

Influence of the Modification of Resol Phenolics on the Properties of Glass and Cotton Fiber Laminates

Parameswaran P. Subramanian^{1,*}, Vaisakh S.S.², Chithra Sekhar V³, Manoj N⁴

Abstract

Fiber reinforced polymer (FRP) composite based on resol phenolics awaits special attention due to excellent inherent properties of the resol phenolics. In this study, modified resol phenolics by unsaturated polyester (UP) and epoxidised novolacs of simple phenol, o-cresol and p-cresol were used to fabricate glass and cotton FRPs. An overall enhancement of 25% in tensile strength and 40% in impact strength is achieved upon modification for both the modified laminates. The amount of modifiers required to achieve this enhancement in the mechanical properties is approximately 10% by weight of resol phenolics. Among the FRPs, glass reinforced composites demonstrated better enhancement in mechanical properties compared to cotton reinforced composites. The results of the water sorption, DMA, and SEM analyses indicate that the modifiers improve the characteristics of the glass fiber-matrix by strengthening the fiber-matrix interface. However, the cotton fiber reinforced composites do not exhibit any appreciable enhancement in the fiber-matrix adhesion by resol modification. Theoretical modelling studies that correlate the volume fraction of fiber with tensile strength of composites have been carried out. It also supports the enhancement of interfacial adhesion in glass-reinforced composites upon matrix modification compared to cotton-reinforced composites. Among the modified resins, UP modified resins impart better properties for the FRP composite than the epoxy modified resins.

Keywords: Resol, modification of resol, FRP, glass laminates, water sorption

INTRODUCTION

Fiber-reinforced polymer complexes have extensive applications across various industries, including high-strength lightweight structures, construction, maritime, aerospace, defense, automotive, sports, and storage tanks [1–4]. Among these, phenolic resins and glass/phenolic composites are particularly noteworthy due to their inherent fire-retardant properties and best flammability performance compared to other thermoset composites. Additionally, phenolics produce minimal level of toxic gases and smoke when subjected to burning [5–7]. Phenolic resins also exhibit several advantages over other thermosetting polymers, such as superior strength, higher hardness, enhanced heat and chemical resistance, and excellent dimensional stability [8–10].

The durability and mechanical properties of phenolic resol resin are insufficient for making complex structural designs. Enhancing these properties is essential to achieve performance levels comparable to other glass/thermoset resin

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composites. Phenolic resins exhibit excellent bondage with natural fibers caused by chemical interactions between the reactive groups in the resin with -OH groups of cellulose in the fibers [11]. However, modifying phenolic resin may affect its bondability with both glass and natural fibers. Studies have shown that the incorporation of unsaturated polyester and epoxidized novolac enhances the properties of phenolic resol resin [12-13]. In this study, these modifiers are utilized to fabricate resol based fiber-reinforced plastics (FRPs), and their properties are evaluated to assess the impact of resin modification on the performance of FRPs.

Here both glass-reinforced and cotton-reinforced laminates were fabricated using modified and unmodified resol phenolic resins. Woven roving glass mats and cotton cloth were employed as reinforcement materials. The influence of modification of resol was evaluated by analysing the tensile strength, impact strength, flexural strength, dynamic mechanical and water sorption properties. These properties are compared with that of the neat composites. The fracture behavior of the laminates was analyzed using scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

The glass mat (WRM-Binani-IS:11272/BS:3749, 610 g/m²) was supplied by M/s Sharon Engineering Enterprises, Kochi, Kerala, India. The cotton cloth, featuring specifications of 100 grams/m² and 40 yarns/ inch², was provided by Ambika Mills, Coimbatore, India. Resol resin in an alkaline medium was sourced from M/s Polyformalin (P) Limited, Thripunithura, Kerala, India.

The neutralization of resol was conducted using glacial acetic acid. Following this process, the neutralized resin was left to rest overnight, after which the aqueous layer was carefully decanted. To eliminate residual traces of water, vacuum was applied for a duration of 12 hours.

Fabrication And Evaluation of Glass and Cotton Reinforced Laminates

The dry resin was blended with 30% methanol and applied to glass and cotton mats. After application, the surplus resol was removed by pressing. A total of 13 piles of glass mats and 14 piles of cotton mats were used to construct the laminate. The resin-impregnated laminates were first cured at room temperature for two days, followed by an additional curing at 70°C for one hour in an air oven. The partially cured laminates were placed between polished steel plates and pressed at 150°C for 30 minutes under a pressure of 180 kg/cm². The final molded sheets had an approximate thickness of 2 mm.

Glass- and cotton laminates were also fabricated using unsaturated polyester (UP) and epoxidized novolac-modified phenolic resins. Optimum modifier concentrations of 7.5 wt.% of UP and 10 wt.% of epoxidised novolacs on resol phenolic basis were used for fabricating laminates [12-13]. The designation and synthesis of UP2, UP2a, UP2b, UP2c, and UP2d have been explained elsewhere [12]. The epoxidized novolac modifiers employed include EPN (epoxidized phenolic novolac), EPCN (epoxidized p-cresol novolac), and EOCN (epoxidized o-cresol novolac). Specifically, six variants of epoxidized novolacs - EPN7, EPN9, EPCN7, EPCN9, EOCN7, and EOCN9—were utilized. The numbers "7" and "9" correspond to the phenol-to-formaldehyde molar ratios of 1:0.7 and 1:0.9, respectively, which were used during their synthesis [13].

Void Content

Void content was calculated as per ASTM 2734-94. Equation (1) was used to calculate void content.

$$\text{Void content, } V = \frac{100(T_d - M_d)}{T_d} \quad (1)$$

T_d and M_d respectively were the theoretical and measured composite density. V is the void content in volume %.

The theoretical composite density can be calculated using the equation (2)

$$T_d = \frac{100}{\left[\frac{R}{D} + \frac{r}{d} \right]} \quad (2)$$

where T_d is the theoretical density. R and D represent respectively the wt.% and density of resin. r and d denote respectively the wt. % and density of the fiber.

Mechanical, Dynamic mechanical and Morphological Studies

The tensile and flexural properties were evaluated in accordance with ASTM D 638 and ASTM D 790, respectively, using a Shimatzu Autograph (AG-I 50 KN) UTM. Impact strengths were determined using a Resil Impact Analyser (Junior), following the ASTM D 256 standard.

A dynamic analyser model TA Instruments DMA-Q 800, was made use to study the damping property of the composites.

The morphology of the fractured surfaces was analysed using a scanning electron microscope, JOEL JSM 840A.

Water Sorption Studies

Moisture ingress into composite materials takes place via three principal mechanisms. [14]. The primary mechanism is the diffusion of water molecules into the microgaps between polymer chains. Additional mechanisms include capillary transport through gaps and flaws at the fiber-polymer interfaces caused by incomplete wetting, as well as the penetration and movement of moisture through microscopic cracks in the matrix, which form during the fabrication process. [15]. Moisture absorption causes irreversible damages in the composite including chemical degradation, debonding etc. These irreversible damages alter the weight gain behavior of the material also [16].

A completely cured thermoset do not undergo sorption. Penetration and diffusion of water primarily occur through the interfacial region of the fiber and matrix. Hence, the strength of fiber-matrix interface plays crucial role in determining the sorption behavior of the composite. Water sorption studies were carried out using 10 mm x 10 mm square samples which were cut from the laminates. The thickness of each sample was noted and weight gain of the samples after immersing it in distilled water was recorded at predetermined time intervals. The weight was recorded until the sample reached equilibrium. The uptake of water in mole percent by 100 g of the sample at time t , Q_t , was plotted against time. The

equation (3) was used to calculate Q_t values [17].
$$Q_t = \frac{M_{(w)} / M_{r(w)}}{M_{i(s)}} \times 100 \quad (3)$$

Where $M_i(s)$ and $M(w)$ are the initial sample mass and mass of water uptake at time t . $M_r(w)$ is the molar mass of water.

The plot of the mole percent uptake against square root of time gives sorption curves. The mole percent uptake when equilibrium was reached is taken as the mole percent uptake at infinite time, Q_∞ . Equation (4) was used to calculate the effective diffusivity, D , from the initial portion of the sorption curves [18]

$$D = \pi \left(\frac{h\theta}{4Q_\infty} \right)^2 \quad (4)$$

where h is the initial sample thickness and θ is the slope of the initial linear portion of the sorption curves.

Using equation (5), sorption coefficient, S , was calculated.

$$S = \frac{M_{\infty}}{M_0} \quad (5)$$

Here, M_0 and M_{∞} respectively represent the mass of the initial polymer sample and the mass of the solvent absorbed at equilibrium swelling. The permeability coefficient (P), reflecting the combined effect of sorption and diffusion, is defined by the following relationship. [19].

$$P = DS \quad (6)$$

RESULTS AND DISCUSSION

Hardness, Density and Void Content of Laminates

Details of the composition, hardness, and density of the composites are presented in Tables 1 and 2. The laminates consist of 51–55% by volume of glass fibers and 42–48% by volume of cotton. The glass-reinforced laminates fabricated with UP-modified resol resins exhibit higher density compared to their unmodified counterparts, with a similar trend observed in hardness values. The composite containing UP-modified resol phenolics has comparatively reduced void volume than the epoxidised novolac modified resols. The cotton fiber-reinforced UP-modified resol phenolic composites display a general reduction in density, with no consistent pattern observed in their void content. The hardness of these composites remains relatively stable. Conversely, the epoxidized novolac-modified resol phenolic composites exhibit increased density and reduced void volume, although their hardness remains unchanged.

Mechanical Properties of FRPs Using UP-Modified Resol Phenolics

Figure 1(a) illustrates the tensile strength of laminates utilizing UP-modified phenolic resins as the matrix. The glass-reinforced composite with modified resins demonstrate higher tensile strength compared to their unmodified counterparts, which can be attributed to the decreased void content and improved bondability of the modified resin with glass fibers. Conversely, the tensile strength of UP-modified resol phenolic–cotton reinforced laminates is slightly lower than that of unmodified laminates. This occurs despite the enhanced void content in the modified composites relative to the unmodified resin composites, suggesting that the presence of UP in the resol phenolic resin diminishes its interaction with the cellulose in cotton fibers.

Table 1. Hardness, density and void content of UP modified resol laminates.

Composite		Glass/cotton vol. %	Hardness (shore D)	Density experimental (g/cc)	Density theoretical (g/cc)	Void content theoretical (vol.%)
Glass/PF	Glass/PF	51.7	78	1.8468	1.9069	3.15
	Glass/PF/UP2	53.1	86.5	1.9263	1.9597	1.70
	Glass/PF/UP2a	51.5	88	1.8548	1.8988	2.32
	Glass/PF/UP2b	51.6	88.5	1.8593	1.9052	2.40
	Glass/PF/UP2c	54.8	88.5	1.9953	2.0236	1.40
	Glass/PF/UP2d	51.4	78	1.8537	1.8975	2.30
Cotton/P	Cotton/PF	45.4	75	1.3320	1.3644	2.37
	Cotton/PF/ UP2	42.5	75	1.3231	1.3563	2.45
	Cotton/PF/ UP2a	42.2	76	1.3475	1.3555	0.60
	Cotton/PF/ UP2b	45.7	75	1.3549	1.3777	1.65
	Cotton/PF/ UP2c	42.8	75	1.3286	1.3570	2.10
	Cotton/PF/ UP2d	42.6	76	1.3450	1.3565	0.85

Table 2. Hardness, density and void content values of epoxy novolac modified resol laminates.

Composite		Glass/cotton (vol. %)	Hardness (shore D)	Density experimental (g/cc)	Density theoretical (g/cc)	Void content theoretical (vol.%)
Glass/PF	Glass/PF	51.7	78.0	1.8468	1.9069	3.15
	Glass/PF/EPN7	51.5	77.0	1.8522	1.8936	2.20
	Glass/PF/EPN9	53.0	78.5	1.8916	1.9482	2.90
	Glass/PF/EPCN7	52.0	78.5	1.8673	1.9105	2.26
	Glass/PF/EPCN9	53.0	77.5	1.8858	1.9514	3.36
	Glass/PF/EOCN7	54.0	77.0	1.9333	1.9929	2.99
	Glass/PF/EOCN9	54.4	75.0	1.9269	2.0065	3.98
Cotton/PF	Cotton/PF	45.4	75	1.3320	1.3644	2.37
	Cotton/PF/EPN7	44.0	75.5	1.3752	1.3598	0
	Cotton/PF/EPN9	47.8	74.5	1.3505	1.3695	1.39
	Cotton/PF/EPCN7	44.2	76	1.3586	1.3604	0.13
	Cotton/PF/EPCN9	45.0	74.5	1.3590	1.3622	0.23
	Cotton/PF/EOCN7	48.0	75.5	1.3494	1.3708	1.56
	Cotton/PF/EOCN9	42.9	75.5	1.3221	1.3572	2.58

Figure 1(b) presents the tensile moduli of the composites. As anticipated, glass-reinforced laminates exhibit higher tensile modulus values compared to cotton laminates. For glass laminates, an upward trend in tensile modulus is observed with the modification of resol, likely due to reduced void volume and enhanced interfacial strength. On the other hand, the tensile modulus of cotton laminates with modified resol is similar to that of the unmodified samples. This suggests that resin modification has a minimal impact on cotton laminates, possibly due to challenges in wetting and bonding between the matrix and fibers.

Figure 1(c) shows the percentage elongation of the modified resin composites. Since the fiber primarily determines the elongation-at-break, the influence of the resin is minimal. No distinct trend is observed in the variation of elongation-at-break upon modification.

Figure 1(d) displays the flexural strength of glass- and cotton-reinforced modified resol phenolics. The glass laminates demonstrate comparatively higher flexural strength, whereas the cotton-reinforced modified resin composites exhibit reduced flexural strength relative to the unmodified resin composites. The matrix composition and interface characteristics play a critical role in influencing flexural properties. Enhanced resin properties and improved wetting contribute to the increased flexural strength observed in the modified glass-reinforced composites. However, in the cotton-reinforced composites, poor bonding and inadequate wetting appear to offset the advantages of the improved resin properties.

Figure 1(e) depicts the flexural modulus of the modified resin composites. The enhanced interaction between glass fibers and the modified resin is likely responsible for the higher modulus values observed in glass-reinforced modified resins compared to unmodified resins. This improvement translates to increased stiffness against flexural deformation in the composite. The modification of the resin has minimal impact on the flexural modulus of the cotton-reinforced modified resin composites. The partial substitution of phenolic resin with UP compromises the interphase between the matrix and fibers. Consequently, the cotton laminates do not exhibit any improvement in properties following resin modification. Fig. 1(f) illustrates the impact strength of the modified composites. The glass-reinforced UP-modified resol laminates display a substantial improvement in impact strength. Similarly, the cotton-reinforced UP-modified resin composites show an increase, albeit to a lesser extent.

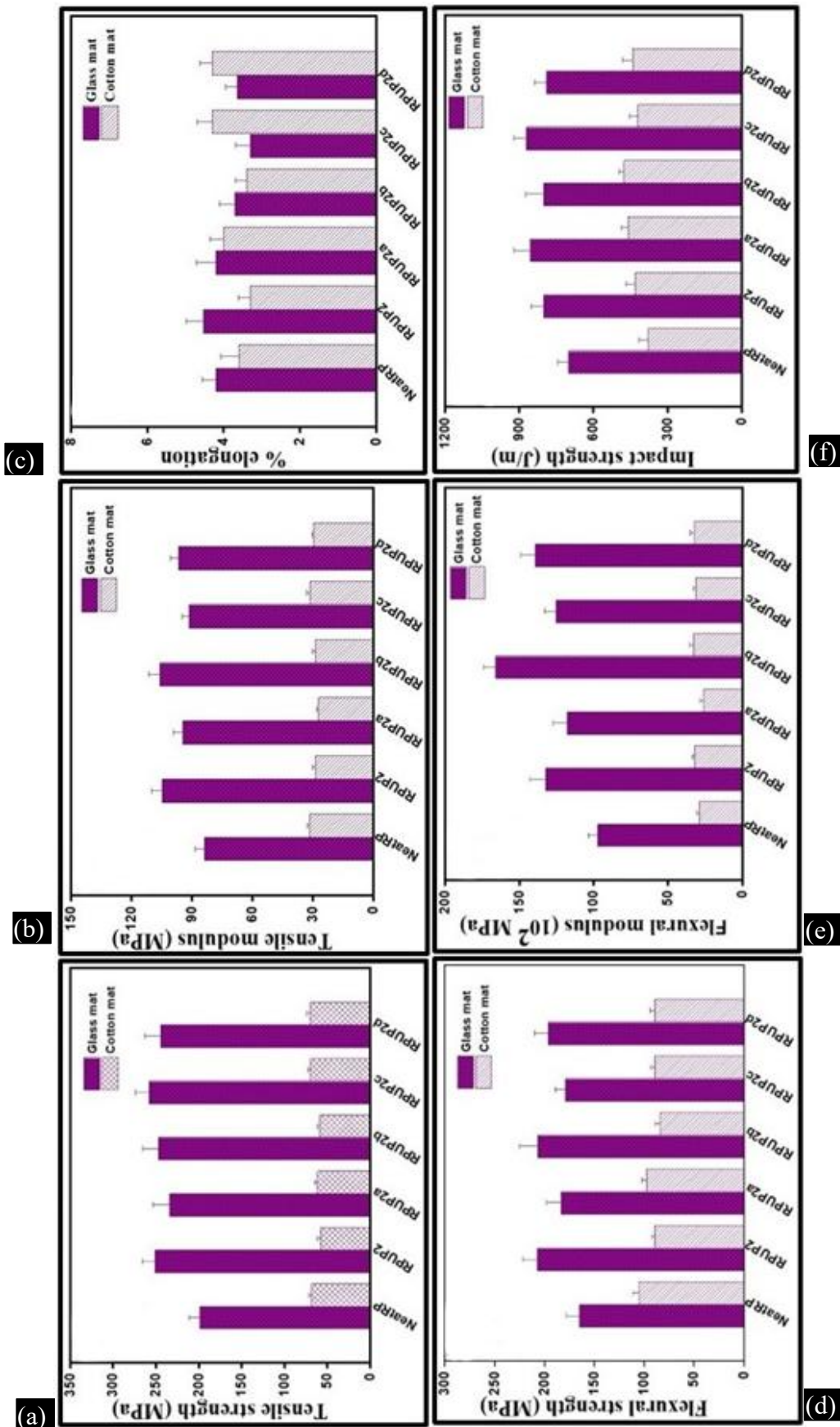


Figure 1. (a)–(f): Mechanical properties of glass and cotton reinforced UP modified resol composites.

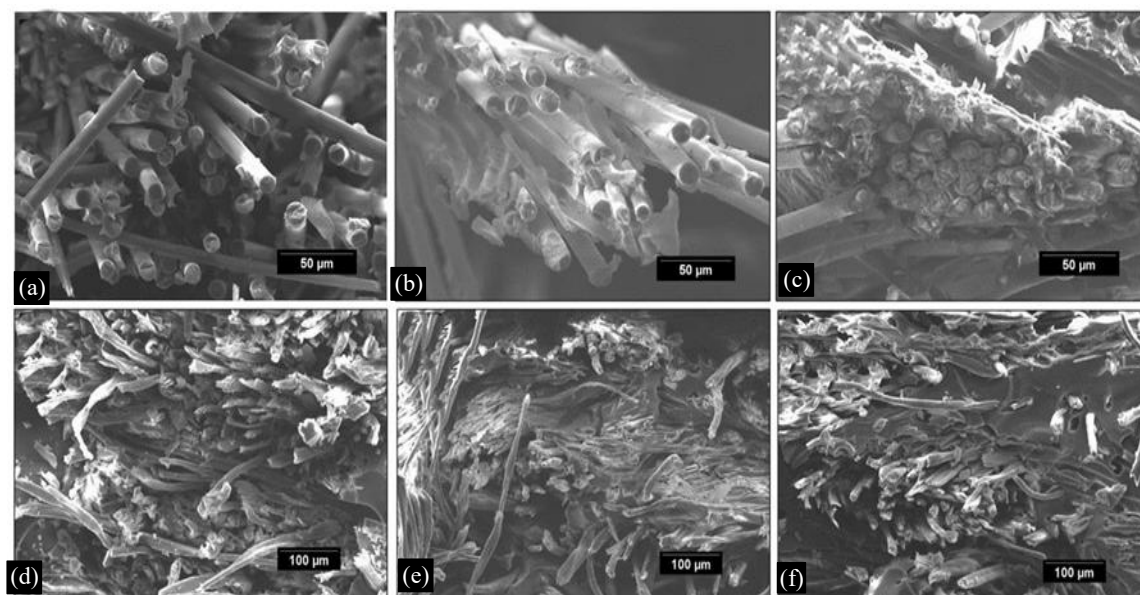


Figure 2. SEM images of the impact-fractured surface of glass-reinforced material (a) NeatRP (b) RPUP2 (c) RPUP2c modified resin composites and cotton reinforced (d) NeatRP (e) RPUP2 (f) RPUP2c modified resin composites.

SEM Studies of the Fractured Surfaces of FRPs of UP-Modified Resol Phenolics

The SEM micrographs of the impact fractured surfaces of UP-modified resol glass and cotton reinforced composites are shown in Figures. 2 (a) to (f).

The glass laminate made from the unmodified resin exhibits weak adhesion between the matrix and fibers, as per evidenced in fiber pullout (Figure 2(a)). Figures. 2(b) and (c) present the SEM images of the glass laminates fabricated using UP2 and UP2c modified resols. In the UP2 reformed composite, the fibers stick to more strongly to the resin, with hollows formed by fiber pullout being noticeable. The rupture surface of the UP2c incorporated resin composite exhibits a uniform cross-section, along with layer separation. This suggests the improvement in impact strength of the UP modified resol/glass reinforced composites.

On the other hand, laminate made of cotton-reinforced neat resin demonstrates a strong interaction between the resin and fibers as it is observed in Figure 2(d). The improved chemical compatibility between the fibers and resins well as uneven surface of the cotton fibers may be responsible for this observation. Replacing the neat resin with UP2 modified resin results in decreased fiber-resin interaction, as shown by clumps of fibers that remain unimpregnated by the resin (Figure 2(e)). The fiber pullout as indicated by the holes in the matrix and the fibers protruding from the fractured surface can be seen in the cotton-reinforced UP2c modified resol laminate (Figure 2(f)). The decreased interfacial adhesion may be responsible for the lowering of tensile strength of cotton laminates, though some improvement in toughness.

Mechanical Properties of FRPs of Epoxy Novolac Modified Resol Phenolics

Figures. 3(a) to 3(f) display the mechanical properties of unmodified and epoxy modified matrix glass and cotton laminates. The tensile strengths of glass- and cotton-reinforced epoxy-modified resin composites are shown in Figure 3(a). The epoxidized novolac-modified resin glass laminates exhibit greater tensile strength compared to the neat composite. However, the cotton-reinforced epoxy composites do not display any significant increase in tensile strength. This may be due to the reduced bondability of resol resins with cellulose fibers upon epoxy modification. The slight improvement in tensile strength observed in these cases may be due to a decrease in void content.

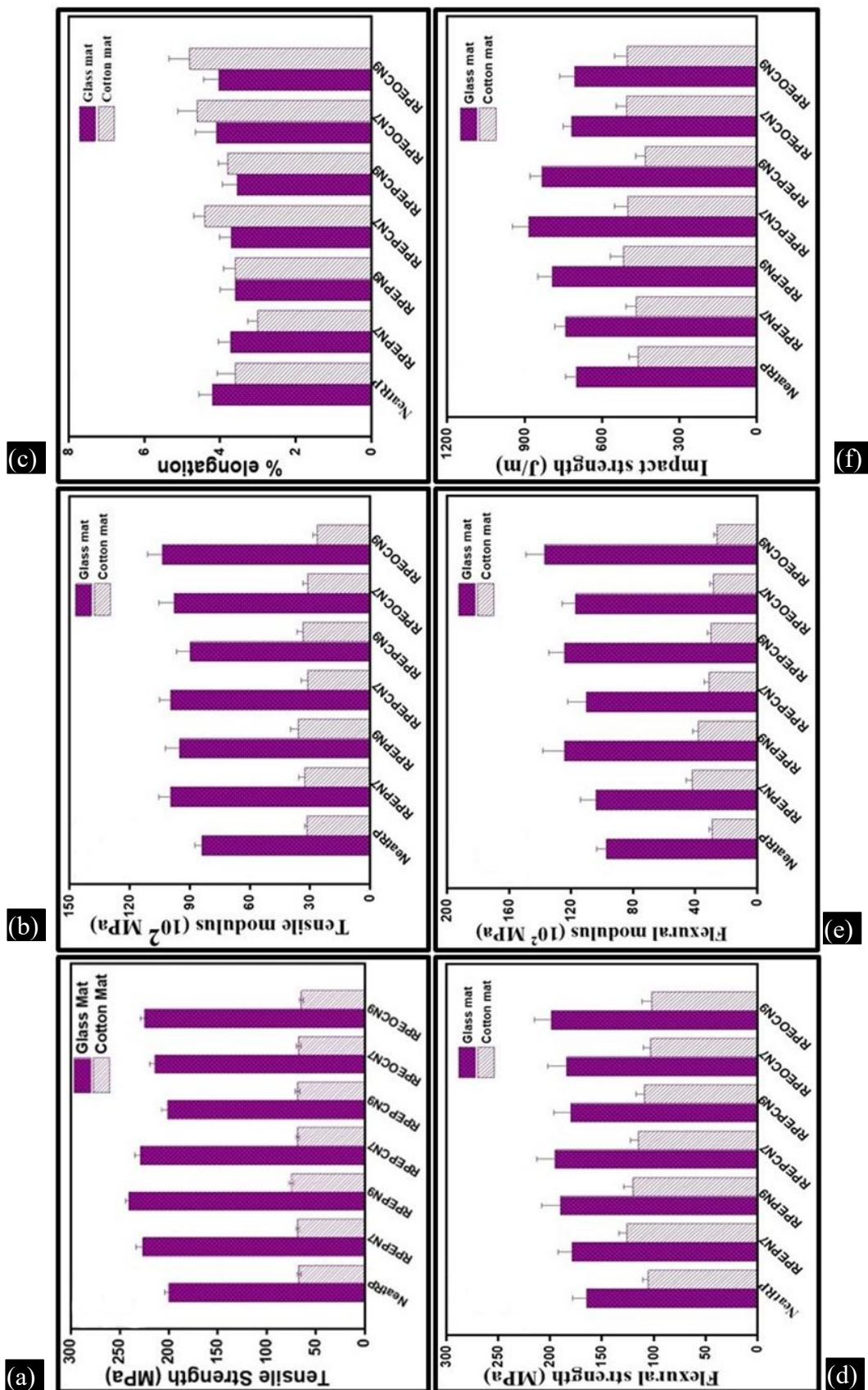


Figure 3. (a)–(f): Mechanical properties of glass and cotton reinforced composites using epoxy novolac modified resol phenolics.

The tensile modulus of cotton-reinforced composites remains almost unchanged compared to the unmodified composite, while the glass-reinforced composites exhibit a rising trend in modulus Figure 3(b). Figure 3(c) illustrates the percentage elongation of the modified composites. These epoxy-modified resol phenolic composites show a slight decrease in percentage elongation, while cotton fiber laminates exhibit increased elongation, particularly with EOCN.

Figures. 3(d) and (e) illustrate the flexural strength and flexural modulus of epoxy-modified resin composites reinforced with glass and cotton fibers. Epoxy modified resol glass laminates exhibit higher tensile strength than the unmodified glass laminates. This improvement is likely due to enhanced wettability and bondability with the glass fibers on epoxy modification. Interestingly, cotton-reinforced composites display a contrasting pattern. The incorporation of EPN-modified resin results in a little enhanced strength and modulus compared to their unmodified counterparts, indicating that the improved properties may be attributed to a decrease in void content within the composites.

Figure 3(f) shows the variation of impact strength of the glass-reinforced epoxy-modified resol resins. Most of the glass-reinforced epoxy-modified resol phenolics demonstrate an enhancement in impact strength. Among the modifiers, EPCN demonstrates the greatest improvement in impact resistance, which is likely attributed to the strengthened fiber-matrix bonding. However, this effect is less significant in cotton laminates, where the increase in impact strength is minimal and not consistently seen across all samples

SEM studies of the Fractured Surfaces of FRPS of Epoxidised Novolac Modified Resol Phenolics

Figure 4 shows the SEM micrographs of the fracture surfaces of glass laminates fabricated using epoxy-modified resol resins. The micrograph of the fractured surface of the neat composite is shown in Figure. 4(a). The glass-reinforced composite containing the unmodified resin shows weak bonding between the resin and fibers, as evidenced by the occurrence of fiber pullout. In contrast, the SEM images of modified composites (Figures. 4(b) to (d), with modifiers EPN9, EPCN7, and EOCN9) show significantly better fiber-to-matrix adhesion. However, even with improved adhesion, delamination and debonding occur. These phenomena can enhance energy absorption and, in turn, improve impact strength.

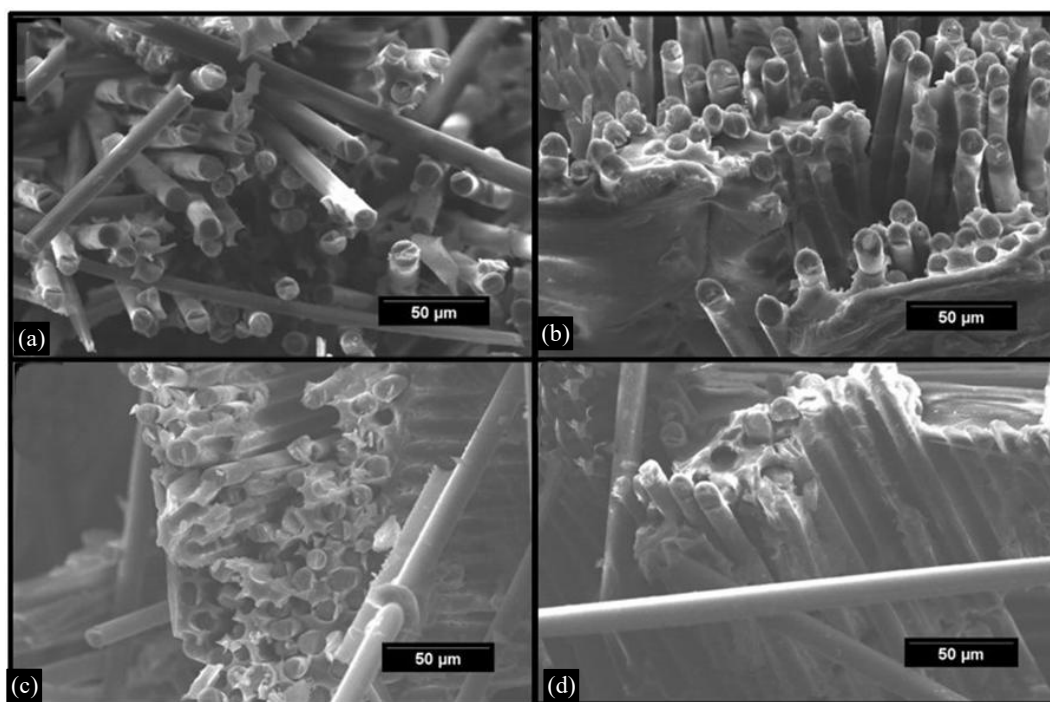


Figure 4. SEM images of the impact-fractured surfaces of glass-reinforced composites: (a) NeatRP, (b) EPN9, (c) EPCN9, and (d) EOCN9-modified resin systems.

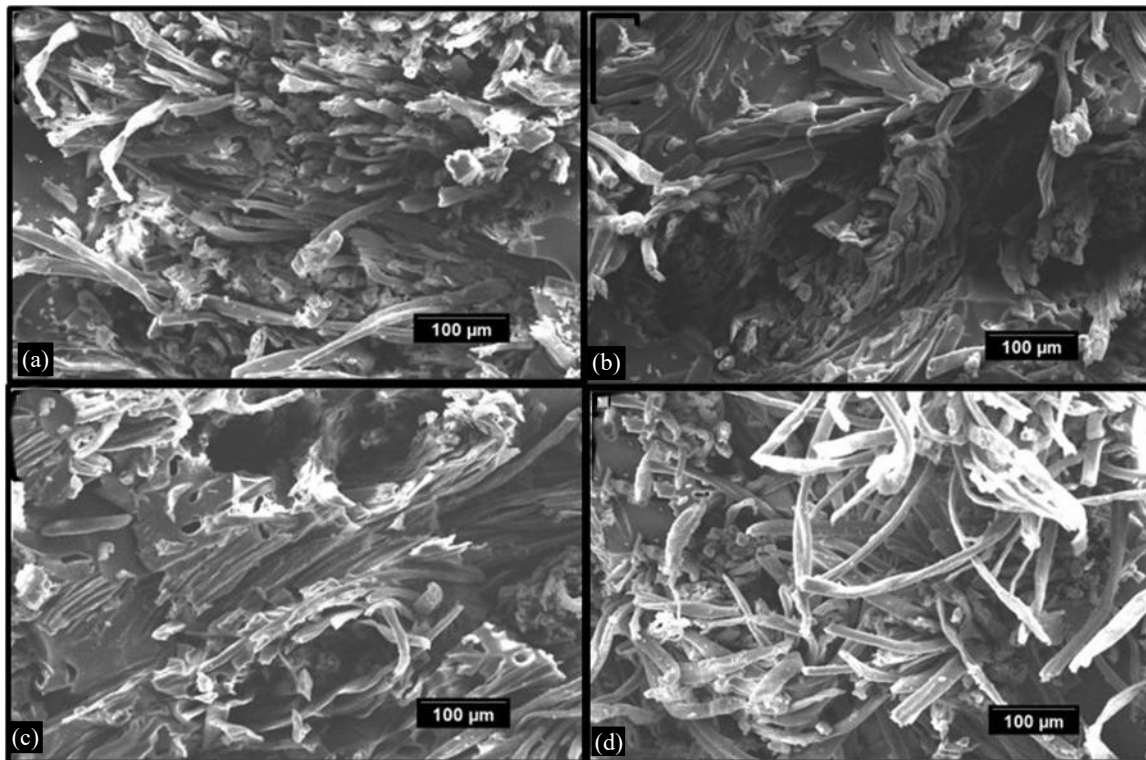


Figure 5. SEM images of the impact-fractured surfaces of cotton-reinforced composites: (a) NeatRP, (b) EPN9, (c) EPCN9, and (d) EOCN9 modified resins.

The impact strength of the cotton-reinforced modified resins shows only a slight improvement over the neat composite. This marginal enhancement could be due to the relatively weak fiber-matrix bonding, which is prone to debonding when subjected to impact. Figure 5 illustrates the morphology of the impact fractured surface of the cotton-reinforced composites made with neat and epoxy-modified resol phenolics. Figure 5(a) presents the fractured surface of the neat resin, which appears smooth and uniform, characteristic of a brittle failure. In contrast, the SEM images in Figure 5(b) to 5(d), corresponding to the composites modified with EPN9, EPCN7, and EOCN9, respectively, exhibit rougher fracture surfaces and visible fiber pullout, suggesting enhanced impact toughness in the modified composites.

Theoretical Modeling

Commonly used models for estimating the tensile strength and Young's modulus of composites include the parallel and series models [20]. Another model used commonly is the modified rule of mixtures (Modified ROM) [21]. This framework takes into account the fiber and matrix fraction along with microgeometry of the composite, knowing that the composite strength is influenced by these factors.

Parallel model

In this model, the tensile strength T_c may be represented as

$$T_c = T_f V_f + T_m V_m \quad (7)$$

where T_c , T_f and T_m are respectively tensile strength of the composite, fiber and matrix.

In a biaxially oriented reinforcement, only 50% of the total fiber content is applicable. This introduces a factor β (fiber efficiency factor) in equation (7).

$$T_c = \beta T_f V_f + T_m V_m \quad (8)$$

Modified rule of mixtures

$$\sigma_{cu} = \sigma'_m(1 - V_f) + \sigma_{fu}V_{fe} \tag{9}$$

σ_{cu} is the ultimate strength of the composite, σ'_m is the strength of the matrix, σ_{fu} is the ultimate strength of the fiber, V_f and V_{fe} are the fiber volume fraction and effective fiber volume fraction respectively. V_{fe} is given by the equation

$$V_{fe} = V_f\beta(1-P) \tag{10}$$

The parameter P, representing the degradation factor for the effective fiber volume fraction, ranges between 0 and 1. It is determined by the composite's microstructure and is influenced solely by the fiber volume fraction and the method of processing. This equation is derived by applying a modified form of the rule of mixtures

$$\frac{\Delta\sigma_u}{\sigma_{fu}} = V_f\beta P \tag{11}$$

where $\Delta\sigma_u$ is the difference between the measured strength and theoretical strength calculated from rule of mixtures.

Since identical types of fibers with nearly equal volume fractions are used, the degradation parameter 'P' is assumed to remain constant throughout the composite. Therefore, any variation in the composite's strength is attributed to the fiber-matrix interaction. To account for this, an additional parameter 'X' is introduced into the equation (11).

$$V_{fe} = V_f\beta(1-P)X \tag{12}$$

Equation (12) enables to calculate the 'X' value of each modified composite. The 'X' value of neat composite is taken as '1'.

Figure 6 presents the experimental and predicted tensile strength values for glass and cotton fiber-reinforced composites made with both neat and modified resol resin.

Figure 6(a) shows the variation between the theoretical and experimental tensile strengths of glass-reinforced epoxy-modified resin composites. The Parallel model exhibits large deviations from the experimental values for the modified composites. This is primarily due to poor interfacial adhesion between the resol and glass fiber. In most cases, the tensile strength calculated using the Modified Rule of Mixtures (Modified ROM) is nearly the same as that of the neat resin.

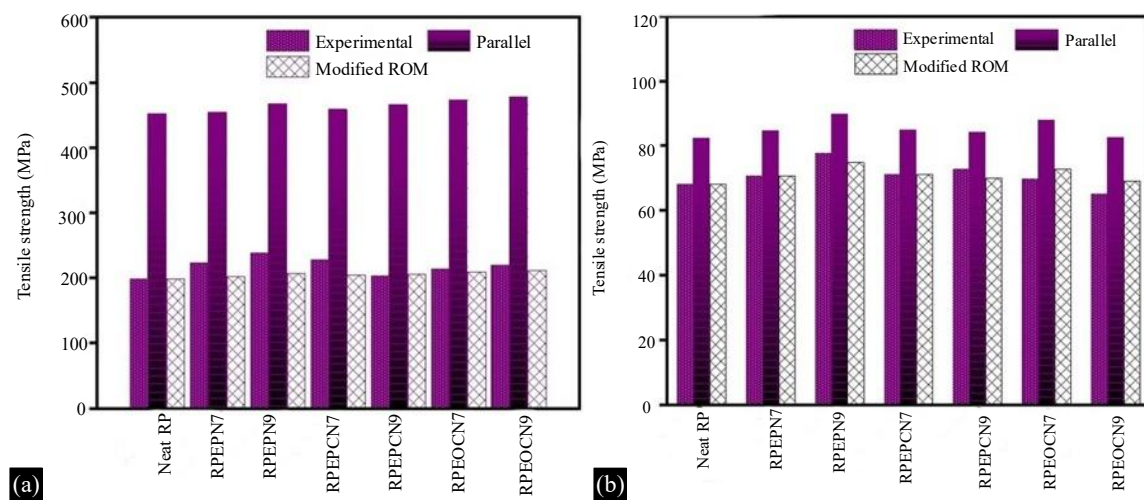


Figure 6. Variation of experimental and theoretical tensile strength values of (a) glass & (b) cotton reinforced epoxy modified resin composites.

Table 3. V_{fe} and X parameters of epoxy-modified resin composites reinforced with glass and cotton fibers.

Composite	V_{fe}	X	Composite	V_{fe}	X
Glass/NeatRP	0.109	1.00	Cotton/NeatRP	0.179	1.00
Glass/RPEPN7	0.122	1.12	Cotton/RPEPN7	0.173	0.99
Glass/RPEPN9	0.131	1.16	Cotton/RPEPN9	0.198	1.05
Glass/RPEPCN7	0.125	1.13	Cotton/RPEPCN7	0.175	1.00
Glass/RPEPCN9	0.111	0.99	Cotton/RPEPCN9	0.187	1.05
Glass/RPEOCN7	0.118	1.03	Cotton/RPEOCN7	0.180	0.95
Glass/RPEOCN9	0.120	1.04	Cotton/RPEOCN9	0.157	0.92

Figure 6(b) presents a comparison between the experimental and theoretical tensile strengths of cotton-reinforced composites made with both neat and modified resins. Unlike the glass-reinforced composites, the deviation from the Parallel model is significantly lower in the cotton-based composites. This smaller deviation could be attributed to the enhanced interaction between the resol phenolic resin and cotton fibers. However, the tensile strengths estimated using the modified Rule of Mixtures (ROM) do not exhibit any consistent pattern.

Table 3 shows the V_{fe} and X values from the modified ROM. The epoxy modification of the resol causes an increase in the ‘X’ values of glass laminates in most cases, indicating improved fiber-matrix adhesion with epoxy modification. However, for the cotton laminates the ‘X’ values are same as those of the neat composite. This suggests that the cotton fiber-matrix interaction is not significantly enhanced by the epoxy modification of the resol.

The theoretical and experimental tensile strengths values of the UP modified resin glass laminates are displayed in Figure 7(a). The Parallel model does not align with the experimental values and exhibits a large deviation. Nonetheless, the increased interfacial adhesion between the fiber and matrix is indicated by the reduced tensile strength measured from the modified ROM.

The tensile strength values of cotton-reinforced composites calculated by both theoretical and experimental methods are compared in Figure 7(b). In these composites, the modified composites deviate more from the Parallel model than the pristine composite. Comparative analysis shows that the tensile strength values determined from the modified ROM are higher than the experimental values. The value of X from the modified ROM is displayed in Table 4.

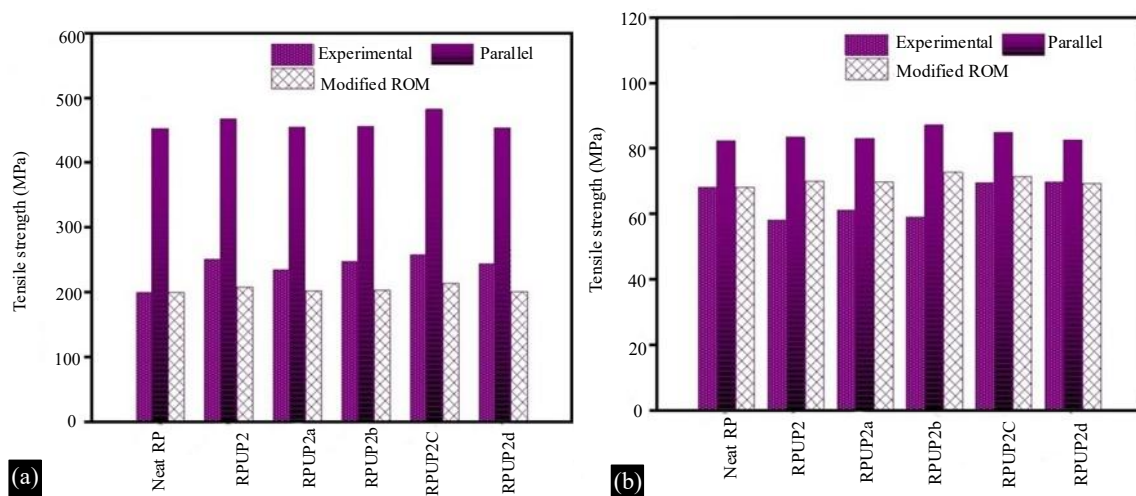


Figure 7. Tensile strength values of (a) glass reinforced UP modified PF resin (b) cotton reinforced UP modified PF resin (calculated by theoretical and experimental methods).

Table 4. The V_{fe} and X values of selected UP modified resol composites.

Composite	V_{fe}	X	Composite	V_{fe}	X
Glass/PF (neat)	0.109	1.00	Cotton/PF (neat)	0.179	1.00
Glass/PF/UP2	0.138	1.23	Cotton/PF/UP2	0.129	0.76
Glass/PF/UP2a	0.128	1.17	Cotton/PF/UP2a	0.138	0.82
Glass/PF/UP2b	0.136	1.24	Cotton/PF/UP2b	0.135	0.75
Glass/PF/UP2c	0.142	1.22	Cotton/PF/UP2c	0.163	0.96
Glass/PF/UP2d	0.134	1.23	Cotton/PF/UP2d	0.170	1.01

The higher ‘X’ value for the UP-modified resol glass laminates indicate the strengthening of the modified matrix/glass fibers interfaces. However, the composites reinforced with cotton show an opposite trend, suggesting a weakening of the interface between the matrix and the cotton fibers.

Dynamic Mechanical Properties of Reinforced Composites

Figure 8(a) depicts a plot of the storage modulus vs temperature for a set of glass laminates. The modified laminates show significantly higher storage modulus compared to the unmodified resol laminate which is a clear indication of improved thermal stability of the glass-reinforced samples. The increase in modulus values also indicates improved interfacial adhesion between the fiber and matrix, with the highest values observed in the UP-modified composites.

Figure 8(b) presents storage modulus of selected cotton reinforced composite at different temperatures. Both the modified and unmodified composites have comparable initial modulus values. But as the temperature rises, the modulus gradually drops, with the UP-modified resin composites showing a more noticeable drop. This implies that the cotton fibers and matrix in the UP-modified composites have relatively weaker interfacial adhesion.

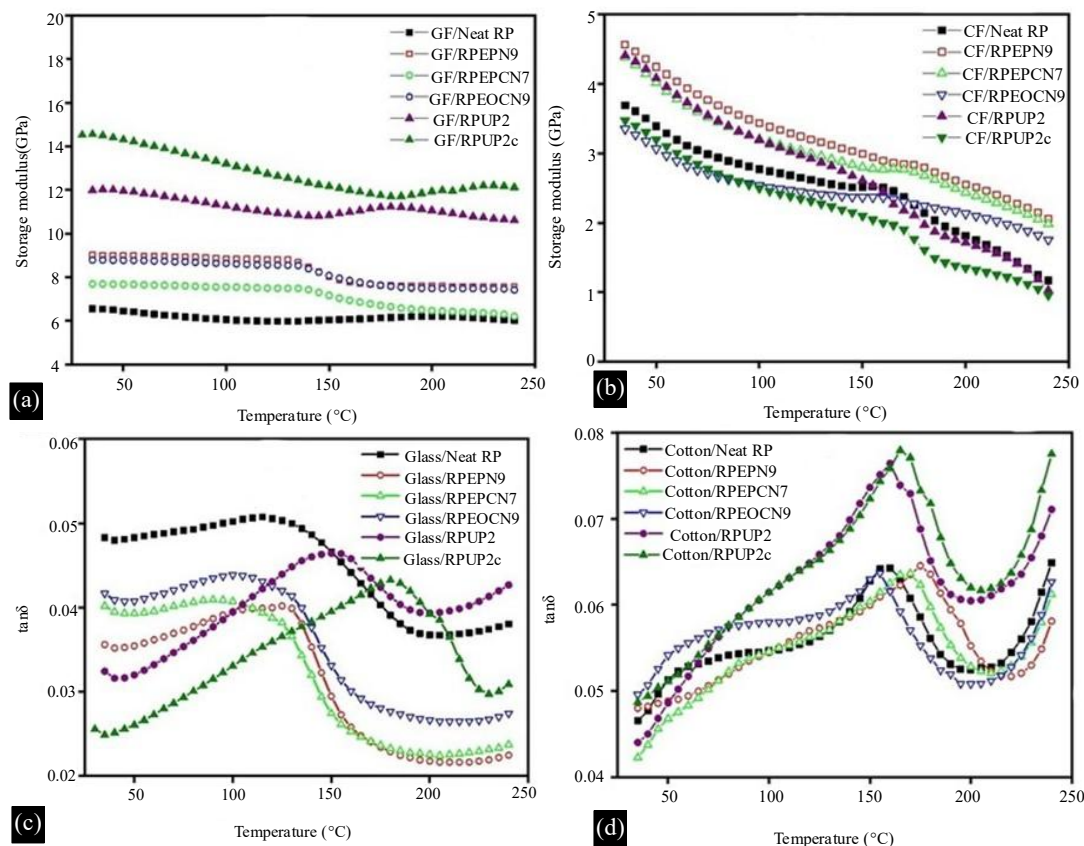


Figure 8. (a) & (b) – Temperature dependence of storage modulus of (a) glass laminates (b) cotton laminates. (c) & (d) – Temperature dependence of $\tan\delta$ for selected (c) glass laminates (d) cotton laminates.

Figure 8(c) shows the temperature dependence of $\tan\delta$ for selected glass laminates. The initial $\tan\delta$ values for the unmodified laminate is higher than that of the modified composites. The damping term $\tan\delta$ and impact strength are inter related. The $\tan\delta$ peak appears in the glass transition region. Here, the material changes to a rubber state from a rigid state. This is attributed to the segmental mobility of the polymer chains, which are initially in a frozen state.

The temperature dependence of $\tan\delta$ is found to be similar for unmodified composites and the epoxidised novolac modified resin composites. The structural closeness between the matrix and the modifier is assumed to be the reason for identical pattern of $\tan\delta$ fluctuation with temperature by both the unmodified composites and the epoxidized novolac modified resin composites. But for UP-modified composites, as the temperature rises, $\tan\delta$ shows an increasing trend, indicating its improved damping properties. Since the molecular chains are more dynamic close to the matrix's glass transition temperature (T_g), the matrix is largely responsible for the composite's damping behavior in those composites. The damping qualities are improved by the UP chains in the modified resin, which offer sufficient space for chain motion. This enhanced damping nature of the UP-modified resins is very well reflected in the composites.

The fluctuation in $\tan\delta$ values with temperature for cotton-reinforced composites is depicted in Figure 8(d). The glass transition temperature (T_g) remains unchanged for both unmodified and modified composites, irrespective of resin modification. In comparison with the unmodified and epoxidized novolac modified resins, the UP-modified resin composites show greater $\tan\delta$ values. Furthermore, compared to previous modified laminates, the glass and cotton laminates made with UP-modified resol exhibit better damping.

Water Absorption Studies of the Modified Resin Composites

Figures. 9 (a) and (b) respectively show water intake w.r.to time of glass and cotton laminates.

Glass laminates Glass-reinforced composites with modified resins exhibit a significant reduction in water uptake compared to those with unmodified resin composite. Specifically, UP-modified resin composites show water absorption reduced to about one-third of that observed in the reinforced neat resin composite. This substantial decrease can be due to various factors, such as structural characteristics of the UP-modified phenolic resin and enhanced adhesion between the glass fibers and the resin matrix. The water uptake by glass laminate made up of EPN modified resol is less compared to EOCN and EPCN modified resol glass laminates. Among all, unmodified laminate shows highest water uptake.

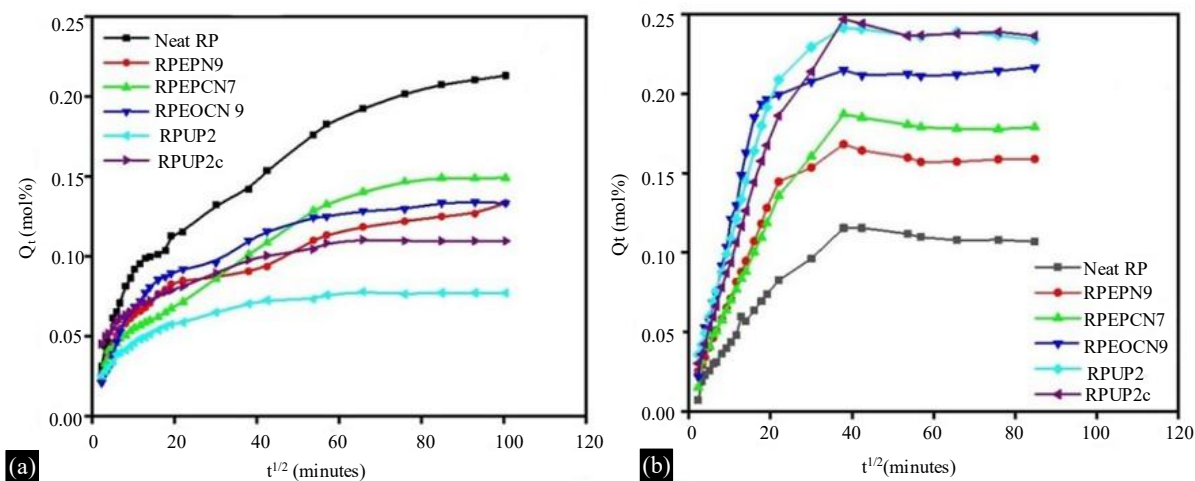


Figure 9. mol % uptake of water against $t^{1/2}$ of (a) glass laminates & (b) cotton laminates.

For the cotton laminates, a contrasting trend in water uptake is observed. When modified resins are used as the matrix, they absorb more water than unmodified resins do. The unmodified composites show the least amount of water uptake while among the modified resins, the UP-modified composites show the most. The resin composites cured with epoxy novolac exhibit intermediate amounts of water absorption.

This trend can be attributed to the reduced interfacial adhesion between the cotton fibers and the modified resins, which creates pathways for water ingress. The structural properties of the modifier resins affect the amount of water uptake; the UP resin contributes to the largest water uptake and the weakest fiber-matrix interaction. This highlights the importance of interfacial bonding in controlling water absorption in fiber-reinforced composites.

Kinetics of Water Sorption

It is believed that the kinetics of water sorption in permeable fiber/polymer composites is a diffusion process that is independent of concentration. Equation (12), an empirical relationship between Q_t , Q_∞ , n , K and t , is used for the study of water sorption mechanism [22].

$$\log\left(\frac{Q_t}{Q_\infty}\right) = \log k + n \log t \quad (12)$$

where Q_∞ is the water uptake in mol% at equilibrium and Q_t is the water uptake in mol% at time t . " k " denotes the interaction between the sample and water, whereas " n " denotes the sorption mechanism. The value of n and k were calculated by linear regression analysis. When the value of ' n ' approaches 0.5, the sorption follows Fickian mode of diffusion and a higher value indicates anomalous diffusion behaviour. A value less than 0.5 indicates non-Fickian diffusion mechanism. The value of " n " for a Fickian mode of diffusion is 0.5. This occurs when the polymer chains' segmental mobility outpaces the permeant molecules' rate of diffusion. This takes place during the diffusion into polymers and that are around 50% of the equilibrium penetrant uptake when temperature is above their glass transition temperature. In rigid polymers with glass transition temperatures significantly higher than room temperature, penetrant diffusion rates are substantially faster than the polymer relaxation process at " n "=1. The diffusion is considered anomalous when the " n " ranges between 0.5 and 1. This occurs when the segmental relaxation rates of polymers and permeant mobility are nearly similar. In this study, linear regression analysis was used to determine the values of " n " and " k ."

Table5. Kinetic parameters and transport coefficients of water sorption studies.

Composite	n	$K \times 10^{-2} \text{ g/g min}^n$	$D \times 10^{-8} \text{ cm}^2 \text{ S}^{-1}$	$S \times 10^{-2} \text{ g g}^{-1}$	$P \times 10^{-9} \text{ cm}^2 \text{ S}^{-1}$
Glass/NeatRP	0.37	8.58	17.60	3.37	5.93
Glass/RPEPN9	0.33	12.29	11.50	2.28	2.62
Glass/RPEPCN7	0.33	10.18	14.60	2.27	3.31
Glass/RPEOCN9	0.43	7.59	23.20	2.33	5.41
Glass/RPUP2	0.21	23.32	7.40	1.36	1.01
Glass/RPUP2c	0.13	33.61	4.08	1.95	0.80
Cotton/NeatRP	0.52	4.20	14.50	1.94	2.81
Cotton/RPEPN9	0.38	7.99	17.40	2.83	4.92
Cotton/RPEPCN7	0.50	4.81	11.30	3.20	3.62
Cotton/RPEOCN9	0.52	5.14	24.20	3.79	9.18
Cotton/RPUP2	0.41	7.06	14.80	4.26	6.30
Cotton/RPUP2c	0.41	6.00	22.40	4.28	9.59

Table 5 lists the water sorption studies' kinetic and transport constants. Glass laminates exhibit non-

Fickian behavior since their "n" value is significantly less than 0.5. The crosslinked structure of the resol resin and the hydrophobic character of the glass fiber may be the cause of this diffusion behavior. It is also noticed that the water absorption is diffusion controlled as the amount of water absorbed increases linearly with $t^{1/2}$ and then approaches the equilibrium plateau. It is observed that the "k" value increases as a result of the resol modification. The structural properties of the polymer and how it interacts with the solvent are the main factors that influence the "k" value. The diffusion coefficient 'D' is less for glass laminates, particularly for UP modified resols. The lowering of the D value indicates enhanced fiber-matrix adhesion. A reverse trend can be seen for cotton laminates. The values of S and P also show an identical trend that supports the improved resol-glass fiber interaction upon UP and epoxidised novolac modification of resols.

CONCLUSION

It has been observed that modification of matrix improves the mechanical characteristics of resol phenolic-glass composites. Both the unsaturated polyester and epoxidized novolac modifiers increased the strength of glass-reinforced composites. On comparing glass-fiber reinforced composites with cotton-fiber reinforced composites, a notable improvement in mechanical properties was noted for glass-fiber reinforced laminates. Among the modified resin, UP modified resol resins show better enhancement in the properties of the composite compared to epoxidised novolac modified resol resin. The theoretical modelling indicates that the fiber-matrix interaction parameter is substantially greater for glass laminates compared to the cotton laminates. The fiber-matrix interaction is higher for the resol resin modified with UP. The SEM and DMA analyses confirm the significance of modification of the resol resin on the damping properties of both the glass and cotton laminates. The kinetic and transport parameters of water absorption studies of the laminates also support the observation of enhanced glass fiber-matrix adhesion for both the modified resols.

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Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

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