavior of the plant-based fiber. The water absorption percentage increased with immersion time, reaching a certain value at a saturation level, beyond which no more water was absorbed, and the water content absorbed by the composite specimens remained constant. The water absorption result obtained is similar to that in other studies in which the water absorption level increased with the abundance of hydroxyl groups —OH on the cellulose molecules in natural fibers. Hydrogen bonds with water molecules can be formed by these hydroxyl groups, thus increasing the water absorption rate of the reinforced composites compared with neat polymer [36, 37]. The roselle fiber treated with a silane coupling agent has the lowest value of water absorption, while the untreated fiber has the highest percentage of water absorption. Initially, the water absorption of the composite samples fluctuated and continuously increased until it reached the saturation point. The untreated and 6% NaOH-treated fibers reached the saturation point at 180 h with a maximum water uptake of 2.2% and 1.75%, respectively. After a 24-h immersion, untreated fiber had the highest percentage of water absorption, followed by 3%, 6%, and 9% NaOH-treated fibers, and the lowest percentage was from fiber treated with the silane coupling agent, with values of 0.83%, 0.68%, 0.65%, 0.54%, and 0.48%, respectively.

Theoretically, alkali treatment affects the chemical composition of the fibers, which can reduce their water absorption. This result might be due to the removal of the lignin and hemicellulose components, the wax and oil of the fiber [38], which is illustrated in Fig. 6. The effect of alkalization by applying an increasing concentration of sodium hydroxide on the fiber was found to be promising because the treatment changes the fiber surface topography and reduces the fiber diameter [39]. In addition, the

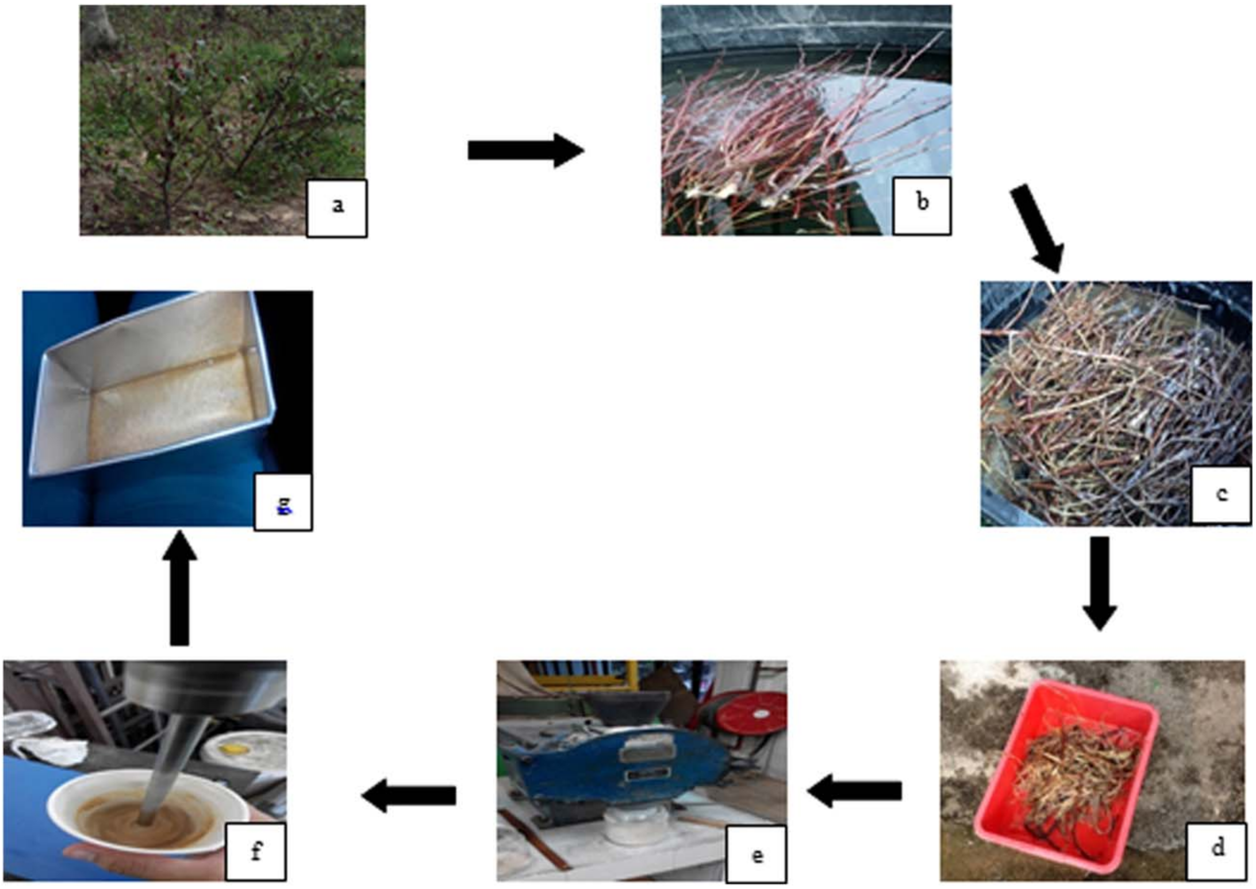

FIG. 4. The fabrication process of roselle fiber-reinforced vinyl ester composites. (a) Roselle plant. (b) The roselle stems were cut and immersed in water for 14 days (water retting). (c) After 14 days, the roselle fibers were ready for extraction. (d) The roselle fiber was dried for 5 days. (e) The grinding process. (f) The roselle fiber was mixed with VE using a mechanical stirrer. (g) The roselle fiber-reinforced vinyl ester composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

affinity of the roselle fiber-reinforced vinyl ester composite toward water was increased, which improved the surface area of cellulose on the surface to promote chemical bonding with the matrix material. A significant amount of water was absorbed through capillary action through the sides of the specimen because the fibers were completely attached to the resin matrix [30]. Roselle fibers are hydrophilic; thus, they can store more water than vinyl ester resin. From the results obtained, the silane coupling agent treatment was the most effective treatment because it reduced the water absorption of the composites and improved their mechanical properties. To apply the silane treatment, the fibers must be soaked in a dilute solution of silane. Silane may be diluted by a water/alcohol or water/ketone mixture. Water will then break silane into silanol and alcohol. Silanol will form stable covalent bonds with the cell walls when it reacts with the —OH groups of the cellulose present in natural fibers [40]. Usage of silane increases the fiber surface area by enhancing the degree of crosslinking in the interface region, which strongly bonds the fiber and matrix [41]. The silane coupling agent generates a water resistant bond at the interface between the matrix and the natural fibers. It has the unique chemical and physical properties of not only enhancing bond strength but also, more importantly, preventing debonding at the interface during composite aging. The improvement of the interfacial bonding between vinyl ester and roselle fiber reduced the water movement into the composite samples, and the number of —OH groups was reduced from the cellulose structure. In the case of the untreated roselle fiber composite, a higher water absorption might be due to the poor wettability and weak adhesion between untreated roselle and vinyl ester and due to defects, such as voids.

CHEMICAL ANALYSIS

The chemical structure of the roselle fiber components was analyzed using FTIR–ATR. The main absorbance peaks of interest in this study were identified and are depicted in Fig. 7. The FTIR spectrum of the roselle fibers shows absorption bands of chemical groups characteristic of lignocellulosic fiber compounds: cellulose, hemicellulose, and lignin. These components are primarily

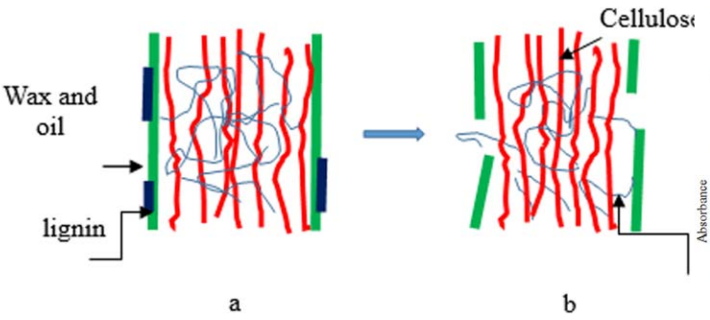

FIG. 5. Water absorption curve for roselle fiber reinforced vinyl ester with different treatments. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

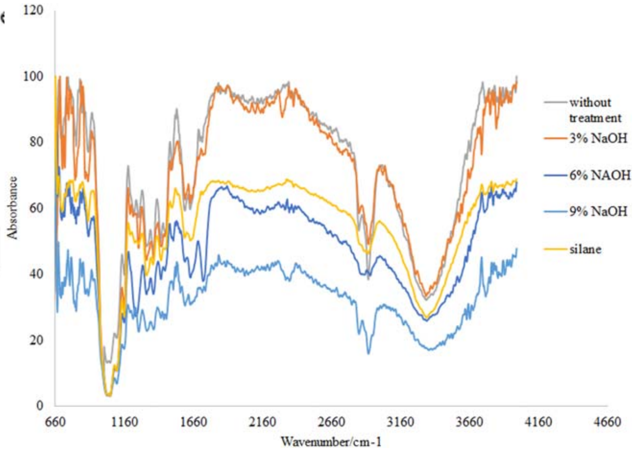

FIG. 7. FTIR spectra of roselle fiber constituents and the treated fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

composed of alkenes, aromatic groups and various oxygen-containing functional groups (esters, ketones, and alcohols) [42]. The functional groups detected in the FTIR spectra also provide evidence of the chemical constituents in the fiber, as discussed in TG/DTG, such as cellulose, hemicelluloses, and lignin [43]. For example, the peaks at 1,000–1,300 cm^{-1} correspond to the C—O group stretching from the lignin in the fiber [42]. Thus, as observed in the roselle fiber without treatment, the characteristic peaks at 1,032 cm^{-1} were assigned to the aromatic C-H in plane deformation and the C—O stretching vibration in primary alcohols (guaiacyl) of lignin. For the silane coupling agent treatment, the peaks shifted to 1,057 cm^{-1}, while for the 3%, 6%, and 9% NaOH treatments, the peaks were at 1,057, 1,056, and 1,054 cm^{-1}, respectively. This result indicated that lignin was removed from the treated fibers. The effects of the different concentrations of NaOH on the removal of lignin were nearly the same according to the absorbance bands, and for the silane-treated fibers, a similar peak to that in the 6% NaOH treatment appeared in the same region. This result indicates that there was no reaction between lignin and the silane chemicals because the fiber was treated with 6% NaOH before the silane coupling agent treatment [44].

The peaks at 2,926 and 2,858 cm^{-1} are the characteristic bands for the C—H stretching vibration from CH and CH_2 in the cellulose and hemicellulose components in the untreated roselle fibers [43]. It can be observed from the graph that the absorbance for this range of peaks is not markedly different, as the peaks are similar. For the 3%, 6%, and 9% NaOH treatments, the peaks were at 2,927 and 2,859 cm^{-1}, 2,924 and 2,854 cm^{-1}, and 2,940 and 2,864 cm^{-1}, respectively. For the silane coupling agent treatment, the peaks were at 2,927 and 2,858 cm^{-1}. The absorbance bands were slightly different between the fibers without treatment, the 3% and 6% NaOH and the silane coupling agent-treated fibers, suggesting that the chemical treatment did not affect the cellulose structure of the fiber. However, degradation of the cellulose and hemicellulose structure was observed for the 9% NaOH-treated fiber, in which the peaks show a lower absorbance compared with the others.

A broad absorption band in the region from 3,600 to 3,100 cm^{-1} corresponds to the characteristic —OH stretching vibration and the hydrogen bonding of the hydroxyl groups. It can be seen that there was a wide range of peaks from 3,200 to 3,500 cm^{-1} for both of the fibers, indicating the presence of OH groups in the fiber, which provided further evidence for the presence of water molecules in the fiber, as discussed earlier. This result was also supported by other studies in which these peak

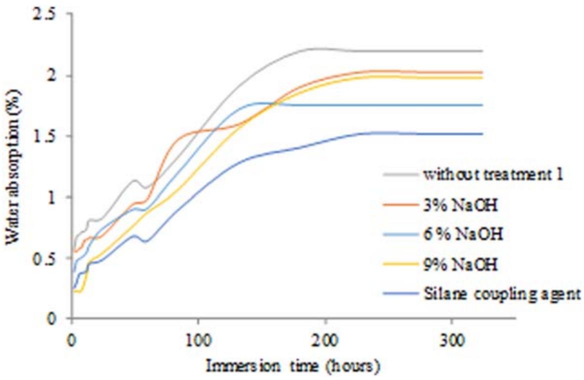

TABLE 1. Thermal degradation analysis of roselle fiber subjected to different treatments.

Roselle Fiber	Weight loss (%) at temperature range of 30 to 110°C	First Degradation phase		Second Degradation phase		Residual char (wt. %)
		T_I (°C)	T_{peak} (°C)	T_{II} (°C)	T_{peak} (°C)	
without treatment	7.96	200–307	312.76	307–400	348.49	24.35
3% NaOH	7.87	200–330	294.04	330–415	362.11	4.781
6% NaOH	7.89	200–337	295	337–410	364.94	17.88
9% NaOH	7.64	200–320	297	320–416	367.43	13.35
Silane coupling agent	7.55	200–311	237.33	311–441	341.20	20.46

ranges were attributed to the stretching of hydroxyl groups due to hydrogen bonding between the molecules. From the results obtained, the silane coupling agent yielded the lowest absorbance. It was observed that the peak of the silane-treated fiber (3,366 cm^{-1}) was slightly shifted to the right compared with the untreated fiber (3,343 cm^{-1}). The absorbance of the NaOH-treated fibers shows slight differences among the NaOH concentrations. The peak of 3% NaOH is 3,343 cm^{-1}, while the 6 and 9% NaOH treatment gives the same peak at 3,349 cm^{-1}. It was also observed that the peak of the treated fiber had a lower absorbance than the untreated fibers, indicating reduced hydrogen bonding. This may be due to the lower absorbances that were detected, suggesting reduced hydrogen bonding because fewer water molecules were present in the treated fiber than in the fiber without treatment; that is, once the fibers have been treated with the chemical (NaOH and silane coupling agent), the water absorption of the treated fibers is reduced. This further supports the obtained results of the water absorption test in which there is a lower water absorption in the treated fiber compared with the fiber without treatment.

THERMOGRAVIMETRIC ANALYSIS

TGA was performed to provide precise information on the thermal stability of roselle fiber subjected to different chemical treatments (alkalization and the silane coupling agent). The thermal stability or thermal degradation of natural fibers is important because the fibers are also affected during exposure to elevated temperatures during the manufacturing process with polymer/resin. It is crucial to confirm that the fiber used in a composite can withstand the temperature applied during the manufacturing process or application of the product.

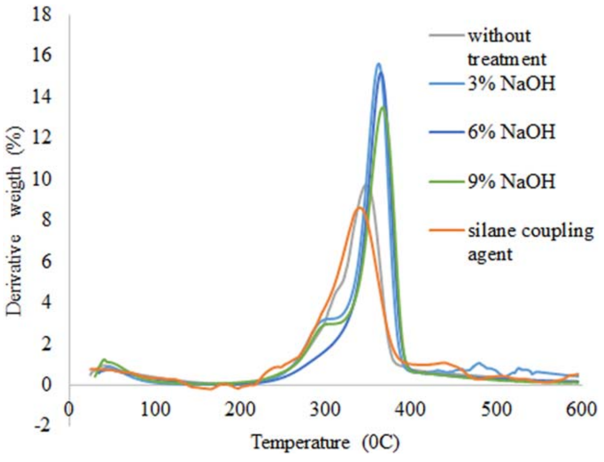

FIG. 8. TGA of roselle fiber with different surface treatment. [Color

Table 1 shows the characteristic data of the thermal behavior of the roselle fiber at high temperatures. Approximately 5 mg of roselle fiber was used to evaluate the thermal behavior. Generally, there are four phases in the thermal degradation of natural fiber. Figures 8 and 9 show the TGA and DTG curves subjected to different chemical treatments, respectively. The results reveal that no significant difference in thermal degradation was found between the treated and untreated fiber. The degradation trends are nearly the same.

Generally, there were four thermal degradation phases of the roselle fiber. The first degradation phase is moisture evaporation, followed by the decomposition of hemicelluloses, cellulose, and lignin, leaving ash as the final residue [45]. The first degradation phase of natural fibers occurs between 30°C and 110°C [43] because of the evaporation of the moisture content in the fiber. In the case of roselle fibers, moisture evaporation occurred over the range from 30°C to 110°C. As the temperature of the fiber increased while it is heated, the fibers became lighter because of the evaporation of bound water and

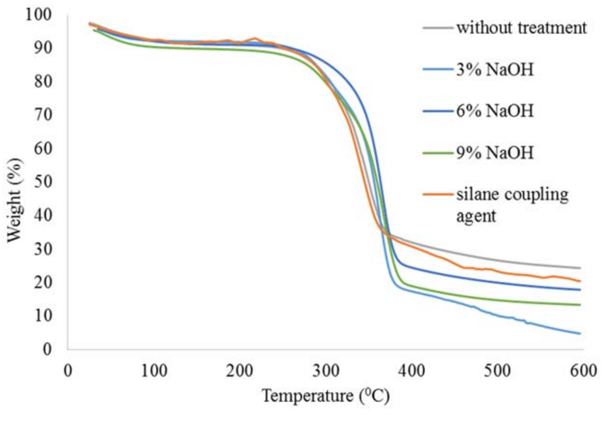

FIG. 9. DTG curves of different treatments of roselle fiber. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

volatile extractives. Although fewer volatile extractives are present, they tend to move toward the outer part of the fiber stem surface. This movement occurs due to the water movement from the inner to the outer part of the fiber stem surface as the water available at the outer part evaporates. From the obtained results, it can be observed that the untreated fiber exhibited the highest percentage of mass loss of 7.96%, while the 3%, 6%, and 9% NaOH-treated fibers had mass losses of 7.87, 7.89, and 7.64, respectively. The lowest weight lost in the first phase of degradation was 7.55%. The mass loss results reflect the moisture content of the roselle fiber.

The second phase of thermal degradation of the roselle fiber is due to the thermochemical change of the hemicellulose content in the fiber caused by the cellular breakdown as the temperature is increased [46]. It was noticed that the degradation of hemicelluloses of the treated and untreated fiber occurs over the range of 200°C–330°C. The peak temperature of the hemicelluloses of the treated fiber was lower compared with the untreated fiber, possibly because of the removal of lignin and hemicelluloses during the alkali treatment [47].

The third phase of degradation involves the cellulose structure. Degradation of cellulose will only begin after the hemicellulose decomposition is complete, primarily because of the higher content of the crystalline chain compared with the amorphous form, causing cellulose to be more thermally stable [45]. Overall, cellulose begins to decompose at 307°C and completely decomposes at 441°C. From the literature, cellulose will start to degrade at a high temperature of 315°C [48]. The range of the cellulose degradation temperature is shown in Table 1. The peak temperature of the cellulose structure of untreated roselle fiber was 348.49°C, and the peak temperature of treated fiber with alkalization increased, thus displaying a higher thermal stability. However, the silane coupling agent-treated fiber shows the lowest peak temperature of 341.20°C. The decrease in the thermal stability of the silane-treated fiber might be because the fibers became rough and more amorphous. The changes in the final phase decomposition temperature indicated that after the treatments, there is a substantial loss in cellulose and lignin degradation, as observed by several researchers [47–49]. Char residue is produced when cellulose is decomposed at high temperature. This is evident in Table 1, the percentage of char residue in treated fiber is lower in comparison to without treatment fiber because the presence of lignin and cellulose which is not removed from without treatment fiber. The result of TGA is in parallel with previous researchers findings which concluded that the thermal stability may be improved through alkali treatment. In addition to that, the reduction in char residue content is a result of decrement in the formation of carbonaceous char.

From the results obtained, it can be concluded that alkalization contributes to the higher thermal stability. As reported in several studies, surface treatments also partially dissolved the lignin and hemicellulose present in the fiber, increasing the amount of exposed cellulose. Furthermore, authors reported that alkali treatment causes a partial loss of cementing material via the rupture of ester linkages between polyuronic acid and lignin, increasing the percentage of crystallinity of alkali-treated fibers. Thermal stability can be enhanced by removing a certain proportion of hemicelluloses and lignin constituents [50].

MECHANICAL PROPERTIES

Tensile Properties

Tensile tests were performed in this study to evaluate the mechanical properties of the roselle fiber-reinforced vinyl ester composites. Two important properties, tensile strength and Young's modulus, were investigated in the tensile test. Tensile strength is an important parameter that can evaluate the maximum force and stress that can be applied until the fiber breaks, which is important for the design of the product, depending on the application. Young's modulus is used to measure the stiffness of an elastic material and is a quantity used to characterize materials. It is defined as the ratio of the stress (force per unit area) along an axis to the strain (ratio of deformation over an initial length) along that axis over the range of stress in which Hooke's law holds. In this study, 5 wt% of roselle fiber was used as reinforcement material to study the effect of the treatments on the mechanical and adhesion properties of the composites.

The effect of the NaOH and the silane coupling agent treatment on the tensile properties of roselle fiber-reinforced vinyl ester can be seen in Fig. 10. From the results obtained, it can be observed that the load increased gradually to the maximum value and then suddenly decreased, implying that a brittle fracture occurred in the material. Figure 10 illustrates the effect of the treated fiber on the tensile strength, and Young's modulus. Overall, the results show that the mechanical properties are substantially changed with the fiber treatments. As expected, the fiber composites resulted in a significant increase in tensile strength. This behavior was observed in both untreated and treated roselle composites, as shown in Fig. 10. The silane coupling agent treatment yields the highest tensile strength, 24.81 MPa, followed by treatment with 9% and 6% NaOH, 20.05 and 19.98 MPa, respectively. The tensile strength of the 3% NaOH-treated fiber is 19.38 MPa and that of the untreated fiber is 17.53 MPa. From the obtained results, the fiber without treatment shows the lowest tensile strength, revealing the weak adhesion between the fibers and the polymer. The weak adhesion between the fibers and the matrix can be seen in Fig. 12b where many pulled-out fibers can be observed. This failure mode is a clear indication of ineffective load transfer between the matrix and fiber. However, the tensile strength of fiber treated with NaOH did not show a significant difference, with results that were similar among the NaOH concentrations tested. Thus, alkalization improves the tensile properties compared to without treatment fiber but the

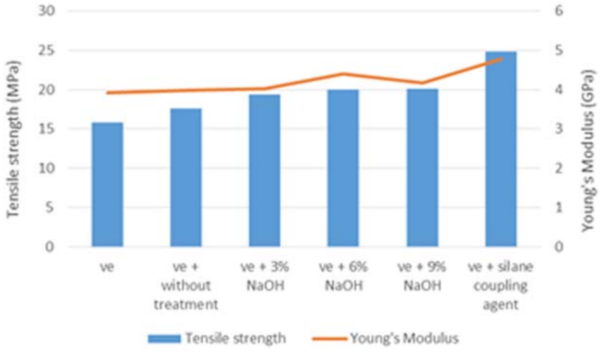

FIG. 10. Effects of chemical treatment of roselle fiber on tensile strength and Young's Modulus for vinyl ester composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

concentrations of alkali chemical does not effect the tensile stress. The silane coupling agent increased the tensile strength by 41% compared with the fiber without treatment. This is due to the good interfacial bonding between fiber and polymer. The interfacial bonding of the silane-treated fiber can be seen in Fig. 12f, where the amount of fiber pull-out is reduced and there is no gap between fiber and polymer. Furthermore, the increased tensile strength is an indicator that the silane conditions promoted good wettability and better fiber–matrix adhesion, allowing efficient stress transfer between the matrix and the fibers [50]. The adhesion between the resin and fiber strongly influences the mechanical properties. Alkali treatment also shows an improvement of tensile strength in which it is increased by approximately 14%. Moreover, as reported in the literature [24], alkali treatment reduces the fiber diameter, which indirectly increases the aspect ratio, thus improving the mechanical characteristics of the composites. However, the different concentrations of NaOH did not result in any significant changes in tensile strength.

Figure 10 demonstrates also the effects of the chemical treatment on Young's modulus of roselle fiber-reinforced vinyl ester. Generally, it was observed that the maximum Young's modulus is from the fiber treated with silane coupling agent, with a value of 4.77 GPa, followed by 6% NaOH at 4.41 GPa. The lowest Young's modulus is for the fiber without treatment followed by 3% and 9% NaOH treatment, with values of 3.97, 3.91, and 4.026 GPa, respectively. There is a significant correlation between Young's modulus and the chemical treatment effect where the treatment improve Young's Modulus of the composites. The higher concentration of NaOH and further treatment, such as with the silane coupling agent, increase Young's modulus of the composite. The results obtained show that the fiber contents and the type of matrix influence the modulus and the tensile strength of the composites.

Impact Test

A material's ability to absorb and dissipate energy under shock loading or impact can be best represented by the impact property [51]. The composites' impact energy level depends on several parameters, such as the nature of the constituents, the construction and geometry of the composites, fiber arrangement, fiber/matrix adhesion, and test conditions. For impact loading, the matrix fracture, fiber/matrix debonding, fiber breakage, and fiber pull-out are important modes of failure in the fiber composites. Debonding may occur if the applied load exceeds the fiber/matrix interfacial bond. This load is normally transferred by shear force to the fibers. The frictional force along the interface may transfer the stress to the debonded fiber. Fibers may break if the fiber stress level exceeds the fiber strength. Ultimately, energy is dissipated when the broken fibers are pulled out of the matrix. The impact strength of composites is influenced by two factors which are the capability of the fiber to absorb energy that can stop crack propagation and poor interfacial bonding which induces micro spaces between the fiber and the matrix, resulting in easy crack propagation [52].

In this study, the effects of chemical treatment (0%, 3%, 6%, and 9% NaOH and silane coupling agent) were evaluated on the impact properties of roselle fiber-reinforced vinyl ester composites. The effects of the treatment are illustrated in Fig. 11. The results show that the presence of roselle fiber reduced the impact strength for treated and untreated biocomposites compared with neat vinyl ester. It could be due to the fiber distribution, which lead to localized stress concentration points and poor interfacial adhesion (as can be seen in the Fig. 13 where some of the composite showed a gap between fiber and matrix). Interfacial adhesion between fiber-matrix influence how the stress should be transferred from the impact load, to the fiber, via the matrix. The highest impact properties of roselle fiber-reinforced vinyl ester are from untreated fiber, with a value of 6.60 kJ/m^2, followed by 3% NaOH and 9% NaOH, with values of 5.68 and 4.89 kJ/m^2, respectively. The lowest impact energy was found in the fiber treated with the silane coupling agent (4.25 kJ/m^2) followed by 6% NaOH (4.46 kJ/m^2). Note that the impact strength for the fiber with 6% NaOH and the silane coupling agent treatment was the lowest of the impact properties compared with the others, possibly because of the good interlocking surface between the fiber and

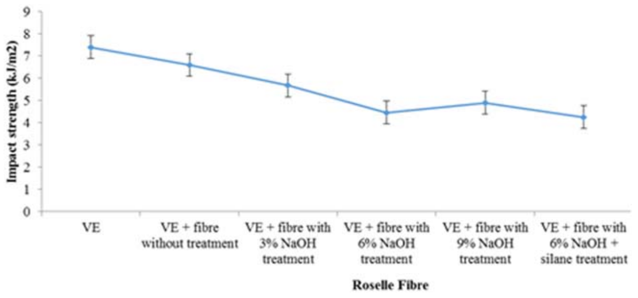

FIG. 11. The effect of chemical treatment on the impact strength of roselle fiber-reinforced vinyl ester. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

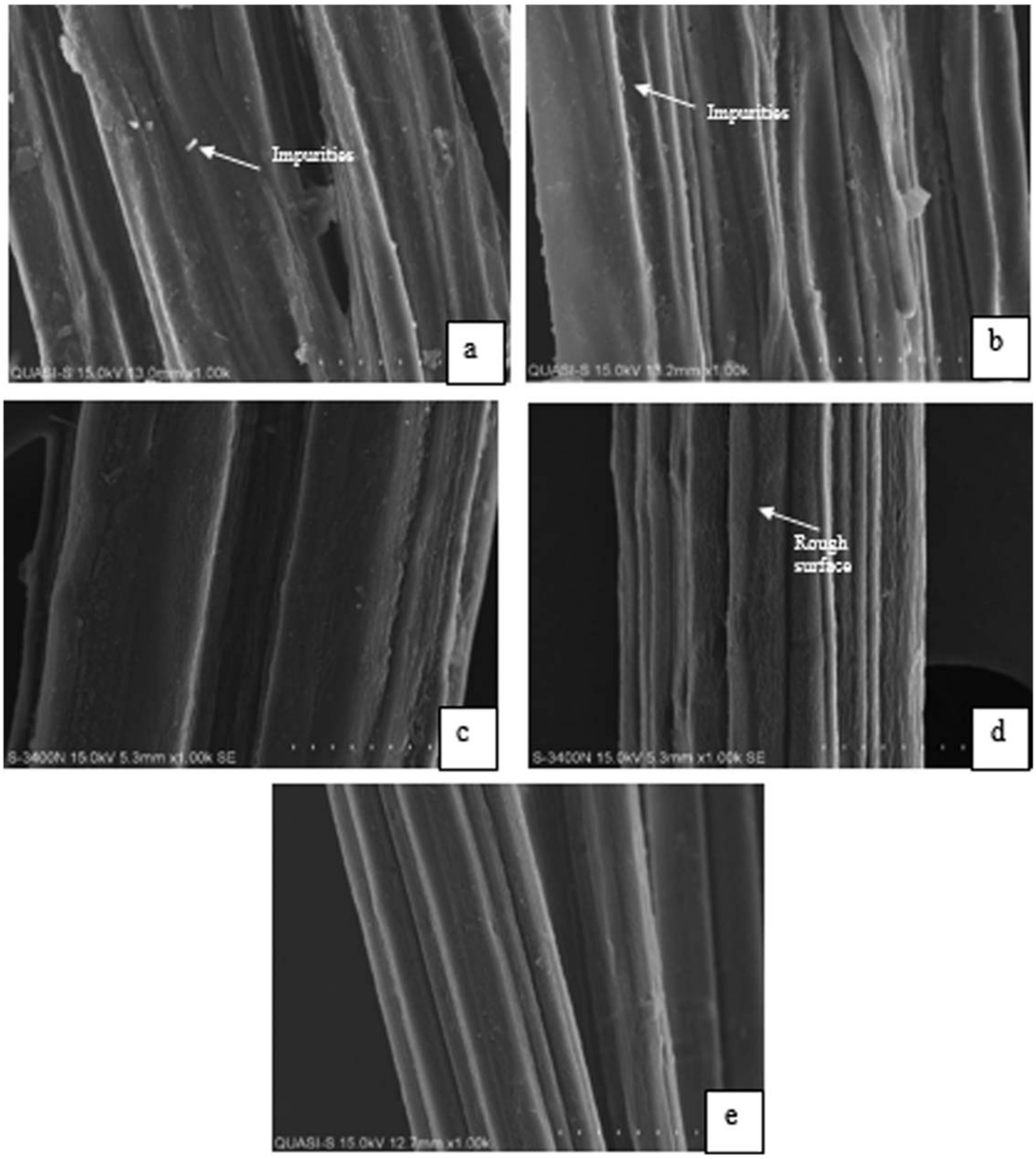

FIG. 12. Scanning electron micrographs of roselle fiber subjected to different treatments [(a) untreated; (b) 3% NaOH; (c) 6% NaOH; (d) 9% NaOH; (e) Silane coupling agent].

matrix of the sample. This result is in line with other studies stating that for a strong fiber-matrix interface, the impact strength of the composites decreases because of the reduction in fiber pull-out. This is because the pullout mechanism absorbed a substantial amount of energy as friction work during impact [53]. It can be seen in the SEM result of the failed samples in Fig. 12d and f that the fiber treated with 6% NaOH and silane coupling agent shows a good interface between fiber and matrix in which a lack of fiber pull-out in the samples was observed. Furthermore, the short fibers used in this study are likely to reduce the elongation at break, and this condition may reduce the impact-absorbing energy. The impact strength may be reduced if there is a stress concentration around the fiber ends or if the adhesive was poorly applied.

In conclusion, the impact test results indicated that the impact energy of the composites decreased when the roselle fibers were treated. This result was expected because the following is known to affect energy consumption during the impact:

1. Fiber–matrix adhesion: as explained earlier, the treatment increases the interfacial strength, thus reducing energy consumption by avoiding fiber pull-out. Under this condition, the fracture occurs with only a slight change in the cracking plane, breaking the fibers instead of pulling them out [53].
2. Fiber mechanical properties: the degradation of properties after treatment is undesirable for impact resistance.
3. Fiber spiral angle: Pavithran et al. found that fibers with small spiral angles form composites with reduced toughness compared to those with high spiral angles. Although

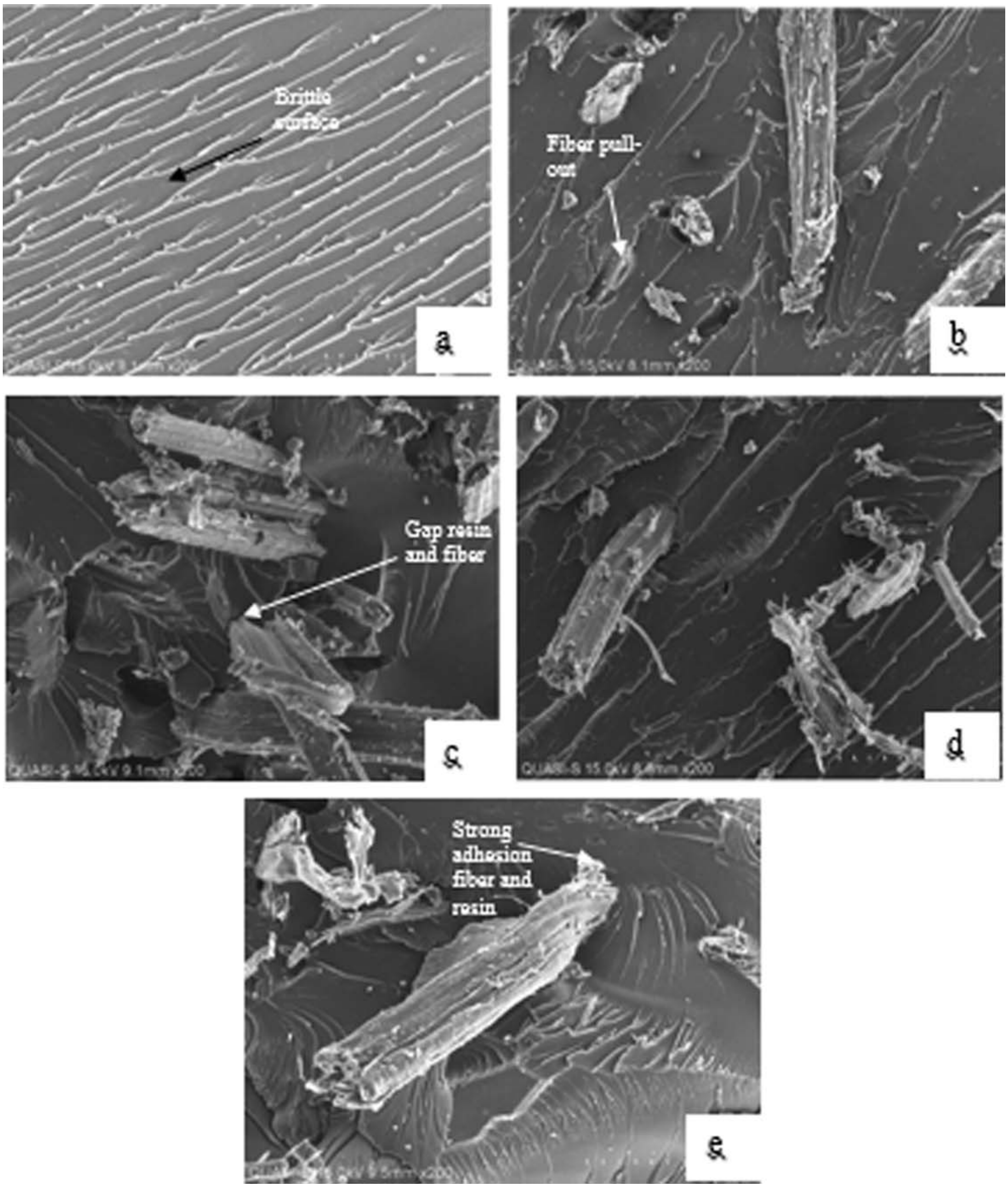

FIG. 13. Scanning electron micrographs of impact fracture samples of roselle fiber-reinforced vinyl ester subjected to different treatments [(a) vinyl ester; (b) without treatment; (c) 3% NaOH; (d) 6% NaOH; (e) 9% NaOH; (f) Silane coupling agent].

the comparison was made among different fibers, the spiral angle decrease was shown to be a factor that damages the composite toughness [54].

Morphology

The effect on surface morphology of the different chemical treatments and the interfacial bonding between fibers and matrix was investigated using SEM. Figure 12a–e shows SEM micrographs of untreated and treated roselle fibers, while Fig. 12a–f shows SEM micrographs of impact fracture surfaces of roselle fiber-reinforced vinyl ester subjected to different chemical treatments. It can be observed in Fig. 12a that the fibers contain impurities and wax, and there are many burrs on the fiber surface. Generally, the wax, impurities and other non-cellulose constituents can be removed by alkalization [55, 56] which can improve their wettability.

Figure 12b shows 3% NaOH-treated roselle fibers, revealing that the impurities remain but are fewer than in the untreated fiber. Thus, 3% NaOH is not a sufficiently high concentration to modify the surface and to remove all the impurities. Figure 12c shows roselle fiber with the 6%

NaOH treatment. It can be observed that the surface of the roselle fiber was smooth, and nearly all of the impurities were removed. The surface is rougher than in fibers without treatment and in those with the 3% NaOH treatment. Figure 12d and e shows the roselle fiber treated with 9% NaOH and the silane coupling agent, respectively. Treatment of the roselle fiber with 9% NaOH and silane removed all the impurities, as shown in the figures. Even the fiber surface is clean, but it appears jagged, and the surface is rougher. From the surface morphology examination, the 9% NaOH and silane treatment of the roselle fiber is the cleanest and roughest among the treatments. From the literature, a rough surface of the natural fiber is the most desired surface because it will increase the interfacial bonding between fiber and matrix [57]. Physically, the presence of a rough surface provides the mechanical lock between the fiber surface and matrix, and it may enhance their interfacial bonding, resulting in good mechanical properties, reduced fiber pull-out and fewer gaps between the fiber and matrix in the composite materials [56, 58]. As mentioned in the literature review, this dewaxing of the fibers improved fiber and matrix adhesion, which can be seen in Fig. 13d and e in which the fibers appear to remain in the polymer matrix and have relatively fewer pull-outs compared with the untreated fibers due to the good interfacial bonding with the matrix. This phenomena specifies a higher interfacial shear strength for the treatment fibers and a good interfacial adhesion between the fibers and matrix [50]. Figure 12e shows the partitioning of cellulose and cleaner surfaces compared with the untreated fiber, and the rough and smooth surfaces offer good adhesion between the fiber and matrix, such as that achieved with alkalization.

SEM micrographs of the failed impact samples of roselle fiber-reinforced vinyl ester composites with different surface treatments are shown in Fig. 13b–f, while Fig. 13a indicates the failed impact sample of vinyl ester. Figure 13b shows that the interfacial bonding between the untreated roselle fiber and the matrix is not good, as shown by the gap between them and the pull-out fibers from the matrix. This might be attributed to the low adhesion between the fiber surfaces and the vinyl ester resin. Therefore, the tensile strength of this composite is low compared with the treated sample. The NaOH and silane coupling agent treatments can eliminate the impurities and wax from the surface of the fibers, enhancing the adhesion with the matrix (Fig. 13d–f). After the treatment, interfacial bonding between the roselle fiber and vinyl ester is markedly better than in the untreated roselle fiber composite, and the mechanical properties are improved. The silane coupling agent-treated fiber composite demonstrated the maximum tensile strength and the lowest impact values because the best interfacial bonding occurred in this composite.

CONCLUSIONS

The effects of alkalization and the silane coupling agent treatment of the fiber on the chemical, physical, thermal, mechanical and morphological properties were analyzed. Chemical analysis was performed using FTIR analysis, revealing that all of the treatments showed lower absorbance compared with the untreated fiber due to the removal of lignin and hemicelluloses during the treatment. The water uptake results show that the treated fiber had lower percentages of water absorption compared with the untreated fiber. Based on the results, the silane coupling agent is an effective surface treatment to improve the water absorption. This result is supported by chemical analysis in which the presence of hydroxyl groups is detected to a lesser extent compared with the untreated fiber. The effect of different surface treatments on the roselle fiber appears to have an inconsistent effect on its thermal properties. Alkalization treatment improved the thermal stability of the roselle fiber due to the removal of lignin and hemicelluloses in the fiber structure, which exposes more cellulose. In contrast to the silane coupling agent, the effect of alkalization on the thermal properties is insignificant. For the mechanical properties of treated roselle fiber-reinforced vinyl ester, there was a positive improvement for the tensile strength, but it was in contrast to the impact properties. The tensile results show that the higher concentration of NaOH provided better tensile properties. However, the silane coupling agent provided the highest value of tensile strength. This result is supported by the SEM results, which showed strong adhesion and less fiber pull-out in the fracture samples. In conclusion, alkalization and the silane coupling agent provided a positive improvement on the properties of roselle fiber-reinforced vinyl ester.

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