Modification of Epoxy Resin by Silane-Coupling Agent to Improve Tensile Properties of Viscose Fabric Composites

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ABSTRACT

The modification of epoxy resin by 3-aminopropyltriethoxysilane (APTES) to improve the tensile properties of warp knitted viscose fabric composites is reported in this study. The study evaluates the efficiency of modification methods adopted to modify the epoxy resin and the influence of the resin modification on various properties of the cured castings. The influence of matrix resin modification on the tensile properties of viscose fabric composite is compared to those prepared from chemically modified fibre. The efficiency of the modification was determined through titration method to determine the epoxide content of epoxy resin, viscosity measurement and FTIR. The effect of APTES modification on various properties of cured castings is studied through differential scanning calorimeter (DSC), contact angle measurement and tensile testing. The addition of APTES into the epoxy resin decreased the epoxide content in the resin as evident from the titration method. The tensile strength of cured castings decreased after the resin modification. The tensile strength and elongation at break of the viscose fabric composites prepared from modified resin, increased up to 14% and 41% respectively. The improved adhesion of APTES-modified epoxy resin to the viscose fibre is confirmed from SEM analysis of tensile fracture surface.

Keywords: Epoxy, modification, APTES, Silane coupling agent, viscose, tensile, composites, regenerated cellulose

INTRODUCTION

The mechanical performance of a composite depends on the properties of the constituents and on the interfacial bonding between the fibre and the matrix. The fibre-matrix adhesion determines how much external stress can be transferred to the load bearing fibres [1]. Thus the stress concentrations are reduced which result in improvement of the overall mechanical properties of composites. The interfacial adhesion between a fibre and a matrix resin can be classified as chemical adhesion, physical adhesion, or mechanical adhesion [2]. The chemical adhesion proceeds through the formation of chemical bonds between fibre and matrix. The main approach for improving the chemical adhesion between fibre and matrix resin is the surface modification of fibre through wet chemical treatment methods like alkali treatment, acetylation, coupling agent treatment or reactive gas treatment methods like corona treatment and cold plasma treatment [3-7]. These surface treatment methods can improve the adhesion between the fibre and the matrix by bringing their surface energy to comparable values. In both cases, this is achieved by incorporating suitable functional groups and by changing the surface morphology by etching. Wide ranges of chemical modification methods to modify fibre to improve the physical properties of composites are discussed in literature [1, 8, 9].

Among various chemical methods available, silane coupling agent modification is a commonly utilised method to modify the glass fibre surface [10, 11] and lignocellulosic fibre surface [4, 12, 13]. Silane coupling agents have a general chemical structure of $R_{(4-n)}$–Si–$(R'X)_n$ (n=1,2), where R is alkoxy (ethoxy, methoxy), X is any organofunctional group such as amino, methacryl, epoxy, or vinyl and R’ is the alkyl bridge connecting the silicon atom and the organofunctional group [5, 12]. Trialkoxysilanes are the type of organo-functional silanes commonly used in the surface modification of lignocellulosic fibres [12]. The alkoxy group in the silane can form a chemical bond with the lignocellulosic fibre surface. The completion of coupling reaction of the silane-grafted on the fibre surface depends on the reactivity between the organo-functionality of silane and the matrix resin. There are several studies which reports the lignocellulosic fibre surface modification with silane coupling agent [14, 15]. These studies reported that the fibre modification with silanes had resulted in the improvement of various physical properties of the thermoplastic and thermoset composites.

The present study differs from the practice of prior art in a way that the silane coupling agent is not used as a fibre surface modifier. Instead, it is directly mixed in the thermoset resin to prepare an alkoxy silane containing thermoset resin. From the composite processing point of view, this is a benefit, as resin modification can be done much easier compared to a surface treatment of a reinforcement. It is well understood from the literature that the chemical surface modification deteriorates the strength of natural fibres [16–18]. Direct mixing of silane coupling agent with epoxy resin and using it in composite preparation is assumed to be eco-friendly and energy efficient. The direct mixing of silane coupling agent with resin and using the modified resin in composite preparation creates less process waste compared to the fibre modification method. The alkali solution or silane solution used to modify the fibre requires waste treatment, which includes additional cost and consumes more energy. Through the matrix resin modification, reactive sites are introduced in the backbone of matrix resin with a higher chemical affinity towards the hydrophilic cellulosic fibre surface without deteriorating the strength of the cellulosic fibre. The organic functionalities such as amino, methacrylate, epoxy, or vinyl groups present in the silane, are capable of forming chemical bonds with compatible reactive moieties in the matrix resin, while the hydrolysable alkoxy groups are capable of reacting with the fibre surface. Thus, it is anticipated to have a good fibre-matrix adhesion through the modification of thermoset resins by silane coupling agents.

Several approaches to modify epoxy resins have been reported in the literature [19–22]. Most of those studies are focused on improving the toughness of the epoxy resin. To improve the crack resistance and prevent interlaminar failure, the epoxy resin has been toughened with elastomers, thermosets, thermoplastics, particlutes or by other miscellaneous methods [19–24]. Epoxy resins have been modified by silane coupling agents to improve the corrosion resistance and the adhesion of epoxy coatings on the aluminium surface [25]. The water resistance of epoxy coatings on metal substrates has been improved through silanes [26]. The potential of silane coupling agents, polysiloxanes, silsesquioxanes, silica and silicates in modification of silane has been reported [27]. Most of the studies related to the silane modification of epoxy resin are in the area of coatings to improve the flexibility, adhesion and/or corrosion resistance. The modification of epoxy resin by silane for use as matrix resin in polymer composites are rarely found in literature. Epoxy resins have been modified with different types of silane coupling agents and the resulting mechanical properties of its composite with carbon fibre were studied by Yang et al. [29]. They reported that the matrix modification improved the tensile strength and flexural properties of carbon fibre composites by 4% and 44% respectively. Kaynak et al. [29] modified epoxy resins by hydroxyl-terminated polybutadiene and reported improvement in mechanical properties, especially the toughness of the composites.

Modification agents, which are specifically used to improve a particular property, can adversely affect other important resin characteristics, which are relevant for composite manufacturing. Thus, studies on the effect of modification on various properties of silane coupling agent modified epoxy resin, cured castings and composites are of special interest. The studies on modification of epoxy resin by silane coupling agent for using it as the matrix resin in regenerated cellulose fibre reinforced composites are rarely reported. The main objective of this investigation was to modify an epoxy resin with an amino functional tri-alkoxysilane and to assess the effect of the modification on the various properties of the resin and cured castings. Also, the tensile properties of modified epoxy/viscose fabric composites are compared with the epoxy/modified viscose fabric to identify the best approach to improve fibre-matrix adhesion.

EXPERIMENTAL

Materials

Prime 20LV, an epoxy resin manufactured by Gurit Ltd was used for modification and composite preparation. An amine hardener (Prime 20LV slow) was used to cure the castings and composites. The main properties of the Prime 20LV resin as given by the manufacturer are listed in Table 1 [30]. The silane coupling agent for epoxy resin modification was 3-aminopropyltriethoxysilane (APTES; 99% purity). All the chemicals used for the titration method to determine the epoxide content of the epoxy resin was of reagent grade and used as received. The fabric used as the reinforcement in the preparation of composites for the tensile test was based on Cordenka 610F viscose yarn with the twist Z40, 2440 dtex linear density and 1350 filaments (Cordenka, Germany). The yarn was processed by warp knitting into unidirectional fabrics with a surface weight of 223 g/m^2 (Engtex, Sweden).

Resin modification method

The epoxy resin modification was done by mixing the epoxy resin with 1 wt%, 3 wt%, and 5 wt% of APTES. No solvents or catalysts were used in the modification of resin. The modification was done for 1 hour at room temperature and at 70ºC. Epoxy resin and the appropriate amount of silane were weighed into a plastic container equipped with a magnetic stirrer and were stirred for 1 hour at room temperature. For the modifications done at 70ºC, the resin and an appropriate amount of silane were weighed into a round bottom flask equipped with a reflux condenser. Stirring was done for 1 hour in a water bath maintained at a temperature of 70ºC (± 3).

Viscose fabric modification method

The viscose fabric modification was done following the procedure explained in our previous study [5]. APTES was added to an ethanol/distilled water (95:5) solution to yield a 2 vol% silane concentration in solution. After 15 minutes the fabrics were dipped in a plastic container containing the reaction solution for 5 min and then dried at room temperature. After 30 min, the fabrics were oven-dried at 110ºC for 30 minutes and cooled in a desiccator.

Preparation of cured castings

A metal mould with dimensions specified for dog-bone shaped tensile specimen according to the ISO 527-2 was placed on the polished glass plate and the edges were sealed with two-sided sticky tape. After proper mixing, the resin was poured into the metal mould. The castings were cured at 65ºC for 7 hours and post-cured at 80ºC for 2 hours. The epoxy resin was mixed with the hardener in 100:26 ratio (by weight).

Preparation of composites

Composites were prepared by vacuum assisted resin infusion method. The mould release agent was applied on a steel mould. The mould was then polished and used after another 30 minutes. Four layers of warp knitted unidirectional viscose fabric were carefully laid (±0/±90/±0/±90) (Figure 1) one after another on the mould surface and finally the vacuum bagging was completed and the infusion was done. The infusion was done in a climate chamber at 65ºC and by applying a vacuum pressure of 0.1 bar. The composites were cured same way as in the case of cured castings and the same amount of hardener was used for curing the composites. The fibre weight percentage in the composites was 38% - 42%. The thickness of the composites was 2.2 mm - 2.4 mm. The details of the modification and designations of the modified resin, cured castings and composites are given in

Table **2**.

Characterization

Epoxide content of epoxy resin

The epoxide content of the epoxy resin was determined according to manual titration method described in ASTM D1652-11. The resin was dissolved in methylene chloride and then titrated with standard perchloric acid in the presence of an excess of tetraethylammonium bromide. The hydrogen bromide generated in situ by the reaction of the perchloric acid with the quaternary ammonium halide rapidly opens the epoxide ring. Therefore, the quantity of perchloric acid consumed can be taken as a measure of epoxy content. The sample was titrated with a perchloric acid reagent to a sharp blue to green end point which was stable for approximately 30 s. The volume of perchloric acid consumed during titratation was recorded. The weight percent epoxide and epoxy equivalent weight were calculated according to Equation 1 and Equation 2 respectively.

$$E = 4.3 \times V \times N/W \qquad \text{(Equation 1)}$$

$$W_{EEW} = 43 \times 100/E \qquad \text{(Equation 2)}$$

Where, E and W_{EEW} are weight percent epoxide and epoxy equivalent weight respectively. V is the volume of perchloric acid reagent used to titrate the sample (ml), N is normality of perchloric acid reagent, the constant 4.3 is the theoretical molecular weight of the epoxide ring 43, adjusted to 4.3 for the calculation to percent epoxide; and W is the weight of the epoxy resin used (g). The value reported is average of two measurements.

Viscosity measurements

The viscosity of unmodified RS0 and silane modified epoxy resins was measured using an Anton Paar MCR 301 rheometer at a constant shear rate of 10 s^{-1} from 25ºC to 65ºC. The measurements were done with a 25 mm plate-plate measuring system at a gap distance of 1 mm. The values reported are average of two measurements.

Contact angle measurements

The contact angle of the surface of the castings was measured to determine the wettability of the cured epoxy resin after silane modification. The measurements were done using a contact angle measurement instrument, OCA20 from Dataphysics Gmbh. The static contact angle of ultra pure water on cured epoxy was measured at room temperature by a sessile drop method. The contact angle value was taken 10s after depositing the drop on the epoxy surface. The results are reported as the average of 5 measurements with corresponding standard deviation.

FTIR spectroscopy

ATR-FTIR spectroscopy was used to characterise the APTES silane modification of the epoxy resin and to characterise the surface of modified cured epoxy castings and composites. The spectra from resins and cured casting surface were recorded on an ATR PerkinElmer-Spectrum One spectrometer. Signals of 8 scans at a resolution of 4 cm^{-1} were averaged before Fourier transformation. The spectrum was recorded over the range 4000 cm^{-1} - 650 cm^{-1}. The spectra from the surface of epoxy/viscose fabric composites were recorded on Bruker Optics-Tensor 27, spectrometer equipped with diamond ATR accessory. Signals of 32 scans at a resolution of 4 cm^{-1} were averaged over the range 4000 cm^{-1} – 400 cm^{-1}.

Differential scanning calorimetry (DSC)

The glass transition temperature from the cured castings was determined using a Netzsch 204 DSC. The samples were first heated from 25ºC to 250ºC at a rate of 10ºC/min and then cooled. The second heating was run from 25ºC to 250ºC at a rate of 10ºC/min. Heating of cured epoxy resin samples to remove any prior thermal history and then cooling before second heat cycle was reported elsewhere [31]. The sample size was 10-11 mg and test was conducted in a nitrogen atmosphere. The glass transition temperature from the second heating scan of the cured castings is reported.

Tensile properties of modified cured castings

The tensile testing of the modified cured castings was conducted according to ISO 527-2:2012 using a Tiratest 2705 tensile testing machine equipped with a 5kN load cell. The cured casting specimen dimensions were 80 mm of the length of the narrow portion, 10 mm of the average width of narrow portion and 4 mm of an average thickness. The gauge length was 50 mm and overall length of the specimen was 150 mm. The testing was carried out at ambient temperature with a testing speed of 2 mm/min. The tensile properties are calculated as the average of five specimens.

Tensile properties of composites

Tensile tests for composites were carried out using Tinius Olsen H10KT universal testing machine. The load cell was 10 kN and test speed was 10 mm/min. Dumb-bell shaped specimens were tested and ISO 527-2:2012 standard was followed. Overall length was 150 mm with the parallel-sided portion of about 60 mm. The width at the parallel-sided portion was 10 mm. The gauge length was 50 mm. The tensile properties are calculated as an average of six specimens.

Scanning electron microscopy (SEM)

Samples for SEM observations were mounted perpendicular on Al-support base with conductive tape, allowing observing the fractured surface. The conductive amorphous carbon paint was used to make contacts with the upper surface; afterwards the samples were coated with few nano-meters thick layer of amorphous carbon (Balzers SCD 050 sputter coater) to achieve conductivity for electrons. The fractured surface was investigated with FE-SEM (Jeol JSM-7600F) at 5 keV using below-the-lens (LEI) secondary electrons detector (SE) to minimize charging on the fibers.

RESULTS AND DISCUSSION

Epoxide content of modified resin

The modification of epoxy resin by APTES silane was verified by epoxide content determination according to ASTM D1652-11. The results are shown in Figure 2. The weight percent epoxide of RS0 resin, RS1-RT resin and RS1-70 resin was determined to be 23.4%, 22.7%, and 22.7% respectively. Irrespective of modification temperatures, the epoxide content of resin after modification with 1 wt% APTES decreased slightly when compared with unmodified epoxy resin. Compared to RS0 resin, a decrease of 1.9% and 2.1% in the epoxide content of RS3-RT (21.5%) resin and RS3-70 (21.3%) resin respectively was recorded. The epoxide content in RS5-RT resin and RS5-70 resin was 20.8% and 20.4% respectively. Compared to RS0 resin, there was a decrease of 2.6% and 3.4% in epoxide content of RS5-RT and RS5-70 respectively. Correspondingly, the epoxide equivalent weight (EEW) increased to 211 g/mol for RS5-70 from 184 g/mol for RS0. The decrease in epoxide content and an increase in epoxide equivalent weight after addition of APTES into epoxy resin confirms the grafting of APTES onto the epoxy resin. The reaction is assumed to proceed by a primary amine in APTES reacting with oxirane ring forming a secondary amine and a hydroxyl. The formed secondary amine will further react with another oxirane ring, resulting in the grafting of the silane as shown in Figure 3 [26, 32]. Seraj et al. [33] modified epoxy resin by APTES to use in cathodic electro-coating application. They also made a similar observation that the reaction of APTES with epoxide in resin increased the epoxide equivalent weight. It was also noticed that the reaction was more favoured at 70^{o}C compared to room temperature when the APTES content was 3 and 5 wt%.

Viscosity of modified resins

The viscosity of RS0 and modified epoxy resins exhibited a decreasing trend with an increase in temperature, as shown in Table 3. The viscosity of the epoxy resin increased with increase in silane content used in resin modification. At room temperature and at the processing temperature (65ºC) the viscosity of 5% APTES-modified epoxy resins was doubled when compared to the value for RS0 epoxy resin. During the cure reaction, viscosity of the thermoset resins will initially decrease due to thermal effects and then eventually increase with rise in the time or temperature due to the formation of cross-linked network [34]. Since the reaction between APTES and epoxide is similar to that of epoxy cure reaction with amine hardener, the increase in viscosity of APTES-modified epoxy resin is attributed to the coupling reaction occurred between silane-amine and epoxide of epoxy resin. The increase in viscosity of modified resin supplements the results obtained from the epoxide content determination test, that a reaction occurred between the epoxy resin and APTES.

FTIR analysis of resins, castings and composites

All the characteristic IR bands for epoxy resin are found in RS0 resin. The absorption bands at 1508 cm^{-1} and 1608 cm^{-1} are assigned to the aromatic ring in epoxy resin. The absorption band corresponding to stretching of C-H of the epoxide ring is at 3057 cm^{-1}. The absorption band at 914 cm^{-1} and 830 cm^{-1} is assigned to the C-O and C-O-C stretching of epoxide group [25, 35]. In epoxy resin, the broad band around 3500 cm^{-1} is assigned to O-H stretching of hydroxyl groups in epoxy resin [33, 36]. It was observed that in the case of RS5-70, the intensity of band at 3481 cm^{-1} corresponding to hydroxyl group increased compared to that of RS0. This indicates the formation of hydroxyl groups via epoxide reaction with silane-amine, as shown in Figure 3. Similar observation was made by Seraj et al. in their study related to modification of epoxy resin by APTES [33]. A comparison of RS0 resin and RS5-70 resin spectra is shown in Figure 4.

The spectra obtained for modified resins seem to be almost similar to RS0 resin with few variations. There is a new absorption band appearing at 1077 cm^{-1} for resins modified with 5 wt% APTES. Some previous studies assign this band to Si-O-C linkage indicating that the ethoxy group in the APTES silane remains unreacted in the modified resin [37]. The absence of absorption band in the region 1040 cm^{-1} to 1020 cm^{-1} and 990 cm^{-1} to 945 cm^{-1} confirms that silanols (Si-OH) are not present in the modified resin. The absence of absorption band corresponding to siloxanes

(Si-O-Si) in the region 1090 cm^{-1} to 1010 cm^{-1} also confirms that the ethoxy group in modified epoxy resin is unreacted [35]. The absorption bands corresponding to the ethoxy and epoxide groups are shown in Figure 5 (a). Generally, it is considered that the peak around 914 cm^{-1} for epoxy resin corresponds to the epoxide group in epoxy resin [25, 32]. It is seen from Figure 5(a) that the intensity of the band at 914 cm^{-1} is decreasing in the case of RS5-RT resin and RS5-70 resin. However, compared to RS0 resin, no difference was noticed in the case of RS1-RT resin and RS1-70 resin.

The absorption bands which remain invariable in a reaction which corresponds to the linkages that do not take part in the cure reaction is used as a quantitative reference for analysing cure reaction of epoxy. This is because the absorption of these bands does not change during the reaction [38-41]. Dividing the area of the reactive band by the area of reference band corrects the variation in mass and thickness of the sample. The normalized area ratio can then be used to compare different spectra. In this study, the absorption band at 1508 cm^{-1} corresponding to the aromatic ring in the epoxy resin is used as a reference band. The peak area of 914 cm^{-1} corresponding to epoxide from all the spectrums were measured by keeping the baseline and integration region constant at 928 cm^{-1} to 883 cm^{-1}. The area ratio of the absorption band of epoxide (914 cm^{-1}) to reference band (1508 cm^{-1}) and the area of absorption band at 914 cm^{-1} are shown in Table 4. The peak area corresponding to epoxide for RS1-RT and RS1-70 resins does not change compared to RS0 resin. However, peak area for RS5-RT and RS5-70 resins decreased considerably when compared to RS0 resin. The decrease in the area of the reactive band (914 cm^{-1}) and the decrease in the area ratio, especially for RS5-RT and RS5-70 resins compared to RS0 resin confirm that the epoxide reacted with an amine in the APTES by resulting in a reduction of epoxide in the modified resins. The results from ATR-FTIR is supporting the results obtained from the epoxide content determination test.

Figure 5(b) and (c) compares the FTIR spectrum of castings and composites prepared from RS-0 and RS5-70 resins. The major difference in spectra of both castings and composites was in the region 1140 cm^{-1} to 840 cm^{-1}. The disappearance of the absorption band at 1077 cm^{-1} in the case of RS5-70-CC castings and composites can be seen in Figure 5 (b) and (c). This absorption band is assigned to the unreacted ethoxy group in modified resin (Figure 5(a)). The tensile test results of composites which will be discussed later, shows significant improvement in tensile properties which indicate that the ethoxy group have undergone reaction with viscose fabric. Another notable difference seen from Figure 5 (b) and (c) is the disappearance of the absorption band at 914 cm^{-1} corresponding to the epoxide in epoxy resin. This indicates that both castings and composites prepared from the modified resin have achieved proper cure as similar in the case of those made from unmodified resin.

Glass transition temperature of cured castings

The glass transition temperature of cured castings is given in Figure 6. The T_g is reported from the midpoint temperature of second heating scan. The ultimate T_g for the castings made from 3% and 5% APTES silane modified epoxy resin slightly decreased when compared to RS0-CC casting. The lowering of T_g after silane modification of epoxy resin has been explained based on the introduction of the flexible silane molecule into the resin structure [42]. According to epoxide titration, the epoxide content in epoxy resin decreased with increase in the APTES silane content. The epoxide content is relatively lower in the modified resins and therefore, less oxirane oxygen takes part in the crosslinking reaction with amine hardener during the curing of the resin. This has resulted in cured castings with low degree of crosslinking in the case of an epoxy resin modified with a higher concentration of APTES silane. The crosslink density is considered to be influencing the T_g of the thermoset resin. A cured system with lower crosslink density is supposed to have lower glass transition temperature [43]. Please refer to Figure S7 and S8 for DSC thermogram of unmodified and modified cured castings.

Contact angle measurements of cured castings

The contact angle measurement of modified epoxy castings was done to determine the wetting properties of cured castings after modification. The contact angles obtained for the modified and RS0-CC epoxy casting surfaces are given in Figure 7. The contact angle of water on silane modified cured castings seems to be increasing with the silane modification. The contact angle gives an indication of wettability of the used liquid on a solid surface. Although epoxy resins have good physical properties, one of its main drawbacks comparing to other commonly used thermoset resin such as unsaturated polyester resins are its low resistivity against water. The water absorption of epoxy resin is related to the presence of hydroxyl groups formed in the ring opening reaction of the epoxide with the amine hardener [44]. A possible explanation for the hydrophobization by silane modification could be the migration of hydrophobic silicon to the surface of cured resin. Honaman and Witucki [45] modified epoxy coating with amino functional siloxanes and silanes including APTES. They found that the modified epoxy coating has poor recoatability. This phenomenon was explained based on the migration of silicon to the surface of amino functional silane modified bisphenol A epoxy coating. It is widely considered that the more hydrophobic a solid surface is, the lower is its wettability. Considering these facts, it could be assumed that the APTES silane modification has increased the hydrophobicity of cured modified epoxy resin compared to the cured unmodified resin.

Tensile properties of cured epoxy castings

The tensile strength of cured castings is as shown in Figure 8. The tensile strength of RS0-CC casting was determined to be 73±2.6 MPa. The tensile strength of the castings prepared from room temperature modified resins decreased in an order of RS1-RT-CC (72±0.5 MPa) > RS3-RT-CC (69±2.1 MPa) > RS5-RT-CC (67±1.6 MPa). There was no significant change observed in tensile strength of RS1-70-CC (70±2.8 MPa) castings when compared to RS0-CC castings. However, the tensile strength decreased with further increase of APTES content for resins modified at 70^{o}C. The tensile strength recorded for RS3-70-CC and RS5-70-CC are 67±1.0 MPa and 62±2.1 MPa respectively. Irrespective of the modification temperatures, the tensile strength of modified castings decreased with an increase in APTES content. The effect of modification temperature on the tensile strength of castings was found to be influenced by the APTES content. The change in tensile strength among RS1-RT-CC & RS1-70-CC and RS3-RT-CC & RS3-70-CC was less significant considering the standard deviation in the results obtained. Whereas, compared to RS5-RT-CC, there is a small decrease in tensile strength of RS5-70-CC.

According to the epoxide content determination test, the epoxide content of epoxy resin decreased with an increase in APTES content, regardless of modification temperatures. For this reason, a relatively low amount of oxirane oxygen will take part in the crosslinking reaction with amine hardener in the case of modified cured castings. This will result in cured castings with lower crosslink density compared to casting prepared from RS0 resin. Crosslink density is a critical parameter governing the properties of the cured resins. Generally, thermoset resins with lower cross-link density are considered to have lower tensile strength [46]. The decrease in the tensile strength of cured castings with increasing APTES content is correlated with the decrease in epoxide content of resin with an increase in APTES content. Thus it is deduced that lower tensile strength of modified cured castings is due to low cross-link density induced by the APTES grafting on the epoxy resin.

The elongation at break of the APTES-modified cured castings is shown in Figure 9. The percentage of elongation at break of the RS0-CC castings was recorded to be 10.5±1.7. Compared to RS0-CC castings, there was no difference observed in the elongation at break of RS1-RT-CC (10.2±1.2) castings. A small difference in the elongation at break of RS3-RT-CC (9.4%±2.0), RS5-RT-CC (9.8%±1.9), RS1-70-CC (9.9±1.2), RS3-70-CC (9.9±2.0) and RS5-70-CC (9.8±2.0) castings compared to RS0-CC are negligible considering the standard deviation. There was no significant change observed for elongation when comparing RS1-RT-CC & RS1-70-CC; RS3-RT-CC & RS3-70-CC; and RS5-RT-CC & RS5-70-CC. This indicates that the elongational strength of cured castings was not affected by the content of APTES or the temperature used for modification. Honaman and Witucki [45] modified epoxy coatings by various silanes and siloxanes to improve the flexibility. They reported that epoxy coatings containing silanes does not improve the flexibility while the flexibility of epoxy coatings containing siloxanes improved. Heng et al [21] synthesized an epoxy resin containing siloxane bridge and found that the elongation at break improved. The increase in elongation was explained based on the siloxane bond formation. Both studies point out that siloxane bond formation have an essential role in improving the elongation of the epoxy resin modified by organo-silicon compounds. In this study, the modified epoxy resin contains non-hydrolysed ethoxy group and hence siloxane bond formation is not favoured. Thus the elongation of resin is not affected by the APTES modification.

Tensile properties of composites

The tensile strength of the epoxy/viscose fabric composites is shown in the Figure 10. The tensile strength of composites prepared from unmodified resin and unmodified fabric (RS0-C) was found to be 71.1 ±2.3. The tensile strength of RS1-70-C, RS3-70-C, and RS5-70-C composites was 70.9 ±1.5, 81.3 ±2.7, and 78.9 ±1.8 respectively. The composites prepared from modified viscose fabric (RS0-FS2-C) exhibited a tensile strength of 55.5 ±2.4. Compared to RS0-C, no significant difference in strength was noticed for RS1-70-C composites. However, in comparison with RS0-C, the strength of RS3-70-C and RS5-70-C composites increased 14% and 11% respectively. A trend observed among the composites prepared from APTES-modified resins is that the tensile strength of composites increases up to an APTES content of 3 wt% in modification and then slightly decreases when the APTES content is 5 wt%. The tensile strength of RS0-FS2-C decreased 22% in comparison to RS0-C composite. Compared to RS0-FS2-C, the strength of RS3-70-C composite is found to be 46% higher. This clearly shows that in this study, the matrix resin modification turns to be better than the chemical fibre surface modification method used.

The elongation at break of the composites (Figure 11) seems to be increasing with increase in APTES content. Compared to RS0-C composites, the elongation at break increased 29% and 41% for RS3-70-C composite and RS5-70-C composites respectively. While, there was a decrease of 40% in elongation of RS0-FS2-C. When compared to elongation of cured resin, the elongation of composite depends more on the properties of reinforcement. It could be considered that the elongation at break of the composites is more influenced by the content and elongation of reinforcing fibre [47]. This is reflected from the elongation of composites prepared from modified and unmodified resins, which is lower compared to the RS0-CC. However, the elongation at break for composites made from modified resins is higher than for the the epoxy composites reinforced with lignocellulosic fibres and glass fibres. Compared to its lignocellulosic counterparts, the elongation at break of viscose fibre yarns used to make the fabric utilised in this study is significantly higher [48]. The increase in elongation in the case of composites made from modified epoxy resins with respect to RS0-C indicate the improved fibre-matrix adhesion attained after the APTES modification of epoxy resin.

The findings from this study suggest that the interfacial adhesion between a warp knitted viscose fabric and epoxy resin improved after the modification of the epoxy resin by APTES. The coupling mechanism can be explained based on the chemical bond formation between the alkoxy containing epoxy resin and hydroxyl groups in the viscose fabric. The presence of unreacted ethoxy (CH_3CH_2O-) after modification of the resin with APTES was confirmed from FTIR analysis (Figure 5(a)). The FTIR analysis of cured castings and composites (Figure 5(b) and 5(c)) show that the absorption band around 1077 cm^{-1} corresponding to (Si-O-C) the ethoxy group, disappears after curing reaction of the epoxy resin. This indicates that the ethoxy groups in the APTES-modified epoxy resin have undergone reaction during the curing of the resin. The tensile strength decreased 8% for RS3-70-CC casting and 15% for RS5-70-CC casting when compared to RS0-CC casting. However, the tensile strength of RS3-70-C composite and RS5-70-C composite increased 14% and 11% respectively. The increase in strength of composites prepared from modified resins with respect to cured castings is obviously due to the improved adhesion between viscose fabric and epoxy resin.

The pre-hydrolysis of the alkoxy group and a temperature above 80ºC are essential for silane modification of cellulose fibre [49]. The low reactivity of Si-OR towards cellulose-OH when compared to Si-OH of the glass surface, was explained based on the poor acidic nature of cellulose-OH [49]. Also, it is seen in literature that the non-hydrolysed alkoxy group (Si-OR) of silane reacted and formed a chemical bond with glass Si-OH [49, 50]. Instead of fibre modification, matrix modification approach is used in this study and thereby the reaction conditions are different from that of cellulose fibre modification. The modification of resin was done in water free and non-humid conditions. Thus the silane grafted resin contains unreacted ethoxy group which was evident from the IR results. The disappearance of the unreacted ethoxy group in modified resins after cure reaction hints the possible reaction occurred during the curing of composites involving ethoxy. This is evident from the improvement of up to 14% in tensile strength and 41% in elongation at break of the composites prepared from alkoxy containing epoxy resin.

Since this study used only one chemical modification method to modify the cellulose fibres, the obtained data is compared to the literature. Recently reported data on the effect of the chemical surface modification on the tensile properties of epoxy composites are compared with the results from the current study and are tabulated in Table 6. Only those studies which reported improvement in the tensile properties of epoxy composites are listed to compare the results from this study and those without improvement is omitted. The percent change in tensile strength for the modified-epoxy/viscose fabric composites prepared in this study is similar to that of the epoxy composites prepared from silane coupling agent modified lignocellulosic fibres [52, 53]. Whereas, the elongation at break of the composites prepared from modified-epoxy resin shows significant increase. The percent change in tensile strength of alkali treated fibre composites obtained from literature is in the range 5.8% - 32.8%. The results from the modified-epoxy resin composites made in this study comes within this range of percent change.

The APTES modification of fabric adopted in this study seems to decrease the tensile strength by 22% and elongation at break by 39.8%. The silane treatment method which gave best result with unsaturated polyester resin (UPR) in our previous study was adopted to modify the fabric [5]. This was selected assuming that the chemical affinity of amine in the silane towards epoxy is higher than that to UPR and was expecting to get better results. It is seen from the Table 6 that the tensile strength of APTES-modified grewia tilifolia/epoxy composites shows an increase in strength when the silane content was 1 vol% in acetone. This might be indicating that the 2 vol% APTES in ethanol/water solution used in this study was excess for the modification. The excess silane is reported to form a physisorbed layer on the chemisorbed silane layer. This layer can act as a lubricant and failure occurs in this region through slippages of physisorbed silane chains [54]. On other hand, the physisorbed layer can prevent the chemisorbed layer from forming chemical bond with the matrix resin [55], which leads to inferior properties.

It is well accepted that chemical treatment methods improve the properties of composites, considering that the optimum treatment conditions are met for each fibre-matrix system under study. However, the established fibre chemical treatment methods are more or less expensive and harmful to environment [56]. The overall time taken from the start of the chemical treatment to drying of the fibres takes minimum 24 hours to maximum of 4 days (excluding the time taken for washing and neutralizing the fibres) (Table 6). The modified-epoxy castings and composites prepared in this study was fabricated after 24 hours of resin modification. Thus in the matrix modification approach the processing time from resin modification to fabrication of composites is same or even less compared to fibre modification methods listed in Table 6. Since the resin modification only takes 1 hour (current study) and because there is no drying step involved, it is also possible to reduce the time after the modification until the fabrication of composites. More research is needed to optimize the process time. Moreover, the direct mixing of the silane in to the resin and using the modified resin in fabrication of composite creates less process waste compared to the hazardous waste generated after the fibre modification. Hence the improvement in tensile properties of composites attained by resin modification approach indicates that it can be used as an alternative for fibre modification approach. Further research is needed to make both the process cost-effective and environmental friendly.

Tensile fractography

SEM images from tensile fracture surface of composites are shown in Figure 12-14. The bundle pull-off in non-load bearing 90^0 layer of cross-ply laminate can be observed from Figure12 (a). Single filaments in the 90^0 layer bundle appears to be clean with less resin covered region and fibre splitting. The polyester yarns used for knitting are also labelled. The appearance of resin rich region is smooth and shiny, but the resin region near polyester knit yarn exhibits micro-textures like river lines. The load bearing 0^0 plies are observed to be more rugged. The internal cracking within the bundle and bundle de-bonding along the fibre-matrix interface is visible from Figure12 (b). Therefore, from the image analysis of RS0-C composites it is assumed that the adhesion between viscose yarns and the epoxy resin is weak.

The SEM images from the tensile fracture surface of RS3-70-C and RS5-70-C composites are shown in Figure 13 (a), (b), (c) and Figure 14 (a) and (b) respectively. Similarly, as in the case of RS0-C composites, pull-out of the non-load bearing 90^0 fibres and fibre imprints are observed also in the case of RS3-70-C (Figure 13 (a)). The RS3-70-C seems to be exhibiting surface features like river lines in the region of polyester knit yarn and also in resin rich region. An improved fibre-matrix adhesion can be seen in Figure 13 (b) through resin smeared bundle as marked. The internal cracking within the bundle in the load bearing 0^0 layer is seen from the image, but the bundle de-bonding along the fibre-matrix interface is less compared to RS0-C composite as seen from Figure13 (a) and (b). Moreover, the fracture surface of RS3-70-C is exhibiting more matrix deformations such as cusps and textured micro flow patterns compared to RS0-C composites as seen from Figure 13 (c). These observations are indicating the improved adhesion of viscose fibre to APTES-modified epoxy resin.

It can be seen from the comparison of Figure 12 (a) and Figure 14 (a) that both fracture surfaces are found to be with fibre rich 90^0 layer. In the case of RS5-70-C composites, the filaments in bundle are well embedded in the matrix resin with less splitting occurring. This point out a better fibre-matrix adhesion in RS5-70-C composite compared to RS0-C composite. As in the case of RS0-C composites, internal cracking within the bundle and the splitting of the load bearing 0^0 layer are visible from Figure 14 (a), but in low degree. It is also seen that the polyester knit yarn also exhibit improved adhesion with 5% APTES-modified epoxy resin. This provide a textured appearance of the resin rich area. The 0^0 bundle smeared with resin can be seen from the Figure 14 (b). Also, resin covered 90^0 bundle is visible. Although, the fibre-matrix adhesion improved, it is also notable that the presence of the polyester knit yarn have initiated bundle de-bonding in the polyester yarn rich region surrounding the load bearing 0^0 bundle. From the observations made from the SEM image analysis, it seems that both RS3-70-C and RS5-70-C composites exhibits improved fibre-matrix adhesion compared to the RS0-C composite.

In cross-ply laminated composites, failure modes such as fibre fracture, delamination between the layers, ply splitting or matrix cracking can develop [57, 58]. Under tension, first failure occurring in a cross-ply laminated composite is the ply cracking in the non-load bearing 90^0 layer. This takes place well before the ultimate failure [59, 60]. In the case of the load bearing 0^0 layer, the main failures observed are the fibre breakages and bundle internal cracking. Same events are assumed to have happened in case of all the composites under study with varying degree of splitting. Generally, a lack of matrix resin on the fibre surface, higher degree of filament pull-out, and matrix cracking within the fibre bundles are taken as an evidence of poor fibre-matrix adhesion [61, 62]. Also, a composite with low fibre-matrix adhesion is supposed to exhibit less matrix deformation patterns such as cusps and textured micro-flows like river lines [61-63]. Taking this into account, it could be assumed that the fibre-matrix adhesion improved with the APTES modification of epoxy resin when compared to RS0-C composite. The improvement in fibre-matrix adhesion is evident from the SEM images corresponding to the RS3-70-C and RS5-70-C composites which exhibits resin smeared fibre surfaces with less fibre splitting and lower bundle de-bonding across the fibre-matrix interface. A notable observation was about the internal cracking within the load bearing 0^0 yarns. This behaviour was exhibited by all the composites irrespective of modification. This is ascribed to the architecture of the warp knitted viscose fabric. In the case of knitted fabrics, each yarns tends to be fairly filament rich with respect to the overall volume fraction of the composite [64]. Thus it is susceptible to bundle internal cracking as observed from the tensile fracture surface images of composites. The bundle de-bonding is associated with the rapid change in the compliance across the bundle boundaries [64]. When the fibre-matrix adhesion improved after resin modification, the degree of de-bonding was found to be lower especially in the case of RS5-70-C composites. However, the presence of knit yarn in the boundary of the bundle initiated the de-bonding in that particular region. The knit yarns are reported to act as initiation sites for damage development in composites with knitted fabric as reinforcement [65]. The tensile strength of the RS3-70-C and RS5-70-C composites were 14% and 11% higher than RS0-C composite. SEM analysis alone could not provide evidences for fibre-matrix adhesion in polymer composite materials. The observations made from the image analysis are supplementing the results obtained from the mechanical testing of composites. Thus it is deduced that the tensile properties of the epoxy/viscose fabric composite improved owing to the improved fibre-matrix adhesion attained after APTES-modification of the epoxy resin.

CONCLUSIONS

The potential of utilising γ-aminopropyltriethoxysilane (APTES) as epoxy resin modifier to improve the tensile properties of fibre reinforced polymer composites was examined in this study.

- The modification of epoxy resin by silane coupling agent was confirmed through a decrease in epoxide content of modified resin and through ATR-FTIR analysis
- In comparison with RS0-CC castings, the tensile strength of cured castings prepared from 3 wt% and 5 wt% silane modified-epoxy resin decreased 8% and 15% respectively. This is due to the decrease in crosslink density after resin modification as evident from change in glass transition temperature.
- There was an increase of 14% in tensile strength and 41% in elongation at break of the composites after the modification of resin with 3 wt% APTES. The improvement in the tensile properties are attributed to the improved fibre-matrix adhesion attained after the resin modification. The fracture surface analysis of tensile specimens also justify the results obtained from the tensile testing of the composites.

The improvement in the tensile properties of composites obtained by resin modification approach is comparable to those attained by fibre modification approach. Moreover, the direct mixing of silane in to epoxy resin generates less process waste compared to that generated after the chemical treatments such as alkalization, acetylation and silylation. More research is needed to optimize both resin modification and fibre modification methods to make it more cost-effective and eco-friendly. Mechanical, water absorption, thermal and burning properties of the viscose fabric composites prepared from silane modified epoxy resin is currently under evaluation. These studies are assumed to provide more insight into the overall performance of these composites.

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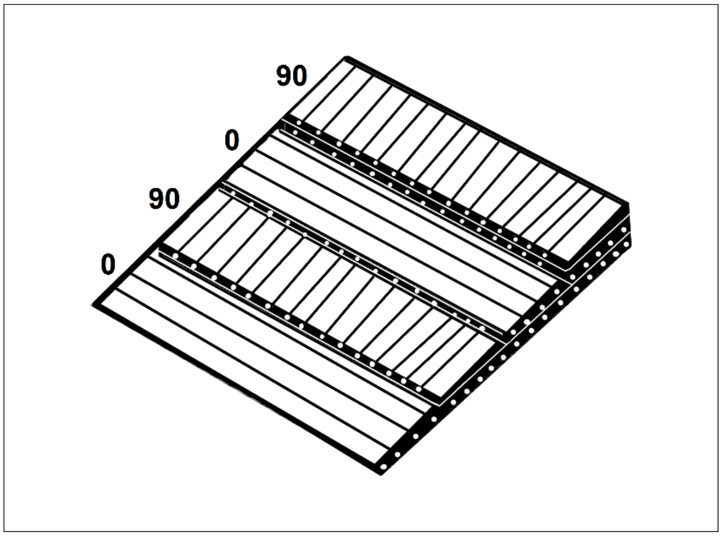


Fig 1. Schematic representation of fabric lay-up in viscose fabric composite

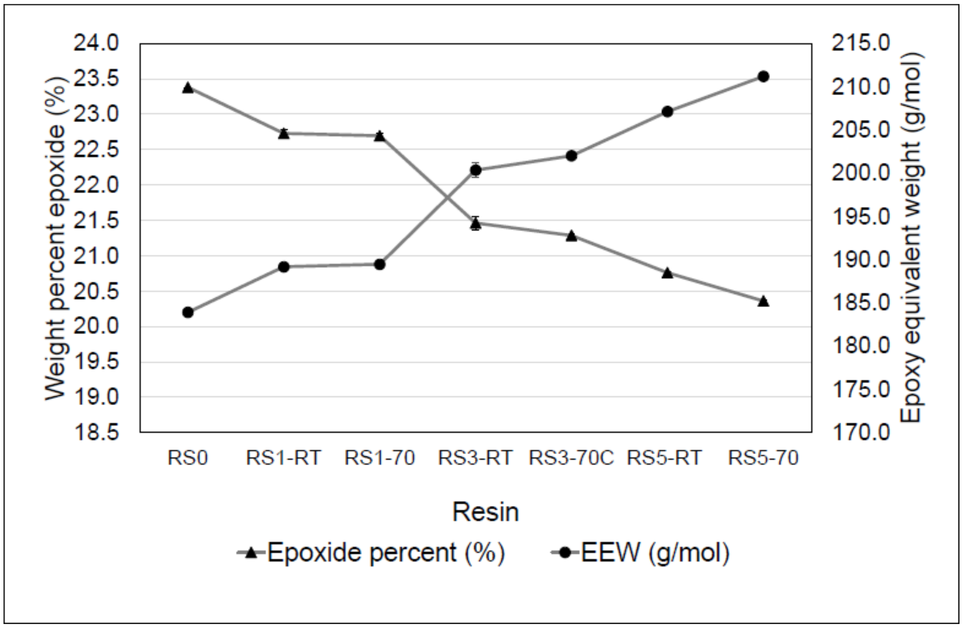


Fig 2. Epoxide equivalent weight of EP unmodified and silane coupling agent modified epoxy resin

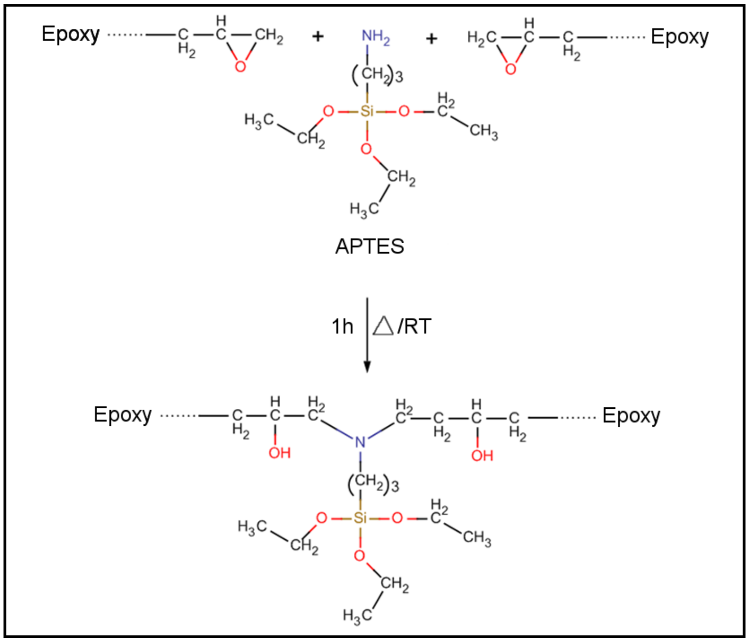


Fig 3. Coupling reaction between 3-aminopropyltriethoxysilane and epoxide in epoxy resin

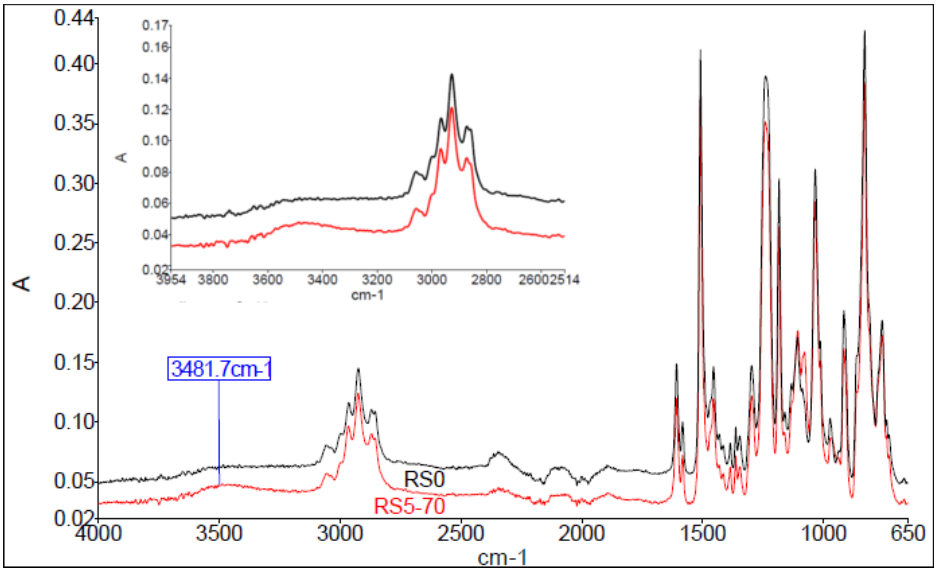


Fig 4. FTIR spectra of RS0 and RS5-70 resins and inset in the region 3954 cm^{-1} – 2514 cm^{-1}

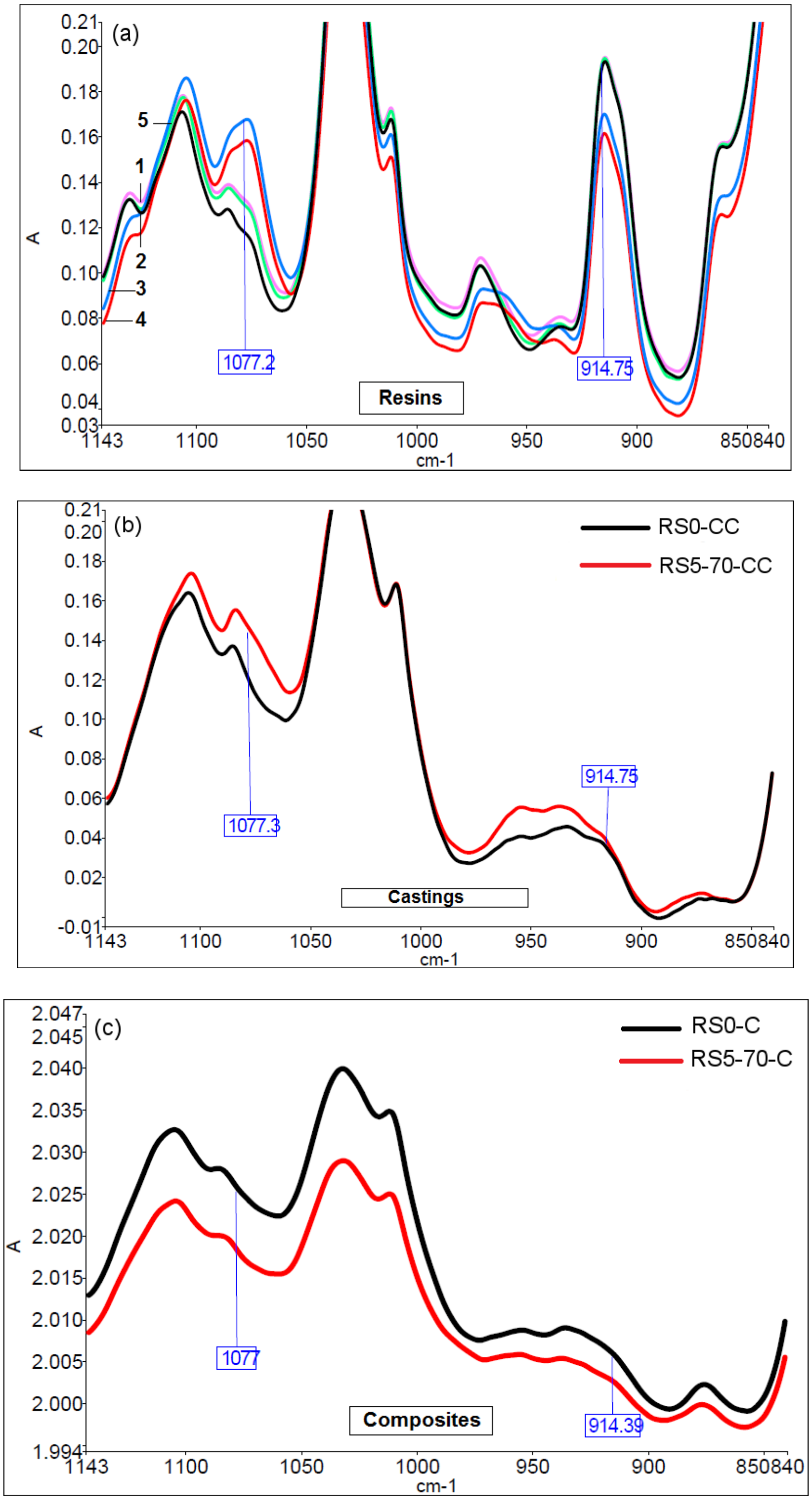


Fig 5. FTIR spectra of epoxy resin, cured castings and composites in the region 1140 cm^{-1} – 840 cm^{-1} (a) Resins- 1: RS1-70, 2: RS0, 3: RS5-RT, 4: RS5-70, 5: RS1-RT (b) castings and (c) composites

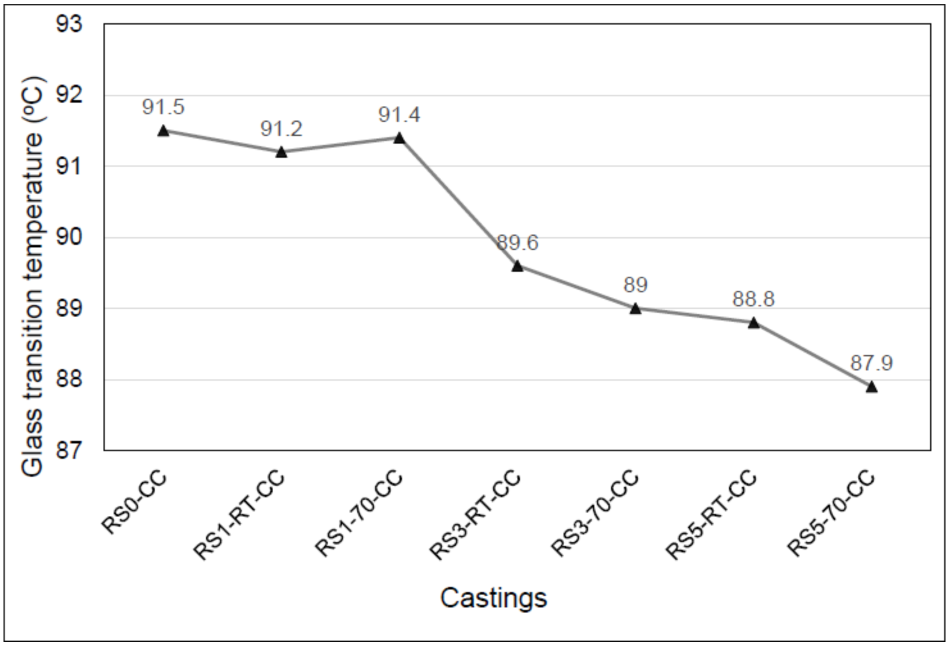


Fig 6. Effect of APTES modification on the glass transition temperature of cured castings

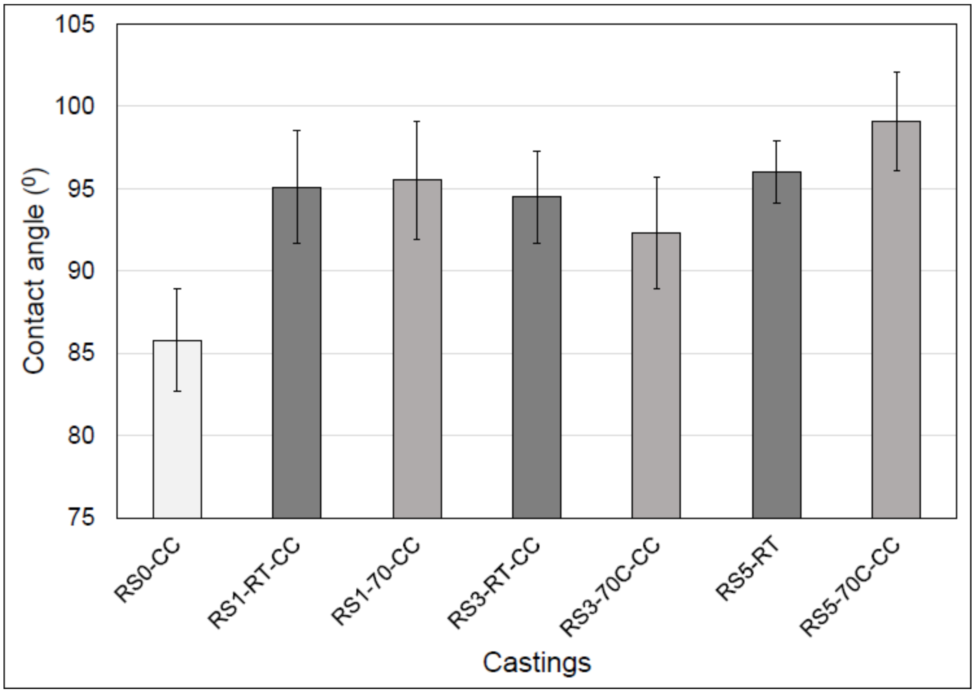


Fig 7. Static water contact angle of modified and unmodified cured epoxy castings

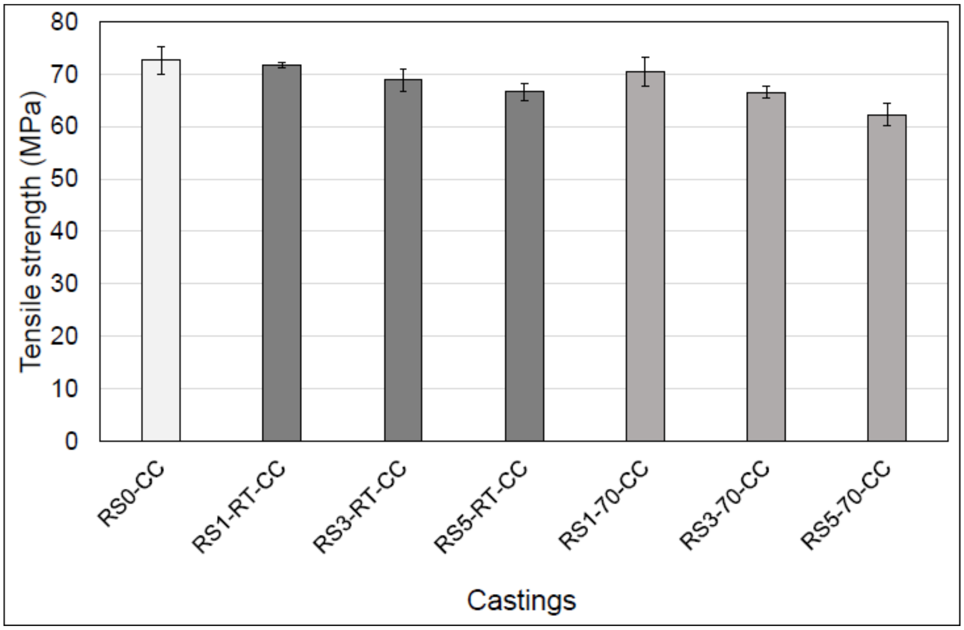


Fig 8. Effect of APTES modification on the tensile strength of cured castings

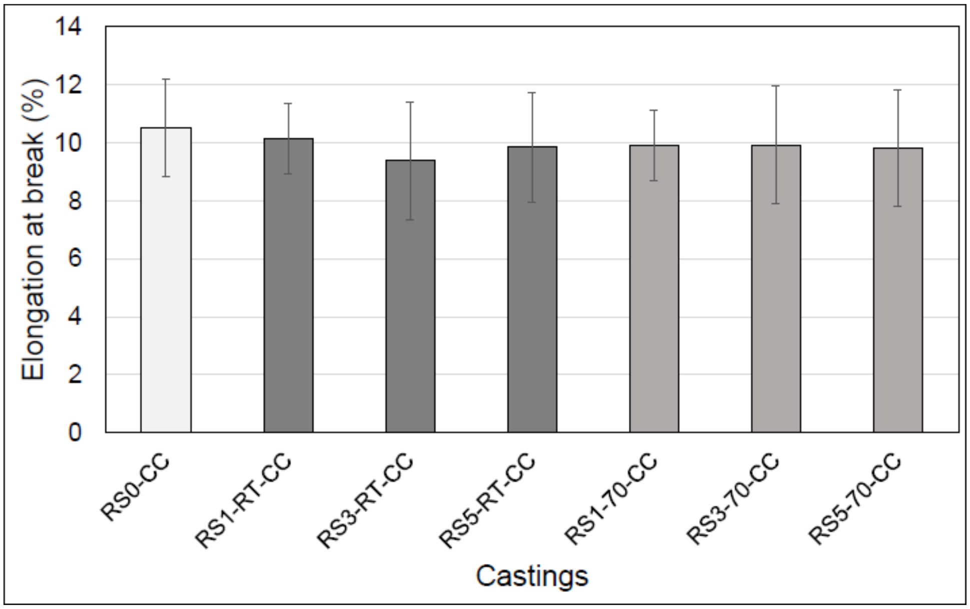


Fig 9. Effect of APTES modification on elongation at break of cured castings

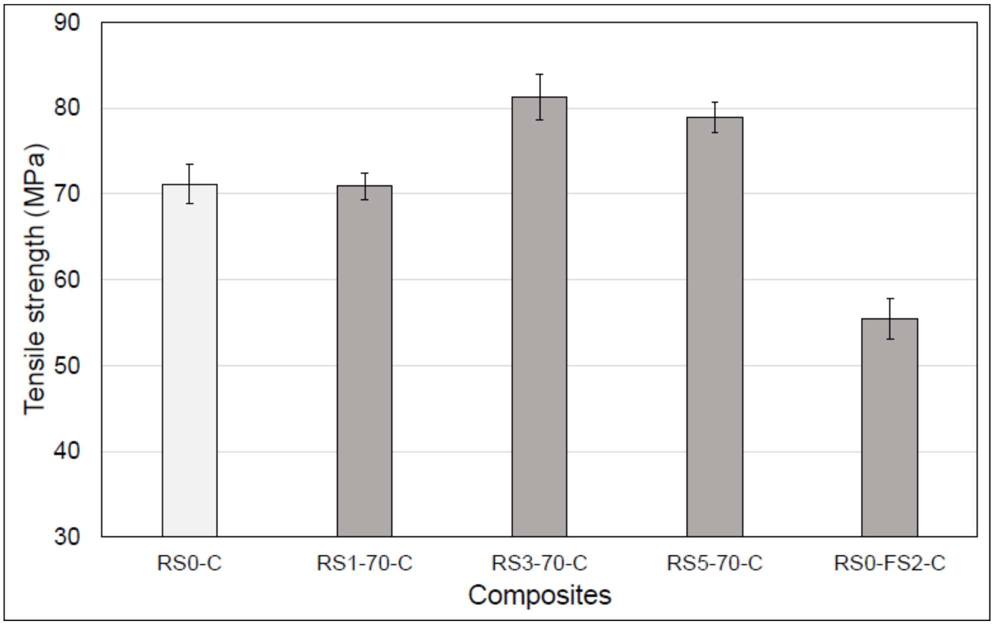


Fig 10. Effect of APTES modifications on tensile strength of epoxy/viscose fabric composites

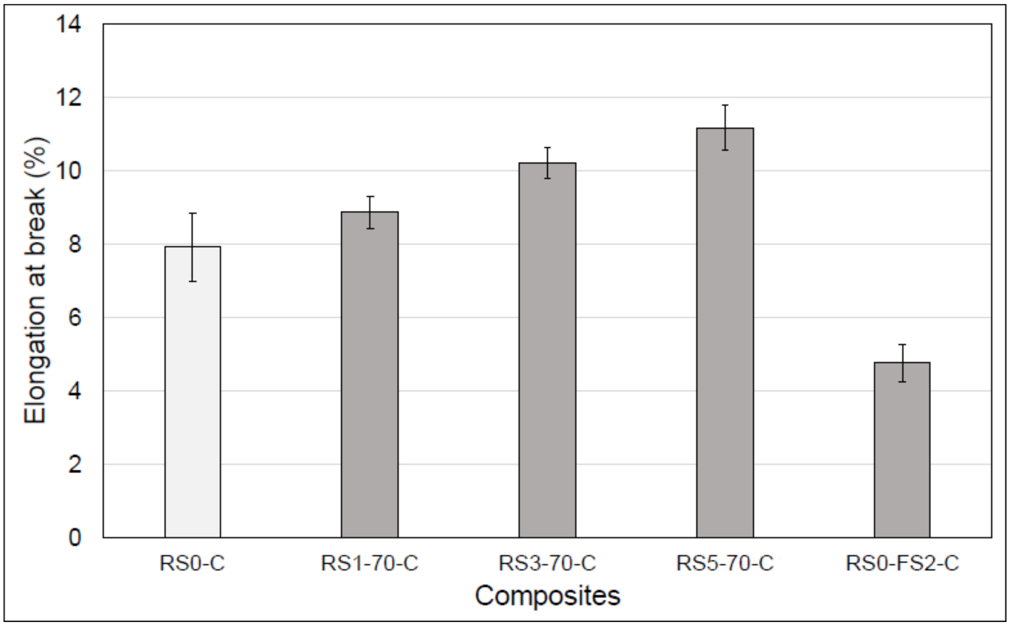


Fig 11. Effect of APTES modifications on elongation at break of epoxy/viscose fabric composites

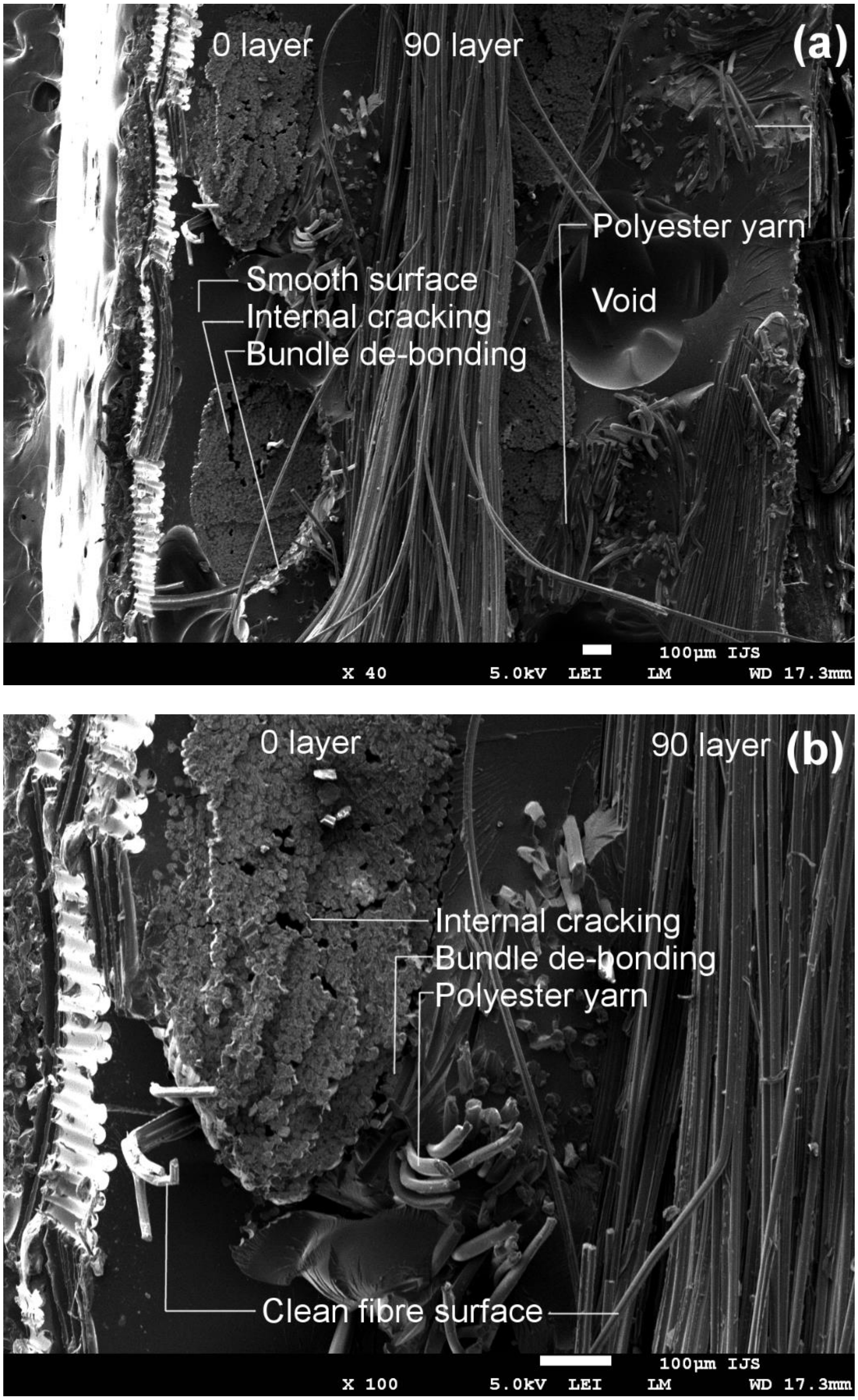
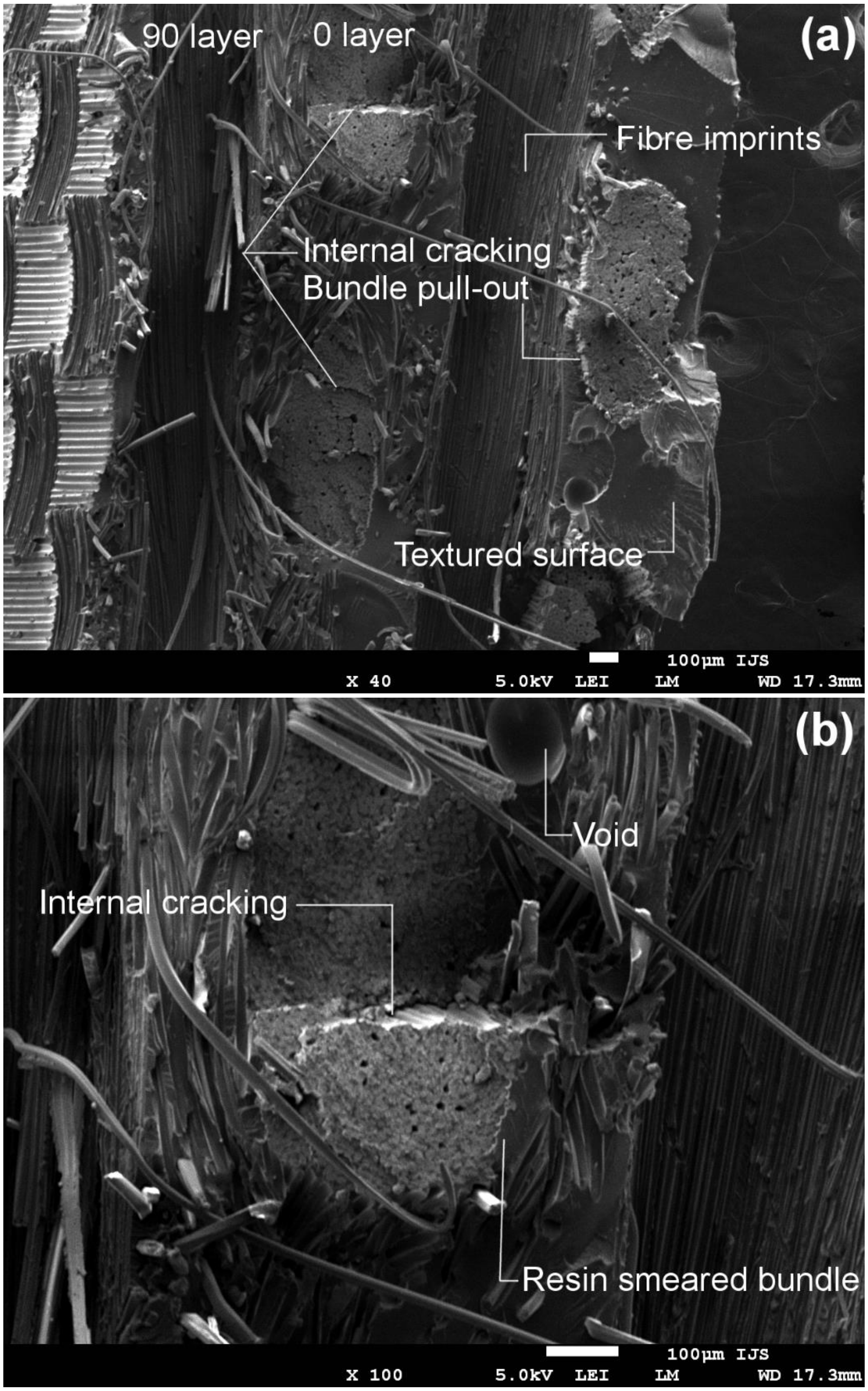


Fig 12: SEM images from tensile fracture surface of RS0-C composites


(a)
90 layer
0 layer
Fibre imprints
Internal cracking
Bundle pull-out
Textured surface
100µm IJS
X 40 5.0kV LEI LM WD 17.3mm
(b)
Void
Internal cracking
Resin smeared bundle
100µm IJS
X 100 5.0kV LEI LM WD 17.3mm

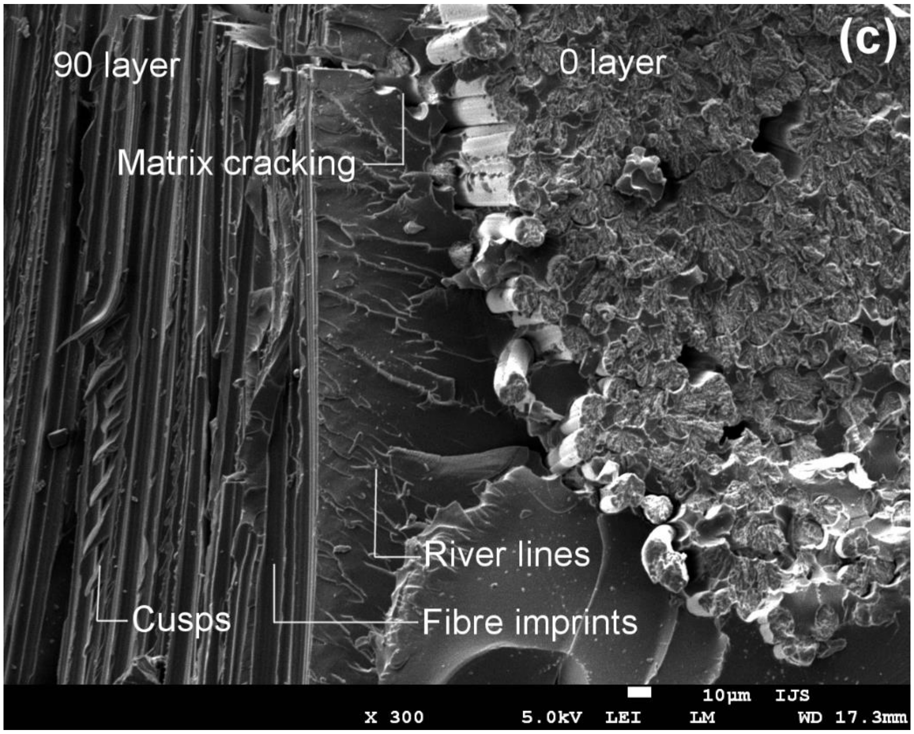


Fig 13: SEM images from tensile fracture surface of RS3-70-C composites

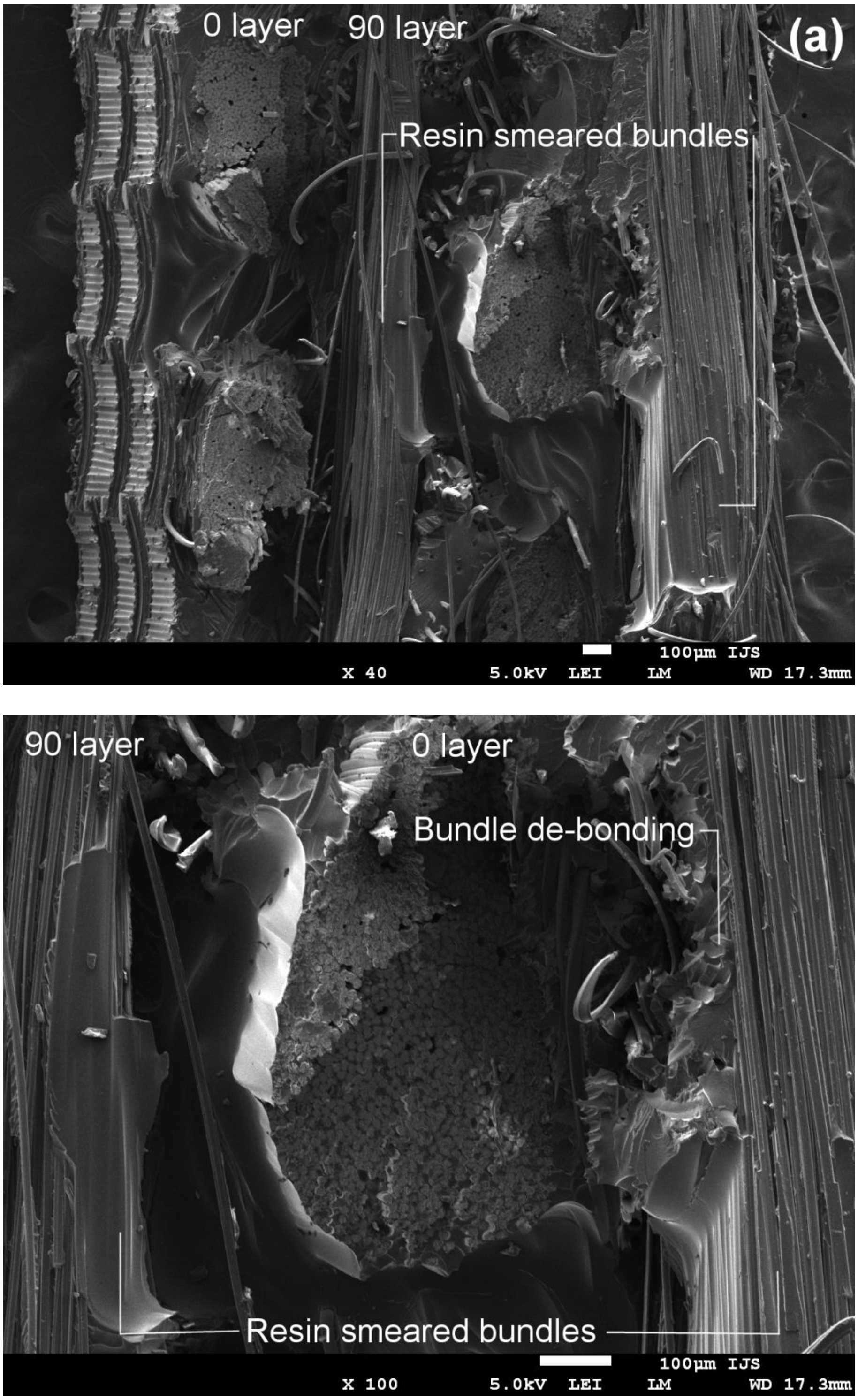


Fig 14: SEM images from tensile fracture surface of RS5-70-C composites

Table 1: Properties of epoxy resin and its cured castings according to the resin supplier

Properties of resin	**Resin**	**Hardener**
Mix ratio (by weight)	100	26
Viscosity at 25ºC (cP)	600-640	15-17
Density (g/cm^3)	1.123	0.936
Properties of cured castings		
T_gUlt (DMTA) (ºC)	87-89	
HDT (ºC)	68	
Tensile strength (MPa)	73	
Tensile modulus (GPa)	3.5	
Strain to failure (%)	3.5	
Cured density (g/cm^3)	1.144	

Table 2: Details of modification and designations of resins, castings, and composites

Modification		**Designation**		
Silane	**Description**	**Resin**	**Cured castings**	**Composites**
0 wt%	No modification	RS0	RS0-CC	RS0-C
1 wt%	Resin modified at room temperature	RS1-RT	RS1-RT-CC	NA
3 wt%	Resin modified at room temperature	RS3-RT	RS3-RT-CC	NA
5 wt%	Resin modified at room temperature	RS5-RT	RS5-RT-CC	NA
1 wt%	Resin modified at 70ºC	RS1-70	RS1-70-CC	RS1-70-C
3 wt%	Resin modified at 70ºC	RS3-70	RS3-70-CC	RS3-70-C
5 wt%	Resin modified at 70ºC	RS5-70	RS5-70-CC	RS5-70-C
2 vol%	Fabric treated at room temperature and dried at 110ºC	NA	NA	RS0-FS2-C

TABLE 3: Effect of silane modification on the viscosity of epoxy resin

Modification	**Viscosity (cP)**	
	25ºC	**65ºC**
RS0	614	36
RS1-RT	704	38
RS1-70	716	61
RS3-RT	872	48
RS3-70	891	48
RS5-RT	1170	59
RS5-70	1185	61

Table 4: Peak area for resins at 914 cm^{-1} and area ratio of reactive band and reference band

Resin	**Peak area**	**Area ratio** **(914 cm^{-1}/1508 cm^{-1})**
RS0	2.43	0.45
RS1-RT	2.40	0.44
RS1-70	2.38	0.45
RS5-RT	2.00	0.40
RS5-70	1.98	0.39

Table 5: A comparison on influence of fibre modification method and resin modification method on tensile strength and elongation at break of epoxy composites

Composite	**Treatment**				**Tensile strength change (%)**	**Elongation at break change (%)**	**Ref**
	Modifier	**Content**	**Time (h)**	**Drying time (h)**			
Sugar palm/ epoxy	NaOH	0.25 (M)	1	96	16.4	-	[51]
Grewia tilifolia/ epoxy	NaOH	5 (wt%)	0.5	-	5.8	-	[52]
Flax/epoxy	NaOH	5 (wt%)	0.5	24	21.9	-	[17]
Bamboo/ epoxy	NaOH	5 (wt%)	0.5	24	32.8	-	[17]
Grewia tilifolia/ epoxy	APTES	1 (vol%) in (acetone)	6	1	14	-	[52]
Bamboo/ epoxy	MPS	0.5 (wt%) in deionized water	4.5	20	15.1	-	[53]
Viscose/ epoxy	APTES	2 (vol%) in 95:5 ethanol/ water	0.8	0.5	-22.0	-39.8	This study
Viscose/ matrix modified epoxy	APTES	3 (wt%)	1	-	14.0	28.9	This study
Viscose/ matrix modified epoxy	APTES	5 (wt%)	1	-	10.8	41.2	This study