# Study on Interfacial Properties of Unidirectional Flax/Vinyl Ester Composites: Resin Manipulation on Vinyl Ester System

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**ABSTRACT:** Flax fibers are widely used as reinforcements in bio-based polymer matrix composites. This study investigated the hydrophilic nature and surface purity of flax fiber that affects fiber/matrix adhesion in combination with hydrophobic structural polymers via matrix modification and the utilization of fiber treatment, specifically in a flax/vinyl ester (VE) composite. A new method to manipulate the vinyl ester system with acrylic resin (AR) was developed to produce flax reinforced. On the other hand, different types of chemical and physical treatments were applied on the flax fiber. FTIR was applied to evaluate the effects of surface treatments. Dynamic mechanical analysis (DMA) was used to analyze the unmodified and modified VE resin system. The surface of untreated and treated flax fibers and their composites were analyzed by scanning electronic microscopy (SEM). Sodium ethoxide-treated flax/ VE with 1% (wt) AR caused the best mechanical performance among all the flax/VE composites evaluated. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 128: 3490–3500, 2013

## INTRODUCTION

Bast cellulosic fibers (e.g., flax, hemp, kenaf, jute, etc.) have an attractive potential as reinforcements in composites. They possess clear advantages over synthetic reinforcing materials, e.g., glass and basalt fibers, such as lower density, relatively higher toughness, comparable strength, and comparable stiffness.[1] They also offer a competitive advantage in terms of insulative properties and offer the potential of biodegradability. Interest in using flax fibers as reinforcements in biocomposites is increasing, and as a result, these type of fibers are being extensively utilized in many automotive applications, including interior dash and trim components as well as underbody shields and covers.[2]

Flax fiber cells are composed of about 70–80% cellulose[3] (dried fiber), which are cemented as fascicle bundles by means of noncellulosic chemicals, e.g., lignin, hemicelluloses, pectin, protein or mineral substances, resins, tannins, waxes, dyes, etc. The selective removal of noncellulosic components is of interest for improving their properties as fibers in composites.[4] Chemical treatments of flax fibers and the ensuing selective removal of noncellulosic compounds is one such technique.

A large presence of available hydroxyl groups in the chemical structure of cellulose increases the hydrophilicity of flax. This hydrophilic behavior of the flax fibers leads to a low compatibility with hydrophobic polymer matrices and amounts to a loss in dimensional stability and structural integrity, as water uptake causes swelling of the fibers. Therefore, the inherent lack of compatibility between lignocellulosic fibers and polymeric matrices leads to low strength of interfacial bonding, and to moderate adhesion between the fiber and the matrix, which collectively affect the final mechanical properties and performance of their composites.[5,6]

Many chemical treatments have been investigated for modifying the surface properties of these lignocellulosic fibers. Some challenges in fiber/matrix adhesion are addressed by treating fibers with suitable chemicals, such as alkaline treatment, and coupling agents that decrease the number of hydrophilic groups, thereby decreasing the net availability of free hydroxyl groups that are hydrogen bonded with cellulose. These surface treatments can also improve the degree of adhesion between flax fiber and polymer matrices.[5,7–19] However, chemical treatments often adversely affect the properties of flax fibers. For example, the alkaline treatment can decrease the tensile modulus of cellulosic fibers.[15]

The second constituent of the composite is the resin matrix, often a thermosetting resin. In terms of liquid molding thermoset resins that are used in composites, the mechanical properties and cost of vinyl ester (VE) are intermediate to those of polyester or epoxy resins. VE offers better resistance to moisture

absorption and hydrolytic attack than polyesters,[20] which is because of a smaller amount of ester groups in the VE structure. These ester groups are readily hydrolyzed, leading to a significant moisture uptake in the cured composites.[21] For flax fiber reinforced composites, the resistance to moisture dictates the service life. Overall, VE is more difficult to process than polyester resin, requiring thorough surface preparation during cure to achieve acceptable levels of adhesion between fiber and VE. The scarcity of ester groups in VE also leads to hydrophobicity, which increases the difficulty of VE bonding with flax fibers. On the other hand, VE can be regarded as a modified form of epoxy because most VE grades are produced by a reaction of acrylic or methacrylic acid using an epoxy resin,[22] typically a bisphenol-A.[23] However, the advantage of VE over epoxy is the cost-effectiveness.

The mechanical properties of flax/VE composites have been studies by many other researchers. However, the effects of modified VE on the mechanical performance of flax/VE composites have not been investigated. Acrylic resin (AR) is obtained either as a thermoplastic or a thermosetting plastic, polymerized from acrylic acid, methacrylic acid, etc. The common uses of AR are in glossing paper, films coating, textile finishing, sealing, and adhesion.[24] AR is often used in combination with a chlorinated binder, where AR serves as a plasticizer. The functional groups of thermosetting AR cross-link with epoxy and polyurethane.[25] Hence, AR possesses the potential to crosslink with VE.[26]

In this study, novel treatment methods have been proposed and analyzed in two areas: (a) Chemical modification on flax fiber and (b) Manipulation of resin system. Within chemical modifications on fibers, sodium hydroxide (NaOH)/ethanol treatment (i.e., sodium ethoxide) was used, which is one of the common treatments used for cellulosic fibers,[15] and fibers hence treated with this method were chosen as the baseline for comparison with other treatments on fibers. Sodium ethoxide can clean the fiber surface without any curling/fiber deformation caused by NaOH water solution. In addition to the NaOH/ethanol treatment, fiber surface was coated with VE to increase the contact area between the fiber and the matrix. Toluene and tetrahydrofuran (THF) were used to disperse VE on the surface of flax fiber because of their comparable polarities with acetone, which were previously established as effective dispersion agents. Bleaching treatment was also investigated because it is particularly effective in decreasing the overall lignin content, which is expected to increase adhesion with the resin. In the resin manipulation study, AR was used to modify the matrix, to be examined for its effectiveness in cross-linking, and ultimately increasing the stiffness of the fiber-reinforced composite. Overall, the chemical surface treatments, namely (1) sodium ethoxide treatment, (2) AR/THF solution treatment, (3) bleaching treatment, (4) VE toluene solution treatment, (5) VE/THF treatment, and (6) AR additive were investigated.

The treated fiber and resin were analyzed using characterization techniques used in processing fiber-reinforced composites. Fourier transform infrared spectroscopy (FTIR) was used to determine the chemical changes caused by the chemical treatments on the fibers and the changes caused by manipulating the resin.

A modified vacuum assisted resin transfer molding (VARTM) method was used to produce unidirectional flax fiber/VE composite panels with a fiber volume fraction varying from 40 to 50%. The flax-reinforced VE composites were tested to determine mechanical properties in tension, flexure, and interlaminar shear. Dynamic mechanical analysis (DMA) was used to study the thermo-mechanical properties. The mechanical and thermal property trends were explained using spectroscopy and electron microscopy analyses on the treated fiber and resin. The surface of untreated and treated flax fibers and the tensile fracture surface of their composites were analyzed by SEM.

## EXPERIMENTAL PROCEDURE

### Materials

Unidirectional flax fibers were obtained from Europe through General Bailey Homestead Farm, Greenfield, NY. The flax fiber was uncut, natural color, from top part of stalk with a density of $\sim$ 1.4 g/cm$^3$. The resin system used for all grades was a vinyl ester resin Hydropel® R037-YDF-40 from AOC resins, and 2-Butanone peroxide (Luperox® DDM-9) solution was used as the hardener, obtained from Sigma-Aldrich. Acronal® 700 L AR was obtained from BASF Aktiengesellschaft, Ludwigshafen, Germany, which is an acrylic resin (copolymer of n-butyl acrylate and vinyl isobutyl ether). THF (puriss. p.a., ≥99 % (GC)) and sodium chlorite (technical grade, 80%) were synthesized in house.

### Surface Treatments

**Alkaline Treatment (N).** Flax fibers were immersed into 10 g/L NaOH/95% ethanol at 78°C for 2 h and then washed with distilled water to reduce color from the treated fibers and to attain a pH ≅ 7.0 (checked with pH paper). 78°C is close to the boiling point of ethanol and the high temperature can increase the reaction rate to clean flax fibers. The treated flax fibers were dried in an oven for 24 h at 80°C.

**VE Resin THF Solution Treatments (N3L, N3F, and N10F).** Three treatments were used, and in each case, the dried, NaOH-treated flax fibers were manually separated and then immersed into either 3 wt % VE/toluene solution (N3L) or 3 wt % VE/THF solution (N3F) or 10 wt % VE/THF solution (N10F) at room temperature for 1 h. The treated fibers were dried in an oven for 24 h at 80°C.

**3% Acrylic Resin THF Solution Treatment (N3AF).** Flax fibers were dried after alkaline treatments, followed by hand–separation and immersion into 3 wt % acrylic resin/THF solution for 1 h at room temperature (23°C, 50% RH). The AR-treated fibers were dried in an oven for 24 h at 80°C.

**Surface Treatment Mechanisms.** The purpose of the treatments used was to cause either (a) dissolution or (b) dissolution and coating. The alkaline treatment can reduce the proteins, waxes, ash, and minerals on the surface of fibers to improve the adhesion between the flax fiber and the vinyl ester matrix. In addition, alkaline treatment partially degrades lignin and helps the cellulose I lattice to partly transform into a cellulose II lattice when the concentration of the alkaline solution is higher than 9% (wt).[27] Cellulose I can also transform by thermal treatment into cellulose II, which is a more stable crystalline structure.[28]

**Table I.** The Nomenclature Used to Denote the Various Grades and Their Chemical Treatments Reinforced Fibers

| | | Treatment | Untreated Flax/VE | NaOH treated Flax/VE | 3% VE Toluene treated Flax/VE | 3% VE THF treated Flax/VE | 10% VE THF treated Flax/VE | Bleaching Flax/VE | Untreated Flax/VE with 1% AR | NaOH treated Flax/VE with 1% AR | NaOH and 3% AR treated Flax/VE |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Resin | Acrylic Resin | (A) | | | | | | | 1A | 1A | |
| Fiber | NaOH | (N) | | N | N | N | N | | | N | N |
| | THF | (F) | | | | 3 F | 10 F | | | | |
| | Toluene | (L) | | | 3 L | | | | | | |
| | Bleaching | (B) | | | | | | B | | | |
| | Acrylic Resin | (A) | | | | | | | | | 3A |
| | | Grade | VE-0 | VE-N | VE-N3L | VE-N3F | VE-N10F | VE-B | 1 A-VE | 1 A-VE-N | VE-N3AF |

VE treatment involves coating, with no chemical reactions between the vinyl ester resin and the flax fiber. For this treatment, toluene solution was chosen initially, as it is a common solvent. Afterward, toluene was replaced with THF as the solvent because of its lower polarity. In the THF solution, flax fiber and vinyl ester resin were expected to have a higher degree of contact than toluene. Often, this increased affinity causes the coated vinyl ester resin to cross-link with VE resin during composite processing.

Bleaching is a conventional treatment for wood fibers that is used to reduce pectin and lignin. An often accepted theory[29] is that oxygen is the key to break down lignin. Another theory[29] is that $Cl_2$ oxidizes lignin. Hydrogen peroxide is the most effective agent for flax fiber bleaching. However, $NaClO_2$ is used predominantly because it is cost-effective over $H_2O_2$.

AR treatment is similar to a VE treatment that coats the surface of flax fibers with acrylic resin using THF as the solvent. Table I shows the nomenclature of the untreated and treated flax fiber composites, according to the corresponding chemical modifications applied.

## COMPOSITE PROCESSING

Composite panels of flax/VE were fabricated using a modified form of VARTM. A caul plate was used underneath the vacuum bag to provide a uniform cross sectional area. This also created a test specimen with a smooth surface on both sides. To obtain similar fiber volume fractions, the VARTM process was aided by compressing the vacuumed flax with 2 metric ton force. The schematic of the processing set-up is shown in Figure 1. The manually aligned dried unidirectional fibers showed a deviation of 0° to 10° with respect to the lay-up direction.

AR was also added in the VE resin to improve the adhesion between flax fibers and VE. AR is a highly viscous liquid that is used particularly in combination with cellulose nitrate. The fibers/VE with 1 wt % acrylic resin composites were also processed by the modified VARTM.

### Characterizations of the Materials

**Density Tests.** The densities of linen flax fiber, linen flax fiber/vinyl ester composites, linseed flax fiber/vinyl ester composites and E-glass fiber/vinyl ester composites were determined using a Mettler Toledo 33360 density determination kit at room temperature. The densities were calculated by eq. (1).

$$\rho = \rho_0(A/P) \tag{1}$$

where $\rho(g/cm^3)$ is the density of the sample of fibers or composites, $A$ (g) is the weight of sample in air, $P$ (g) is the buoyancy of the sample in distilled water, and $\rho_0$ (g/cm$^3$) is the density of distilled water at the given temperature.

The fiber volume fraction of composite samples was calculated using eq. (2).

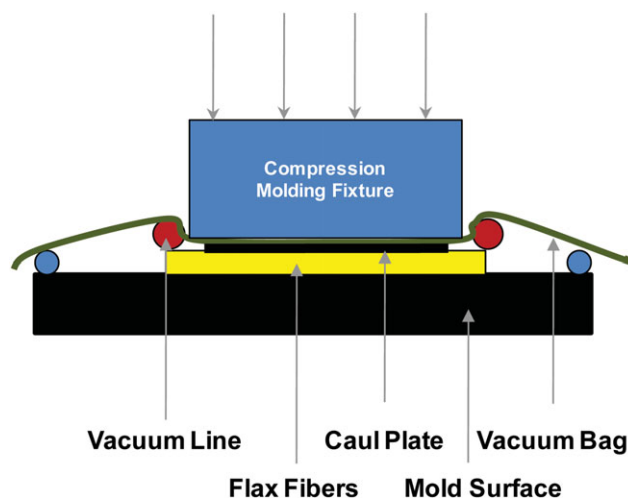$$V_f = W_f(\rho_c/\rho_f) \tag{2}$$



**Figure 1.** A schematic of compression-aided VARTM process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

where $V_f$ is the fiber volume fraction in composite, $\rho_c$ (g/cm$^3$) is the density of the composite, $\rho_f$ (g/cm$^3$) is the density of the fiber, and $W_f$ is the weight percent of fiber in composite. $W_f$ was calculated by measuring the weight of the fiber and resin before the composite is processed and the weight of the composite after processing.

**Fourier Transform Infrared Spectroscopy.** FTIR was used for studying the functional group modifications. FTIR spectra were obtained for all grades of composite materials processed. A total of 32 scans were acquired at a resolution of 4 cm$^{-1}$ between 4000 cm$^{-1}$ and 650 cm$^{-1}$ for each spectrum on a Nicolet 6700 FTIR spectrometer equipped with Spectrum software. The fibers bundles were twined and secured over the zinc selenide ATR crystal to scan the fiber surface for the spectrum.

**Dynamic Mechanical Analysis.** Dynamic mechanical properties were measured using TA DMA Q800 (TA Instruments, New Castle DE) in dual cantilever mode at 1 Hz scanning at 3°C/min temperature ramp. A 2.5 mm thick $\times$ 12.7 mm wide coupon samples used that were cured at room temperature with and without 1 wt % AR prior to the test. The recorded $T_g$ was the temperature at the peak of the tan $\delta$ curve in the glass transition region. The span of the glass transition in the tan $\delta$ curve was determined as the width across the curve when it decreased to half of its peak value, i.e., full-width at half-maximum (FWHM).

**Interlaminar Shear Strength.** Interlaminar properties were assessed using short beam strength tests, according to ASTM D2344. Short beam shear tests were carried out in displacement control at a rate of $\sim$ 1 mm/min on an Instron 5567 load frame. Five specimens for each sample were tested. Interlaminar shear strength (ILSS) was also calculated using ASTM D2344 [eq. (3)] to analyze the interlaminar properties for each sample set.

$$\tau = \frac{0.75P}{bh} \qquad (3)$$

where $P$ (N) is the maximum load, $b$ (m) is the width of the beam tested, and $h$ (m) is the depth of the beam tested.

**Flexural Strength and Flexural Modulus.** Flexural analysis was performed through a three-point bend testing, as specified in Procedure A of ASTM D790, using an Instron model 5567 load frame. The speed of the cross-head was dependent on sample thickness, and was on an average, $\sim$ 1 mm/min. Five specimens were tested for each sample. The flexural strength and flexural modulus were calculated using eq. (4).

$$\sigma_f = \frac{3PL}{2bd^2}$$
$$E_m = \frac{L^3 m}{4bd^3} \qquad (4)$$

where $\sigma_f$ (Pa) is the flexural strength, $P$ (N) is the maximum load, $b$ (m) is the width of the beam tested, $d$ (m) is the depth of the beam, $L$ (m) is the span length of the supports, $E_m$ (Pa) is the flexural modulus, and $m$ is the slope of the linear region in the stress–strain plot.

**Tensile Strength and Elastic Modulus.** Tensile mechanical testing was performed to ASTM D3039 on a 5-specimen sample set using an Instron model 5567 load frame. The speed of the cross-head was approximate by 1 mm/min. The specimens were tested until tensile failure. The specific tensile strength and specific tensile modulus were calculated.

**Scanning Electron Microscopy.** SEM images of untreated, bleached and 10% VE-treated linen flax fiber and their composites after tensile failure were obtained using a JEOL JSM-6490LV scanning electron microscope (JEOL, Peabody, MA) at an accelerating voltage of 15 kV in the secondary electron contrast mode. The fiber samples were attached to aluminum mounts with adhesive carbon tabs or colloidal silver, and sputter-coated with gold-palladium (Model SCD 030, Balzers, Liechtenstein).

## RESULTS AND DISCUSSION

### Fourier Transform Infrared Spectroscopy

The FTIR spectra of untreated and treated flax fiber are presented in Figure 2. The spectrum of VE–0 flax fiber showed characteristic bands for cellulose. These bands included a hydrogen bonded ─OH stretching[30] at 3600 cm$^{-1}$ to 2995 cm$^{-1}$, the ─CH stretching at 2906 cm$^{-1}$ and 2844 cm$^{-1}$, the ─OH bending[31] at 1575 cm$^{-1}$, the ─CH$_2$ bending at 1409 cm$^{-1}$, the ─CH bending at 1377 cm$^{-1}$, and the C─O stretching at 1018 cm$^{-1}$. The spectrum of all specimens showed the bands for cellulose.

The hydroxyl region is detailed in Figure 2(a), showing the characteristic bands at 3340 cm$^{-1}$ which is from intramolecular hydrogen bond in cellulose. The spectra for the untreated flax and bleached flax show prominent methylene stretching at the 2850 cm$^{-1}$ and 2920 cm$^{-1}$ that represent the presence of waxy constituents.[29] Weak presence of these bands was observed in the VE-N, VE-N3F, and VE-N3AF treated flax fiber spectra, showing the effectiveness of these treatments in eliminating waxes from the flax fiber structure. The spectra of VE-N3F showed wide, low-absorbance peaks from 3573 cm$^{-1}$ to 2973 cm$^{-1}$, which indicated a decrease in H-bonded ─OH. However, the 3340 cm$^{-1}$ band showed a decrease in absorbance with VE THF and AR treatments and VE-N showed a broad peak for ─OH stretching at 3600 cm$^{-1}$ to 2995 cm$^{-1}$. These spectral characteristics support NaOH treatment exhibiting a strong effect on the functional groups of cellulose.[31] The second derivative spectra in the 2980 cm$^{-1}$ to 2920 cm$^{-1}$ range obtained from untreated- and NaOH/ethanol-treated flax are shown in Figure 2(b). The band observed at 2954 cm$^{-1}$ in the alkaline-treated fiber spectra can be attributed to the ─CH stretching in Cellulose II.[32] The bands at 2966 cm$^{-1}$ and 2944 cm$^{-1}$ in both untreated and VE-N (NaOH/Ethanol) are illustrative of ─CH stretching in Cellulose I.[32] Hence, these distinct differences in spectra support the formation of Cellulose II from Cellulose I using the NaOH/Ethanol treatment in the flax fiber. During the alkaline treatment, small amount of Cellulose I in flax fiber transformed into Cellulose II. However, there are still large amount of Cellulose I in flax fiber existing after the treatment. Thus, the typical bands for Cellulose I are shown in the spectrum after the alkaline treatment.
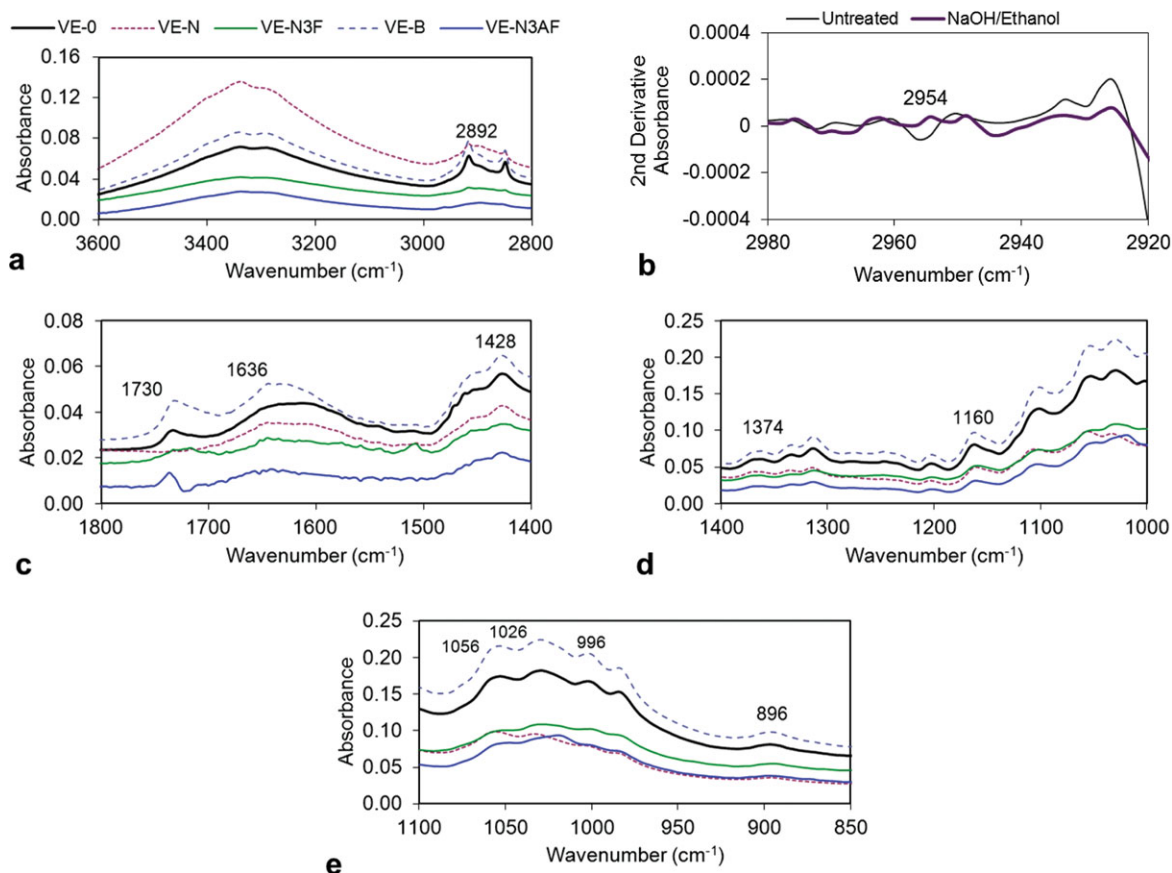
**Figure 2.** FTIR spectra of untreated and treated flax fiber showing (a) hydroxyl region, (b) second derivation of –CH stretching, functional groups of (c) carbonyl region, (d) cellulose II, and (e) microcrystalline cellulose. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The FTIR spectra representing bands from transient products of the surface treatments are shown in Figure 2(c). As shown, the band at 1730 cm$^{-1}$ exhibits an oxidation product that was absent in VE-N/VE -N3F/VE-N3AF treatments when compared with the untreated flax. This band signifies a C═O stretching in unconjugated ketones, carbonyls, or esters.[32,33] However, in VE-B, the 1730 cm$^{-1}$ band was present with a significant intensity. The spectrum of VE-B shows a peak at 1685 cm$^{-1}$, which is illustrative of C═O stretching.[32] The presence of carbonyl group peak supported sodium chlorite oxidizing the hydroxyl groups in lignin to form carbonyl groups and reducing the color of flax fiber. A minor peak was observed at 1677 cm$^{-1}$ that resulted from the C═O group of vinyl ester.[34] The 1636 cm$^{-1}$ (adsorbed water) band was seen in the untreated and VE-B, but to a lower degree in VE-N and other treatments used in this study. CH$_2$ scissoring in Cellulose II is a representative of Cellulose II and amorphous cellulose and often detected in the spectra at about 1430 cm$^{-1}$, was present in all treated and untreated fibers with a varying degree of absorbance. This band is exhibited by the crystalline region of the fiber.

The bands at 1374 cm$^{-1}$ (C─H deformation in Cellulose II) and 1160 cm$^{-1}$ (C─O─C vibration from $\beta$-glycosidic link in Cellulose II[34]) are shown in Figure 2(d). These bands are understood to be representative of Cellulose II. The spectra in Figure

2(d) showed the presence of these bands in all treated/untreated fiber, with VE-B exhibiting higher absorbance over the other treatments. The representative microcrystalline cellulose bands are shown in Figure 2(e). The bands of interest in this region are 896 cm$^{-1}$ showing a C─O─C valence vibration of $\beta$-glycosidic link or deformation in cellulose II.[34] This band is exhibited by the amorphous region of the fiber. The 896 cm$^{-1}$ band showed the lowest absorbance in treatments other than the baseline and bleaching, hence was supporting of the utilization of the surface treatments in increasing the overall crystallinity of the fibers.

The FTIR spectra of VE-0 and 1 A-VE are shown in Figure 3. In the VE-0 spectrum, C─H stretching (2899 cm$^{-1}$, 2807 cm$^{-1}$), carbonyl group (1706 cm$^{-1}$), C─H bending of CH$_2$ group (1450 cm$^{-1}$), and C─O (1114 cm$^{-1}$) were observed. The comparison of these two spectra indicated the presence of common chemical groups, e.g., the peaks from 2954 cm$^{-1}$ and 2869 cm$^{-1}$ are from C─H stretching, the peak at 1731 cm$^{-1}$ is from carbonyl group, the peak at 1479 cm$^{-1}$ is from C─H bending of CH$_2$, and the peak at 1160 cm$^{-1}$ is from C─O. All these peaks showed a shift to a higher wavenumber and with a higher absorbance. The peak shift can be caused by the similarity in functional groups of VE and AR and because of the modification of carbonyl behavior of AR by other functional groups
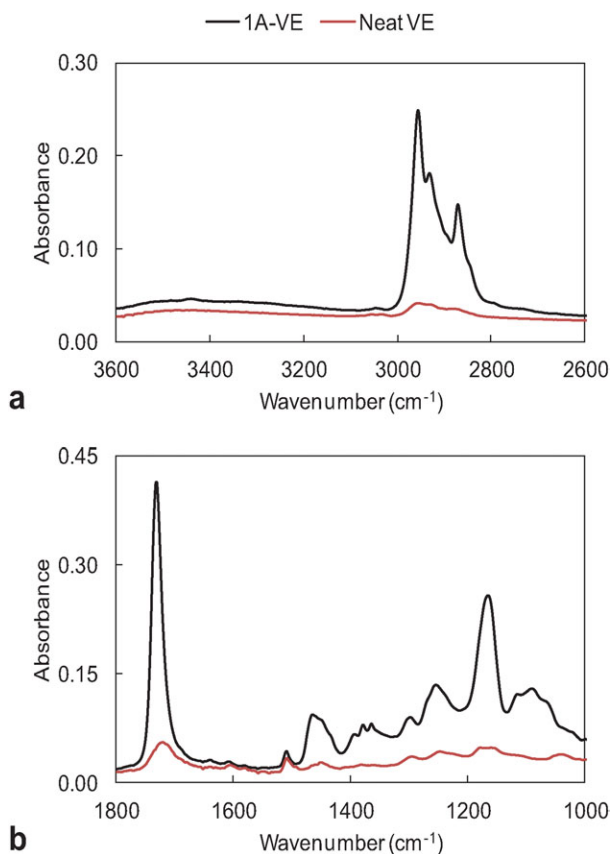
**Figure 3.** FTIR spectra of neat VE and VE with 1% AR (1A-VE). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

present. A sharp peak was also observed at about 1444 cm$^{-1}$ in the spectrum of 1A–VE, which is representative of C—H bending of CH$_3$ from AR.

Overall, the FTIR spectra showed that all the chemical treatments modified the flax fibers. Specifically, NaOH treatment changed the crystal structure of flax fibers, VE-based treatments coated the surface of flax fibers, bleaching reduced the content of lignin, and AR increased the amount of carbonyl groups in VE.

**Mechanical Properties**
The density[35] of the cured vinyl ester is about 1.10 g/cm$^3$. The density of flax fiber was measured using immersion density technique, and was determined to be 1.42 $\pm$ 0.02 g/cm$^3$. The densities of the flax/VE composites were observed to be between 1.19 g/cm$^3$ to 1.32 g/cm$^3$ and the fiber volume fraction of flax fiber composites were then found to vary from 40 to 50%. Since both density and volume fraction showed variation, specific interlaminar properties, specific tensile properties, and specific flexural properties were calculated to normalize the observed effects.

**Dynamic Mechanical Properties.** The storage modulus ($E'$) and tan $\delta$ curves of the cured VE-0 and 1A-VE are presented in Figure 4. The peak position and transition breadth of the tan $\delta$ of each resin were determined using the crosslink density. The

$T_g$ of VE-0 was 128°C and the $T_g$ of 1A-VE was 127°C, and thus, similar storage modulus values were observed for both the resin systems. In addition, the transition breadth of the tan $\delta$ curve of 1A-VE was sharper than that of the neat VE. These differences in both the $T_g$ and the transition breadth indicated that the crosslink density of VE with 1 wt % AR was lower than that of the neat VE. The concentration of the crosslinking monomer is varied within a network and the changes in $T_g$ are dependent on the additive nature of the crosslinking effect and the copolymer effect. Overall, the effect of AR is to reduce the effective crosslink density of VE system during its curing.

**Interfacial Properties.** Table II provides values of ILSS; Table III and Figure 5 show the specific interlaminar shear strength of untreated and treated flax fiber composites measured by short beam shear tests (ASTM D2344). Interfacial properties are dictated by fiber-to-matrix bonding.[35] Higher ILSS values indicate a stronger bonding between the fiber and the matrix. Compared with the untreated and treated flax composites, all chemical modifications showed improvements in ILSS, which indicates that all treatments enhanced the adhesion strength between matrix and fibers.

The specific ILSS properties of NaOH treatment showed an approximate two-fold increase compared with VE-0 composite. VE-N was used as a baseline treatment for cellulosic fibers because it can lead pectin to hydrolyze and lignin to
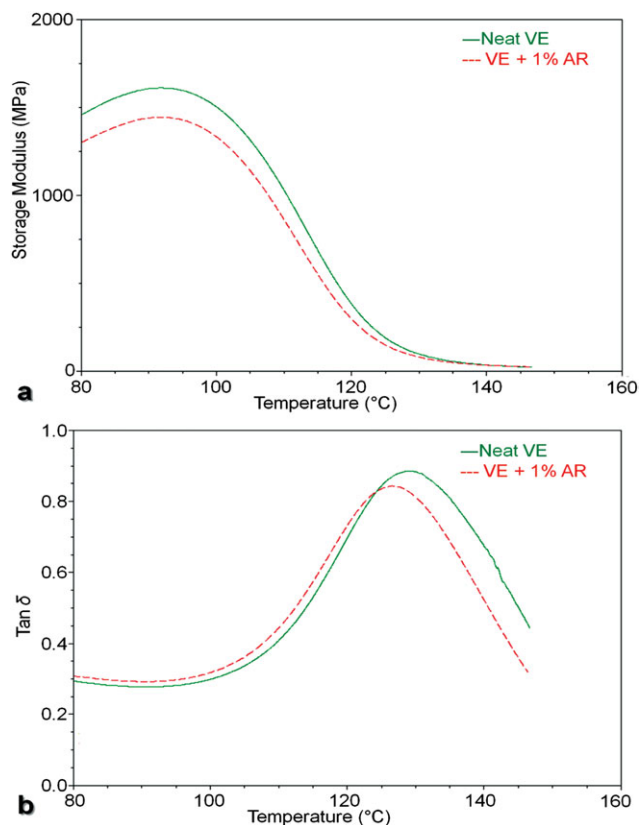


**Figure 4.** DMA plots of (a) storage modulus and (b) tan $\delta$ versus temperature for neat VE and VE with 1 wt % AR (1A-VE). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**Table II.** Mechanical Properties of Flax/VE Composites Include ILSS, Flexural Properties, and Tensile Properties

|  | ILSS (MPa) | Flexural strength (MPa) | Flexural modulus (GPa) | Tensile strength (MPa) | Tensile modulus (GPa) |
|---|---|---|---|---|---|
| VE-0 | 8.53 ± 0.22 | 280.95 ± 31.11 | 35.57 ± 3.12 | 76.32 ± 14.67 | 12.30 ± 0.85 |
| VE-N | 27.38 ± 2.01 | 332.97 ± 24.27 | 35.47 ± 3.05 | 166.89 ± 43.70 | 10.50 ± 1.02 |
| VE-N3L | 26.60 ± 1.12 | 286.14 ± 40.44 | 27.69 ± 2.92 | 141.26 ± 22.34 | 10.41 ± 1.18 |
| VE-N3F | 26.98 ± 0.57 | 216.34 ± 19.88 | 20.28 ± 2.74 | 141.22 ± 22.62 | 8.66 ± 0.71 |
| VE-N10F | 29.00 ± 0.91 | 223.17 ± 28.18 | 23.71 ± 3.42 | 215.02 ± 12.84 | 10.46 ± 1.31 |
| VE-B | 16.85 ± 1.78 | 191.12 ± 27.02 | 20.10 ± 2.10 | 112.48 ± 19.65 | 9.84 ± 0.85 |
| 1 A-VE | 12.95 ± 1.12 | 277.97 ± 25.30 | 36.84 ± 1.58 | 101.68 ± 26.69 | 12.73 ± 0.67 |
| 1 A-VE-N | 28.90 ± 1.93 | 334.50 ± 17.87 | 34.11 ± 2.50 | 216.13 ± 34.43 | 13.23 ± 1.15 |
| VE-N3AF | 15.34 ± 1.18 | 170.13 ± 17.23 | 30.28 ± 3.23 | 115.98 ± 26.62 | 10.74 ± 1.58 |

degrade.[5,7,8] Moreover, alkaline solution also potentially removes chemicals, e.g., waxes, dyes, and ashes, to cause a rough fiber surface and can improve the adhesion between fibers and matrix.[7,8] A common agent used for alkaline treatment is NaOH solution.[5] Nevertheless, the shrinkage of flax fibers because of an alkaline treatment is a challenge that ultimately affects the overall properties of their flax fiber composites. Since flax fibers were required to be taut, a NaOH/ethanol system was used to reduce shrinkage and ensuing twisting effects.

Among the VE treatments, VE -N10F showed a factor of 2.2 in improving specific ILSS over VE-0 composites and a marginal 4% in specific ILSS over VE-N. Nevertheless, VE-N3L showed 2% lower specific ILSS than VE-N. Both VE-N3F and VE-N10F showed a higher specific ILSS than VE-N3L. This effect is likely because of the higher mechanical interlocking between the coated vinyl ester resin and the flax fiber. The polarity of THF is higher than toluene and the carbon chain of flax fibers are more movable in THF solution. Therefore, the contact area of vinyl ester resin and flax fiber in THF is higher compared with that in toluene. VE resin is more effective in filling up the apparent surface flaws in flax fiber and cause better adhesion.[36] VE-N3AF treatment is similar to a VE treatment, involving AR coating on flax fiber surface. Although AR THF treatment improved the interfacial bonding between flax fibers and VE, it showed lower specific ILSS than other treatments, including VE-N, VE-N3L, VE-N3F, VE-N10F, VE-B, and 1A-VE-N.

Bleaching treatment is a common method for wood fibers and cotton, which can oxidize lignin and change the color of the fibers.[29] However, since the lignin content in the flax fiber used in this study was only 2 wt %, a major improvement was not expected.

Within all the surface treatments analyzed, 1A-VE-N showed the highest specific ILSS with 230% increase over VE-0. The specific ILSS of 1A-VE was about 50% higher than VE-0. These results suggest that a combination of the chemical treatment on flax fiber and the chemical additive in VE matrix can show significant improvement in the interfacial properties of flax/VE composites.

**Flexural Properties.** In Table II, the flexural properties of untreated and treated flax fiber reinforced composites, measured by three-point bending tests (ASTM D790), are shown. In Table III, Figure 6(a, b), the specific flexural properties are presented. As seen, an improvement in flexural properties was not obtained with all treatments. Moreover, only VE-N, 1A-VE, and 1A-VE-N were comparable with VE-0 composites in overall properties.

As seen from Figure 6(a), VE-0, VE-N3L, and 1A-VE-N showed higher specific flexural strength over VE-0 composites. The 1A-VE-N shows about a increase over 22% VE-0, which was similar to the ILSS behavior. The mechanical properties of flax fiber/VE composites depend on the mechanical properties of flax fiber, the mechanical properties of the VE matrix, and the efficiency

**Table III.** Specific Mechanical Properties of Flax/VE Composites Include ILSS, Flexural Properties, and Tensile Properties

|  | Specific ILSS MPa/(g/cm³) | Flexural strength MPa/(g/cm³) | Flexural modulus GPa/(g/cm³) | Tensile strength MPa/(g/cm³) | Tensile modulus GPa/(g/cm³) |
|---|---|---|---|---|---|
| VE-0 | 6.85 ± 0.22 | 216.12 ± 24.01 | 27.35 ± 2.41 | 59.16 ± 11.36 | 9.52 ± 0.66 |
| VE-N | 21.01 ± 1.54 | 255.51 ± 18.63 | 27.22 ± 2.34 | 129.38 ± 33.88 | 8.14 ± 0.80 |
| VE-N3L | 20.09 ± 0.82 | 236.15 ± 33.38 | 22.85 ± 2.41 | 106.66 ± 18.16 | 7.86 ± 0.89 |
| VE-N3F | 20.67 ± 0.44 | 163.28 ± 15.00 | 15.31 ± 2.07 | 107.00 ± 17.14 | 6.56 ± 0.54 |
| VE-N10F | 21.97 ± 0.69 | 188.12 ± 23.75 | 19.98 ± 2.88 | 164.71 ± 9.84 | 8.02 ± 1.00 |
| VE-B | 13.45 ± 1.42 | 145.53 ± 20.58 | 15.30 ± 1.60 | 90.33 ± 17.67 | 7.90 ± 0.68 |
| 1 A-VE | 10.11 ± 0.87 | 216.98 ± 19.75 | 28.75 ± 1.23 | 82.58 ± 21.68 | 10.34 ± 0.54 |
| 1 A-VE-N | 22.83 ± 1.53 | 264.32 ± 14.12 | 26.95 ± 1.98 | 175.18 ± 27.90 | 10.72 ± 0.93 |
| VE-N3AF | 12.15 ± 0.94 | 134.80 ± 13.65 | 24.00 ± 2.56 | 92.45 ± 21.22 | 8.56 ± 1.26 |
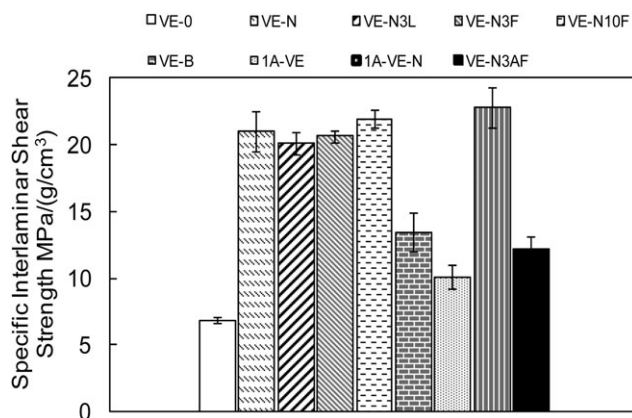
**Figure 5.** A plot of specific interlaminar shear strength comparison of the various composites.

of load transfer. AR additive increases the hydrophilicity of VE, which leads to better wettability between flax fibers and VE. However, VE-N3F and VE-N10F show a lower specific flexural strength than VE-0 composites. The VE-B and VE-N3AF showed lower specific flexural strength over all other treatments, consistent with the observed ILSS behavior. For flax fiber composites, the interface between flax fiber and orientation of microfibrils are also important. For all THF solution treatment (VE-N3F, VE-N10F, and VE-N3AF), some coiled fibrils in flax fibers are loosened and exposed in THF solution during treatments.[15] These fibrils can contribute to uncoiling when a bending force is applied, which leads to the reduction in interfacial stress transfer.

From Figure 6(b), 1A-VE is observed to have about 5% higher specific flexural modulus over VE-0 composites, which indicates that adding AR in VE may not affect the flexural modulus of flax fibers. The specific flexural modulus of VE-N and 1A-VE-N are almost equivalent to that of untreated flax/VE composites, which indicates that VE-N exhibits a minimal affect on the flexural modulus of flax fibers. Other treatments show a decrease in specific flexural modulus. The decreases in flexural modulus of composites are related to the structural variation in the flax fiber cells. The swelling and partial removal of noncellulosic chemicals in flax fibers decrease the resistance of microfibrils to stretching.[37]

**Tensile Properties.** The tensile properties of flax/VE composites are presented in Table II, and the specific tensile properties are shown in Table III, Figure 7(a, b). The specific tensile strength of all treatments were observed to be higher than VE-0 composites, consistent with the ILSS behavior. However, the composites with 1% AR added in VE alone showed a higher specific tensile modulus than the VE-0 composite.

The specific tensile strength of 1A-VE-N was seen to be the highest among all flax/VE composites, ∼ 200% higher than VE-0. This increase supported that the addition of AR to VE led to a better load transfer from the flax fibers to the VE matrix while maintaining the required fiber strength. The VE-N10F and VE-N showed an ∼ 180% and 120% higher specific tensile strength than VE-0 respectively, similar to the results of ILSS. This
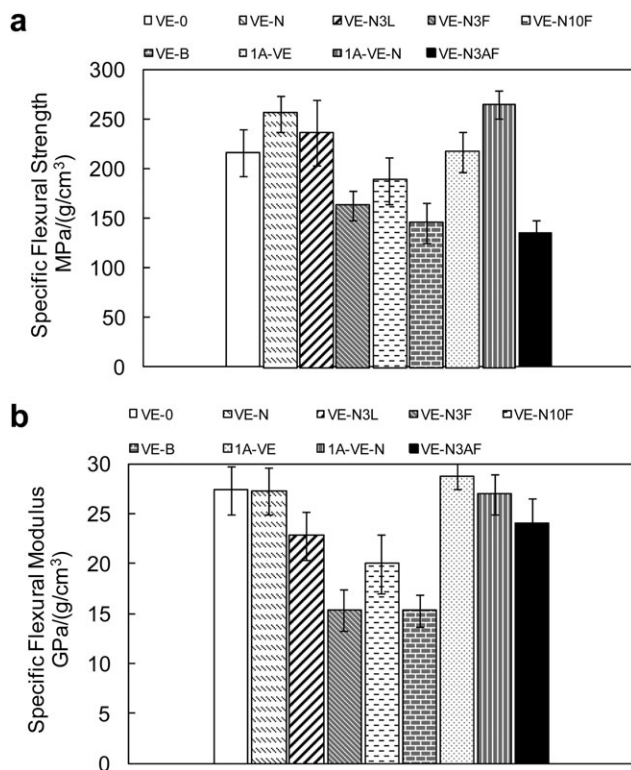


**Figure 6.** A comparison of (a) Specific flexural strength and (b) specific flexural modulus of untreated and treated flax/VE composites.
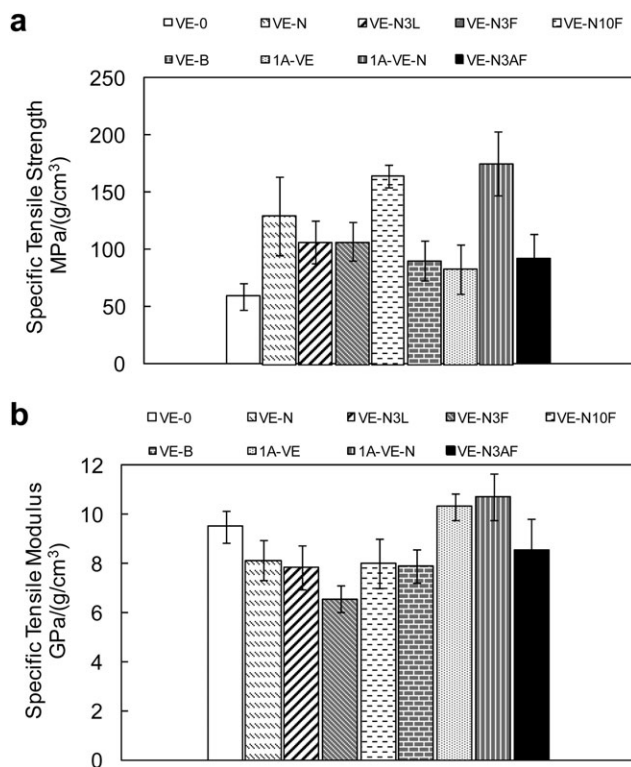


**Figure 7.** A comparison of (a) specific tensile strength and (b) specific tensile modulus of untreated and treated flax/VE composites.
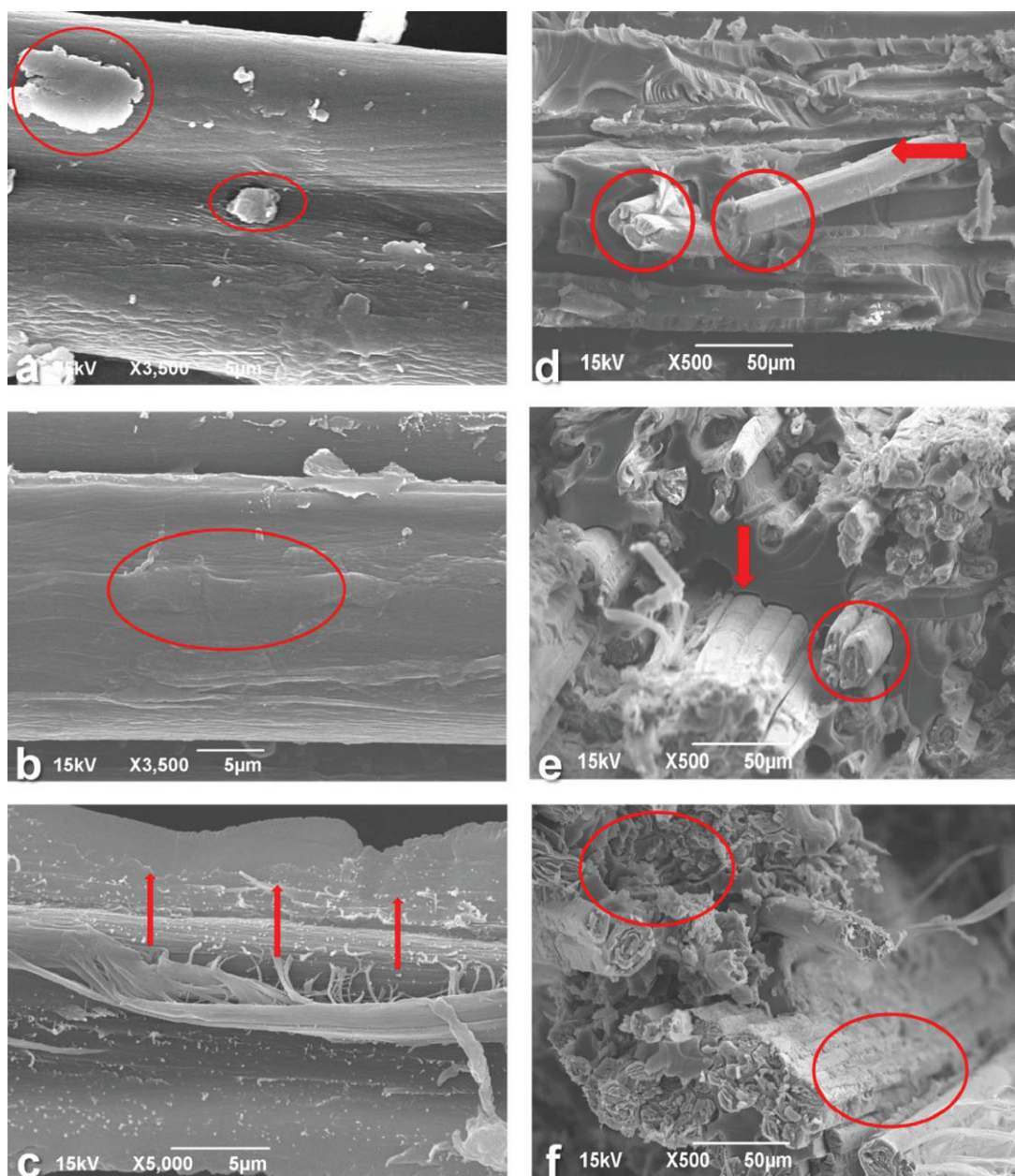
**Figure 8.** SEM images of untreated, treated flax and their composites: (a) untreated flax, (b) bleaching flax, (c) VE-treated flax, (d) VE-0, (e) VE-B, and (f) VE-N10F. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

significant increase in specific tensile strength can be attributed not only to an effective interfacial load transfer, but also to the enhanced crystallinity and thereby the structure of cellulose because of the alkaline treatment.[15,31,34]

Specific tensile modulus of most of the treatments used in this study showed a decreasing effect on the properties of flax fibers, except AR-added VE. The specific modulus of VE-N was about 15% lower than that of untreated flax/VE, which indicated that the NaOH treatment could affect the properties of flax fiber. Flax fibers have been known to show a lower modulus after an NaOH treatment.[15] Considering the tensile modulus values, all three VE treatments showed a lower specific tensile modulus than VE-0, which was similar to the specific flexural modulus

behavior. Toluene and THF are common polar solvents and they assist VE to disperse and to coat on the surface of flax fibers. Meanwhile, the variation in structure of flax fibers may have led to change in tensile modulus.[38] However, AR additive showed an increase in specific tensile modulus, 1A-VE and 1A-VE-N showed about 9% and 13% increases over VE-0 respectively in specific tensile modulus. Chemical modification on VE matrix and the combination of surface treatment on flax fibers and chemical modification on VE showed the greatest potential for property optimization of flax fiber composites.

**Scanning Electronic Microscopy.** Electron microscopy analysis is shown in Figure 8. The SEM images of the various flax fibers [Figure 8(a–c)] and their composites [Figure 8(d–f)] are shown

in the collage. The SEM image of untreated flax fibers showed deposited material on the surface. Compared with the untreated flax, the bleached flax fiber [Figure 8(b)] exhibited a considerably cleaner surface, but with residual matter on the surface. The SEM image of VE THF [Figure 8(c)] treated flax fiber also showed a coating of VE resin, and in this case the coating layer was observed to be substantially thicker than the coating formed as a result of the acrylic acid treatment.

As shown in the SEM image of VE-0 [Figure 8(d)], the fibers were pulled out from the matrix. The debonding between flax fiber and matrix was also seen, which could be attributed to the weak adhesion between untreated linen flax and the matrix. As shown in the SEM image of VE-B [Figure 8(e)], the fibers were pulled out, accompanied by additional debonding. In the SEM image of VE-N10F [Figure 8(f)], pullout of the fibers and debonding are barely visible. Hence, the VE THF treatment showed improved interfacial properties as compared with the other two types of composites. The observations and resulting differences between these SEM images supported the trends of the observed interfacial mechanical properties.

## CONCLUSIONS

In this study, all chemical treatments investigated were seen to improve the interfacial bonding between flax fibers and VE matrix to a certain degree. However, each treatment possessed a unique effect on the modulus of flax/VE composites. To improve the adhesion between the flax fibers and the vinyl ester matrix, individual modifications to flax fibers (VE-N, etc.) and polymer matrix (1A-VE, etc.) were used. Also, a combination of treatments to both polymer and the fiber simultaneously (1A-VE-N, etc.) was used.

Overall, these conclusions were extracted from this study:

- NaOH treatment caused a decrease in tensile modulus over the baseline– untreated flax composites.
- NaOH treatment as a common treatment for cellulosic fibers caused an increase in interfacial properties, tensile strength, and flexural strength over the untreated fibers.
- AR as an additive in VE contributed to increases in mechanical properties, apart from the established advantages of being time-efficient and cost-effective compared with most surface chemical treatments.
- NaOH treatment combined with AR added in VE showed the highest improvement in the properties among all flax composites.
- The interfacial characteristics of the untreated fibers and the composites supported the interfacial modifications brought about by the various fiber surface treatments.
- The combination of fiber treatment and matrix modification improves ILSS, tensile properties, and flexural properties of flax fibers reinforced composites.

The methods used in this study can be used as basic treatments for improvements in flax fiber reinforced composites. However, these treatments were determined as being sufficient for the current size of panel, which was limited because of the size of mold. Possible extensions to this work are to (a) optimizing and scaling-up the fiber treatments, and (b) manufacturing

composites in various forms to assess the effectiveness of these treatments.

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