

Synthesis and Characterization of Polymethylhydrosiloxane-Modified Phenol-Formaldehyde Resin

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Abstract: Resol phenol-formaldehyde (PF) resin was modified with 2.5 and 5.0 wt% polymethylhydrosiloxane (PMHS). This study characterizes the modified resin and its subsequently fabricated glass fiber (GF) reinforced composites (30–60 wt% GF). Formation of an organic-inorganic hybrid network, via reaction between Si-H groups of PMHS and hydroxyl (-OH) groups of the resol resin, was confirmed by FTIR and ¹H NMR. DSC and TGA/DTG revealed an enhanced thermal stability for PMHS-modified resin: the decomposition temperature of Resol-PMHS 5.0% increased to 483 °C (neat resin: 438 °C), and char yield at 800 °C rose to 57% (neat resin: 38%). The 60 wt% GF-reinforced Resol-PMHS 5.0% composite exhibited tensile, flexural, and impact strengths of 145 ± 7 MPa, 160 ± 7 MPa, and 71 ± 5 kJ/m², respectively, superior to the unmodified resin composite (136 ± 6 MPa, 112 ± 6 MPa, and 51 ± 5 kJ/m²). SEM observations indicated improved fiber-matrix interfacial adhesion and reduced delamination. These results demonstrate PMHS modification effectively enhances the thermo-mechanical properties of the PF resin and its composites, highlighting potential for industrial applications.

Keywords: Phenol-formaldehyde resin; Polymethylhydrosiloxane; Glass fiber reinforced composites; Thermal stability; Mechanical properties; Organic-inorganic hybrid

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1. Introduction

Phenol-formaldehyde (PF) resins, particularly the resol type, have long been established as one of the most crucial thermosetting polymeric materials in industrial applications. Attributed to an optimal balance of good mechanical properties, high thermal and dimensional stability, superior chemical resistance, coupled with excellent electrical insulation and reasonable production costs, resol PF resins are extensively utilized in the manufacturing of adhesives, protective coatings, molding compounds, engineered laminates, and notably, as matrix materials for high-performance composites in demanding sectors

such as the automotive, aerospace, and construction industries [1,2]. Resol resins, synthesized via the condensation reaction of phenol and formaldehyde under alkaline catalysis with an excess formaldehyde-to-phenol molar ratio, possess reactive methylol (-CH₂OH) groups. These functional groups enable them to cure readily upon heating, forming a highly durable three-dimensional crosslinked network [3,4].

Nevertheless, unmodified PF resol resins exhibit certain inherent limitations, including brittleness, insufficient impact toughness, and, in some instances, thermal stability or fire retardancy that may not fully meet the increasingly stringent requirements of advanced applications [2,3]. To overcome these drawbacks and further broaden the application potential of PF resins, extensive research has focused on their structural modification [5-7].

Copolymerization and blending with synthetic or bio-based modifying agents have demonstrated significant improvements in the thermo-mechanical properties of PF resins. Cardanol, derived from cashew nut shell liquid (CNSL), is a natural phenol possessing a long, unsaturated aliphatic side chain. When copolymerized with phenol and formaldehyde, this aliphatic chain can enhance the flexibility of the PF network, thereby significantly improving its toughness and impact strength [8]. Studies indicate that increasing cardanol content generally leads to enhanced flexibility and fracture toughness, albeit often accompanied by a reduction in flexural modulus and crosslink density. However, a common consequence is a potential decrease in thermal stability at higher cardanol loadings [9]. Cardanol-modified PF resins find applications in adhesives, coatings, and rubber additives. Lignin, an abundant natural polyphenolic polymer, is a promising candidate for partially replacing phenol in PF resin synthesis, contributing to product sustainability [10]. Incorporating lignin into the PF structure can enhance thermal stability and adhesive strength [11]. However, owing to its complex structure and lower reactivity compared to phenol, lignin often requires pre-treatment or chemical modification—such as methylolation, phenolation, demethylation, or succinylation—to improve its compatibility and performance within the PF network [12]. Blending or copolymerizing PF resin with epoxy resins is a common strategy to combine the high thermal resistance of PF with the toughness and good adhesion of epoxies [13]. These hybrid materials often exhibit superior mechanical properties and improved oxidation resistance [14]. Incorporating rubbery phases, such as nitrile rubber, or certain amino silane compounds into the PF matrix is an effective method to enhance the toughness of inherently brittle PF resins [15]. Other toughening agents like cashew phenol, polyurethane prepolymers, or polyvinyl acetal have demonstrated similar efficacy [16,17]. This soft phase can absorb and dissipate energy upon impact, thereby impeding crack propagation [18]. Phenolic-rich bio-oils, obtained from biomass pyrolysis, can also be used to modify or blend with PF resins. Studies suggest this approach can potentially improve thermal stability and adhesive strength, particularly at low substitution or blending ratios [19]. The phenolic constituents in bio-oils can participate in the PF network formation, while other components might act as plasticizers or fillers [20].

Several chemical agents are also employed for modifying and improving the properties of PF resins. Phosphoric acid is used to incorporate P-O-C and P=O linkages into the PF resin structure, forming heterocyclic structures with higher thermal stability and aromaticity, leading to improved heat resistance and mechanical strength [21]. KH550 (γ -aminopropyltriethoxysilane) can be grafted onto the PF resin, capping the polar phenolic hydroxyl groups. This modification reduces water absorption, increases volume resistivity, enhances electrical insulation properties in humid environments, and improves adhesive strength [22]. The addition of HBP-NH₂ has been reported to promote the curing process (reducing gel time, lowering curing temperature), increase molecular

weight, and improve adhesive strength through co-condensation reactions with the PF resin [23].

Polymethylhydrosiloxane (PMHS), a linear polysiloxane characterized by highly reactive Si-H groups and hydrophobic methyl groups attached to a flexible Si-O-Si backbone, has emerged as a promising modifying agent [24-26]. The presence of these active Si-H bonds allows PMHS to chemically interact with the abundant hydroxyl (-OH) groups in resol resins, potentially forming an organic-inorganic hybrid network. The incorporation of siloxane segments into the PF structure is anticipated not only to improve thermal stability and hydrophobicity but also to enhance toughness, mechanical properties, and, crucially, interfacial interactions when combined with glass fibers for composite fabrication [27-29].

The present work focuses on the comprehensive synthesis and characterization of resol PF resin modified with PMHS at various contents (2.5 wt% and 5.0 wt%). Furthermore, this study aims to evaluate in detail the impact of this modification on the properties of glass fiber-reinforced composites, with fiber content varying from 30 wt% to 60 wt%. The main objectives include: (i) elucidating the chemical structure formation of the modified resol resin using Fourier-transform infrared spectroscopy (FTIR) and proton nuclear magnetic resonance (^1H NMR); (ii) investigating the influence of PMHS on the curing behavior (via Differential Scanning Calorimetry, DSC) and thermal stability (via Thermogravimetric Analysis/Derivative Thermogravimetry, TGA/DTG) of the resin; and (iii) evaluating key mechanical properties of the composites, including tensile strength, flexural strength, and impact strength, to clarify the role of PMHS in enhancing mechanical performance. The fracture surface morphology of the composites will also be analyzed using scanning electron microscopy (SEM) to gain further insight into failure mechanisms and fiber-matrix interactions.

The successful development of composites from PMHS-modified PF resin holds significant scientific and practical importance. This research not only provides an in-depth understanding of the mechanism by which PMHS affects the structure and properties of resol resin but also offers valuable experimental data for the optimization of composition and processing parameters, thereby contributing to the development of advanced composites with superior performance. By conducting a detailed performance comparison between the PMHS-modified resol resin and its unmodified counterpart, this study will elucidate the role of PMHS in enhancing key material characteristics, potentially paving the way for new applications of phenolic resins in fields requiring materials with high strength, excellent thermal resistance, and improved mechanical flexibility.

2. Chemicals and Methods

2.1. Chemicals

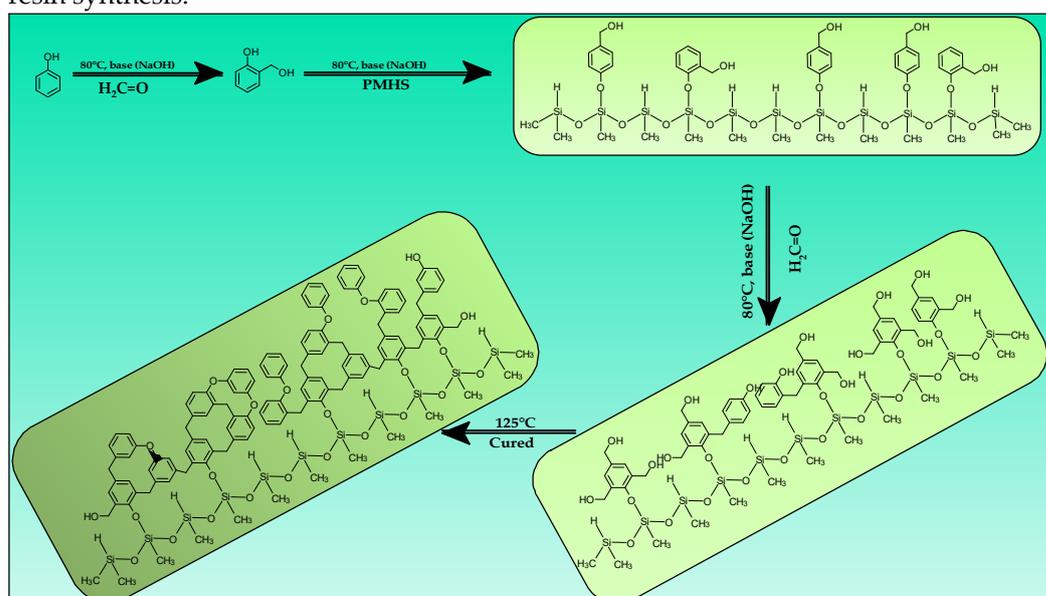
Phenol (purity $\geq 96\%$), sodium hydroxide (NaOH, purity $\geq 97\%$), and polymethylhydrosiloxane (PMHS, viscosity 15–40 mPa·s at 20 °C) were supplied by Sigma-Aldrich. Formaldehyde (37–41% aqueous solution) and isopropanol (IPA, purity $\geq 99.5\%$) were purchased from Fisher Chemical. E-glass fibers (chopped strand mat) were supplied by Shenzhen Feige Composite Fiber Co., Ltd. (China).

2.2. Synthesis of Materials

Synthesis of Resol Resin: Resol resin was synthesized in a 500 mL three-neck round-bottom flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser. The synthesis procedure was as follows: Initially, 47.0 g of phenol and 20.8 g of formaldehyde solution (37-41 wt% in water) were charged into the reaction flask.

Subsequently, an NaOH solution (prepared by dissolving NaOH pellets, equivalent to 0.5 wt% of phenol, in 5 mL of distilled water) was added as a catalyst. The reaction mixture was then heated to 80 °C and maintained at this temperature for 1 hour under continuous stirring. After this period, the remaining 40.0 g of formaldehyde solution (37-41 wt%) was slowly added to the mixture. The reaction was continued at 80 °C for another 3 hours. Finally, water and other volatile components were removed from the product mixture by vacuum distillation at 80 °C until no further condensation was observed. The resulting product was a transparent, brown, viscous resol resin.

Synthesis of PMHS-Modified Resol Resin: The synthesis procedure for PMHS-modified resol resin (Scheme 1) was similar to that for neat resol resin, with a key modification. Specifically, after the initial 1-hour reaction period at 80 °C (between phenol and 20.8 g of formaldehyde) and before the addition of the remaining 40.0 g of formaldehyde solution, a pre-calculated amount of polymethylhydrosiloxane (PMHS) (corresponding to X wt% relative to phenol, e.g., 2.5% or 5.0%) was slowly added dropwise into the reaction flask under continuous stirring. The mixture was then maintained at 80 °C for 1 hour to facilitate the reaction of PMHS. Subsequently, the remaining 40.0 g of formaldehyde solution was added, and the remaining synthesis steps, including the vacuum distillation stage, were carried out as described for the neat resol resin synthesis.



Scheme 1. PMHS modified resol resin synthesis process.

Fabrication of Composite Samples: The resol resin (neat or PMHS-modified) was dissolved in IPA at a ratio of 3.0 g resin to 1.0 mL IPA to prepare a resin solution. E-glass fibers at various contents of 30, 40, 50, or 60 wt% (based on the dry resin weight) were added to the resin solution and thoroughly mixed. This mixture was then allowed to stand for 6 hours to ensure thorough impregnation of the fibers by the resin, after which it was poured into a steel mold treated with a release agent. Next, the mold was vacuum-dried at 60 °C for approximately 3 hours – initially at atmospheric or low vacuum pressure, then gradually increasing the vacuum level – until the IPA solvent completely evaporated and the resin surface became tacky. Finally, the resulting prepreg was hot-pressed at 150 °C for 30 minutes to achieve full curing, thereby forming the composite material. The mold was allowed to cool naturally before demolding the sample.

2.3. Characterization of Materials

The successful synthesis of resol and PMHS-modified resol resins was confirmed by Fourier-transform infrared (FTIR) spectroscopy (Tensor II, Bruker, 400–4000 cm^{-1} , resolution 4 cm^{-1} , KBr pellet technique) and proton nuclear magnetic resonance (^1H NMR) spectroscopy (AvanceNEO 600 MHz, Bruker, solvent DMSO-d_6). The curing behavior of the neat and modified resol resins was investigated using differential scanning calorimetry (DSC). The thermal degradation behavior was analyzed by thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) over a temperature range of 40 $^\circ\text{C}$ to 800 $^\circ\text{C}$ under an air atmosphere. The microstructure of the composite materials was observed using scanning electron microscopy (SEM, JEOL-JMS 6490).

The mechanical properties of the composite materials were evaluated according to standard test methods. Tensile strength was determined following ASTM D3039; five specimens of each sample type were tested, and the average value with standard deviation was reported. Flexural strength was measured according to ASTM D790, with five specimens tested for each material to determine the average value and standard deviation. Impact strength was evaluated using ASTM D256; three specimens of each material were tested, and the results were reported as the average value accompanied by the standard deviation, ensuring the accuracy and reliability of the data.

3. Results and Discussion

3.1. Synthesis of PMHS-Modified PF Resin

Figure 1 presents the Fourier-transform infrared (FTIR) spectra of pure polymethylhydrosiloxane (PMHS), unmodified resol resin (neat resol), and resol resin modified with 2.5 wt% PMHS (Resol-PMHS).

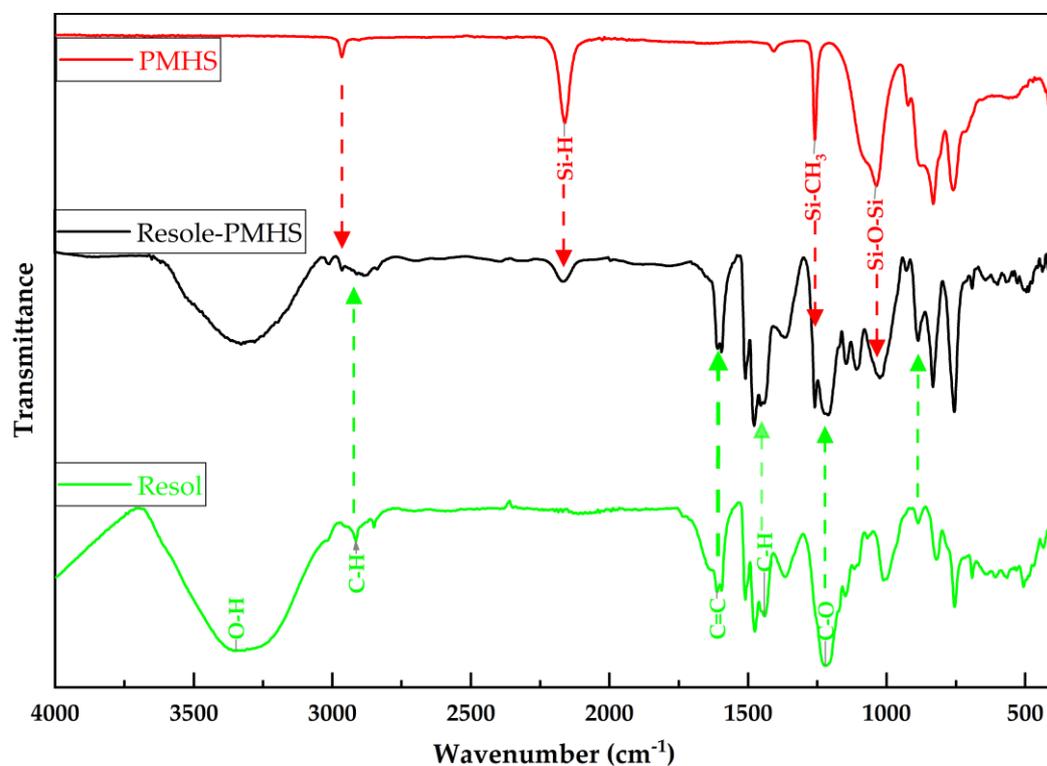


Figure 1. IR spectrum of PMHS (red), Resol (blue) and Resol-PMHS (black).

The FTIR spectrum of the neat resol resin (blue line) exhibits a broad and strong absorption band at 3342 cm^{-1} , characteristic of the hydroxyl ($-\text{OH}$) stretching vibration ($\nu(\text{O-H})$), encompassing both phenolic $-\text{OH}$ and methylol ($-\text{CH}_2-\text{OH}$) groups. The breadth and intensity of this band indicate the presence of strong intermolecular and

intramolecular hydrogen bonding within the resin structure. Peaks observed at 2915 cm⁻¹ and 2848 cm⁻¹ are attributed to the C-H stretching vibrations (ν C-H) of methylene (-CH₂-) and methylol groups. The absorption region between 1700–1500 cm⁻¹ is associated with the aromatic ring structure, featuring characteristic peaks at 1612 cm⁻¹, 1510 cm⁻¹, and 1475 cm⁻¹, corresponding to the C=C stretching vibrations (ν C=C) of the benzene ring. The absorption peak at 1371 cm⁻¹ can be assigned to the C-H bending vibration (δ C-H) of the methylol group. A strong peak at 1221 cm⁻¹ is characteristic of the C-O stretching vibration (ν C-O) of the phenolic group. The peak at 1011 cm⁻¹ is attributed to the C-O bending vibration (δ C-O) of the methylol group and/or may include contributions from ether linkages (C-O-C) formed during condensation. The 1000–650 cm⁻¹ region contains absorption peaks at 889 cm⁻¹, 820 cm⁻¹, and 755 cm⁻¹, characteristic of out-of-plane C-H bending vibrations (δ C-H) of the benzene ring, indicating substitution patterns on the aromatic ring [30].

The FTIR spectrum of PMHS (red line) displays its characteristic absorption peaks. These include a peak at 2965 cm⁻¹ (C-H stretching vibration, ν C-H, of methyl (-CH₃) groups) and a very prominent and sharp peak at 2161 cm⁻¹ assigned to the Si-H stretching vibration (ν Si-H) of the PMHS backbone. Other notable peaks include 1259 cm⁻¹ (Si-CH₃ bending vibration, δ Si-CH₃), peaks at 832 cm⁻¹ and 759 cm⁻¹ (Si-CH₃ rocking vibration, ρ Si-CH₃), and a strong peak at 1038 cm⁻¹ characteristic of the siloxane (Si-O-Si) stretching vibration (ν Si-O-Si) [31].

The FTIR spectrum of the PMHS-modified resol resin (Resol-PMHS, black line) reveals the presence of absorption peaks characteristic of both the resol structure and PMHS, confirming the incorporation of PMHS into the resol matrix. Peaks related to the -OH groups, benzene ring vibrations, and C-H as well as C-O bonds of the resol component are largely preserved. Crucially, the appearance of characteristic PMHS peaks, such as the Si-CH₃ vibrations (1259 cm⁻¹, 832 cm⁻¹, 759 cm⁻¹) and the Si-O-Si vibration (1038 cm⁻¹), is evident in the Resol-PMHS spectrum. Furthermore, a significant reduction in the relative intensity of the ν Si-H peak at 2161 cm⁻¹ is observed in the Resol-PMHS spectrum compared to that in pure PMHS. This reduction becomes particularly clear when its intensity is considered relative to other PMHS peaks less likely to participate in reactions, such as the Si-CH₃ bending vibration at 1259 cm⁻¹. The formation of Si-O-C linkages in phenolic-silicate systems has been confirmed by FTIR analysis, with characteristic peaks appearing around 1020-1040 cm⁻¹ representing these new covalent bonds [32]. This diminution provides strong evidence that the Si-H bonds of PMHS have participated in a chemical reaction, most likely with the hydroxyl groups of the resol resin, leading to the formation of new Si-O-C covalent linkages [33].

The proton nuclear magnetic resonance (¹H NMR) spectra of the unmodified resol resin (neat resol) and the PMHS-modified resol resin (Resol-PMHS) are presented in Figure 2.

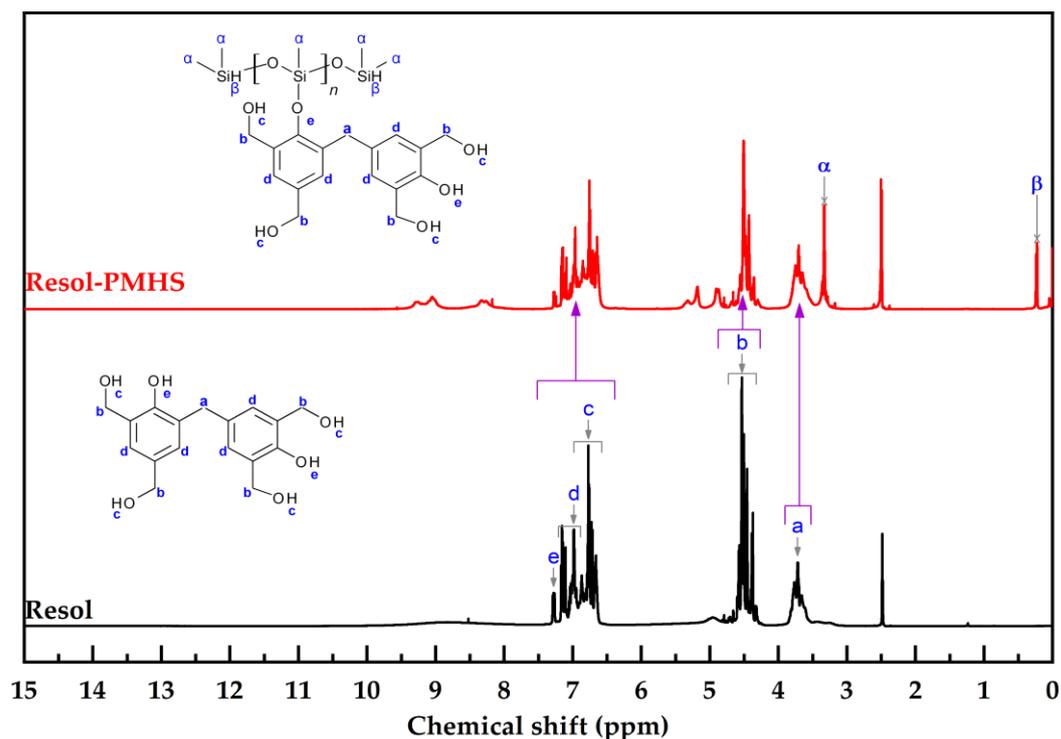


Figure 2. ^1H NMR of resol (black line) and Resol-PMHS (red line).

In the ^1H NMR spectrum of the neat resol resin (Figure 2a), characteristic proton signals are observed at various chemical shifts (δ). Specifically, protons of the methylene bridges connecting phenol units ($\text{Ar-CH}_2\text{-Ar}$) appear in the range of $\delta = 3.6\text{--}3.8$ ppm (signal a). The methylene protons of the methylol groups ($\text{Ar-CH}_2\text{-OH}$) resonate in the range of $\delta = 4.3\text{--}4.6$ ppm (signal b). A complex group of signals is recorded in the $\delta = 6.6\text{--}7.3$ ppm region, encompassing protons from the aromatic rings and hydroxyl groups. Within this region, aromatic protons (Ar-H) are primarily identified in the range of $\delta = 6.9\text{--}7.1$ ppm (signal d). A broad signal at $\delta = 7.2\text{--}7.3$ ppm (signal e) is attributed to the hydroxyl protons of the phenolic groups (Ar-OH). Signal (c), observed between $\delta = 6.6\text{--}6.8$ ppm, may comprise contributions from other aromatic protons and/or hydroxyl protons (originating from either phenolic or methylol groups).

For the ^1H NMR spectrum of Resol-PMHS (Figure 2b), the characteristic signals of the parent resol structure are largely retained, indicating that the main framework of the resin was not significantly disrupted during the modification process. However, important changes were also recorded. Most notably, the intensity of signal (e) ($\delta = 7.2\text{--}7.3$ ppm), assigned to phenolic hydroxyl protons, decreased markedly. This reduction provides strong evidence for the participation of phenolic hydroxyl groups in the reaction with PMHS. Furthermore, new signals, characteristic of the presence of PMHS, appeared at approximately $\delta \approx 0.2$ ppm and $\delta \approx 3.3$ ppm. Based on the PMHS structure, the strong singlet signal at $\delta \approx 0.2$ ppm is assigned to the protons of the methyl groups directly attached to silicon ($-\text{Si-CH}_3$). The signal at $\delta \approx 3.3$ ppm, despite exhibiting a shift from the typical value for Si-H protons in pure PMHS (which usually resonate around $\delta \approx 4.7$ ppm), can be attributed to these Si-H protons [34]. This alteration in chemical shift is likely due to the influence of the new chemical environment following PMHS incorporation into the resin network, or potentially due to the formation of new covalent bonds. These results align with the established mechanism for silane modification of phenolic resins, where the reaction between silane agents and phenolic hydroxyl groups proceeds through dehydration condensation. The formation of Si-O-C bonds is evidenced by the characteristic shifts in the NMR spectrum, confirming a successful grafting process [22].

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Combined with the results from FTIR spectroscopy (which indicated a decrease in the intensity of the ν Si-H peak), the changes observed in the ^1H NMR spectra – particularly the diminished signal of phenolic -OH groups and the appearance of Si-H as well as Si-CH₃ signals – provide convincing evidence of a chemical reaction between PMHS and the resol resin. This reaction is proposed to occur primarily through the interaction of Si-H groups on PMHS with the phenolic hydroxyl groups of the resol resin, leading to the formation of Si-O-C linkages.

Thermal Characterization

To evaluate the effect of PMHS modification on the thermal characteristics of the resol resin, Differential Scanning Calorimetry (DSC) measurements were performed. The DSC curves for the neat resol resin and samples modified with 2.5% and 5.0% PMHS are presented in Figure 3.

The DSC thermogram of the neat resol resin (black curve) displays a distinct exothermic peak with a peak temperature (T_{cure}) of approximately 163°C. This peak is characteristic of the resin's thermal curing, which proceeds via condensation reactions between methylol groups and phenolic rings to form a three-dimensional network. The observed peak temperature is in excellent agreement with the 134–163°C range reported in the literature for this curing process [30,35].

As the temperature increases further, a second, broad exothermic peak emerges around 474°C (T_d). This event is attributed to the thermo-oxidative degradation of the previously cured phenolic network. Compared to the neat resol resin, the PMHS-modified samples exhibited significant changes in their thermal behavior. Regarding the curing process, both Resol-PMHS 2.5% (red curve) and Resol-PMHS 5.0% (blue curve) showed a shift in T_{cure} towards higher temperatures, approximately 172°C and 171°C, respectively. This increase in T_{cure} by about 8–9°C suggests that the presence of PMHS influenced the initial curing kinetics or mechanism, possibly due to interactions or steric hindrance by the polysiloxane chains.

The most pronounced changes were observed in the thermal degradation region. The degradation profiles of the modified samples became more complex, with the appearance of at least two main exothermic events. Multi-stage thermal degradation behavior is characteristic of silicon-containing phenolic systems, where the presence of polysiloxane components creates distinct decomposition pathways compared to conventional phenolic resins [36]. One thermal event was recorded at approximately 465–466°C, slightly lower than the T_d of the neat resol. More notably, a second, distinct, and strong exothermic peak emerged at significantly higher temperatures, around 525°C (for 2.5% PMHS) and 527°C (for 5.0% PMHS). The appearance of this high-temperature degradation peak (> 520°C) provides convincing evidence that the thermal stability of the resol resin was substantially improved after modification with PMHS. The enhanced thermal stability is a direct consequence of integrating the silicone structure into the resin, which introduces intrinsically highly stable Si-O-C linkages. Indeed, research has shown that these bonds (specifically Si-O-Ph) are exceptionally robust, with decomposition temperatures exceeding 520°C. More importantly, upon exposure to extreme temperatures, the pyrolysis of these stable linkages leads to the in-situ formation of a silica-rich ceramic phase. This ceramic phase subsequently acts as an effective thermal barrier, significantly enhancing the overall protection of the material [33].

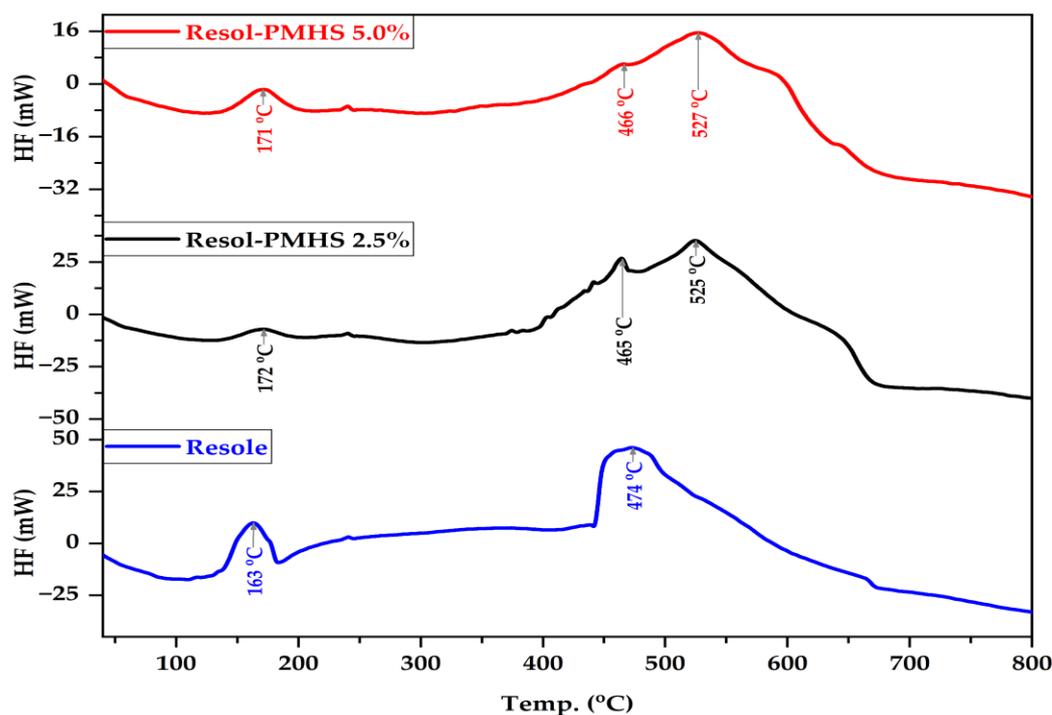


Figure 3. DSC thermodiagram of resol, and PMHS modified resols.

Comparing the two PMHS contents, it is evident that increasing the content from 2.5% to 5.0% did not significantly alter the temperature positions of the degradation peaks. However, the relative intensity of the high-temperature exothermic peak ($\sim 527^{\circ}\text{C}$) appeared more prominent in the 5.0% PMHS sample, suggesting that a higher PMHS content might promote the formation of thermally stable structures more effectively, contributing to the overall thermal stability of the hybrid material. Thus, the DSC results confirm that the incorporation of PMHS into the resol resin structure successfully enhanced the material's thermal stability.

Analysis of Thermal Stability and Degradation Process by TGA/DTG

The thermal stability and mass degradation characteristics of the neat resol resin and the Resol-PMHS hybrid materials were further elucidated through thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG), as presented in Figure 4.

Analysis of the DTG curves reveals characteristic mass loss events. In the low-temperature region ($< 200^{\circ}\text{C}$), a mass loss peak was observed for all samples. For the neat resol, this peak had a maximum ($T_{\text{max,cure}}$) at $\sim 137^{\circ}\text{C}$, corresponding to an initial mass loss of approximately 8-10% in the TGA curve. This event occurred within the temperature range of the exothermic curing process observed by DSC ($\sim 163^{\circ}\text{C}$). Therefore, this DTG peak is attributed to the release of small molecules, primarily water, generated from condensation reactions during the curing of the resol resin.

For the modified Resol-PMHS 2.5% and 5.0% samples, this low-temperature mass loss peak shifted to higher temperatures, with $T_{\text{max,cure}}$ reaching approximately 170°C . This shift is fully consistent with the increase in the exothermic curing peak temperature observed in the DSC analysis (to $\sim 171\text{-}172^{\circ}\text{C}$). This further corroborates that this initial mass loss primarily reflects the curing process and that the presence of PMHS altered its kinetics, requiring higher temperatures to achieve the maximum rate of reaction and byproduct release.

In the higher temperature region, the main degradation of the cured network structure occurred. For the neat resol, the maximum degradation rate temperature ($T_{\text{max,decomp}}$) was observed at $\sim 438^{\circ}\text{C}$. In contrast, both modified Resol-PMHS 2.5% and 5.0% samples exhibited a significant increase in their main degradation temperature, with $T_{\text{max,decomp}}$ shifting to $\sim 483^{\circ}\text{C}$. This increase in the main decomposition temperature

by approximately 45°C is a clear indication that the thermal stability of the polymer structure was substantially improved after PMHS incorporation.

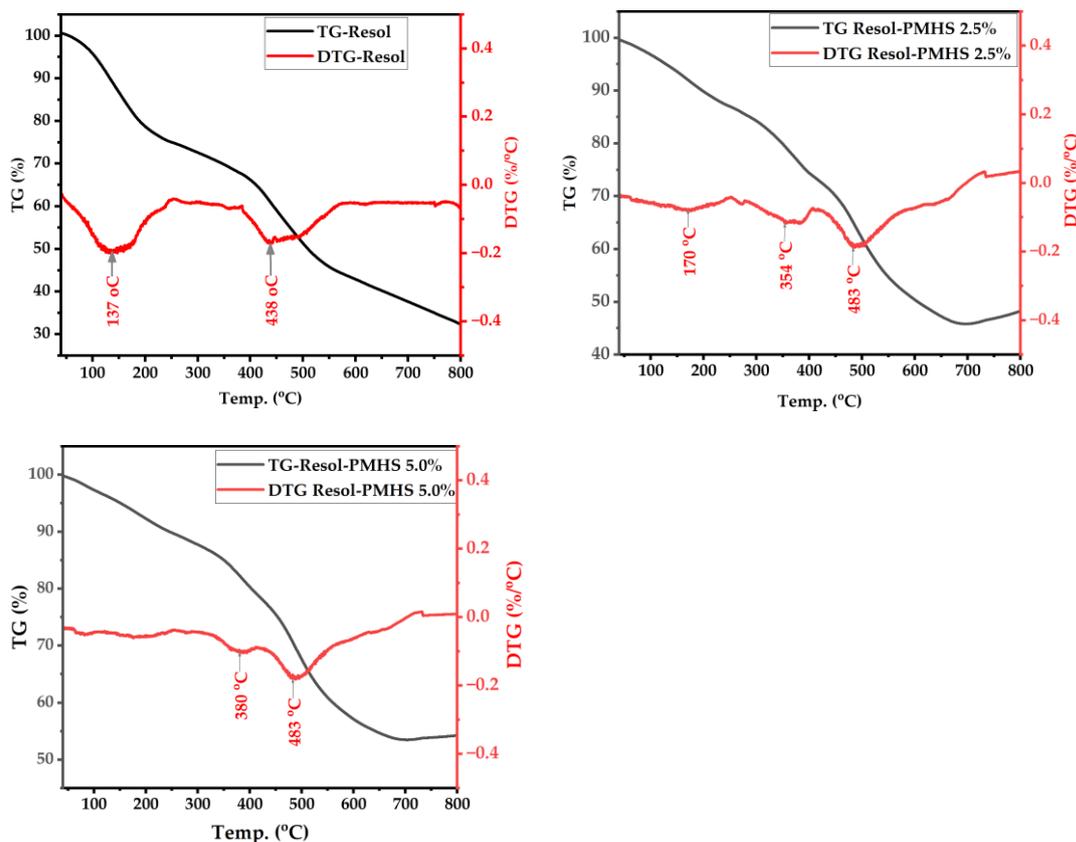


Figure 4. Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) curves of neat resol, Resol-PMHS 2.5%, and Resol-PMHS 5.0%.

Furthermore, the amount of material remaining at 800°C (char yield) also confirmed the thermal stabilizing effect of PMHS. The char yield increased from ~38% for the neat resol to ~53% for Resol-PMHS 2.5% and further to ~57% for Resol-PMHS 5.0%. The significantly higher residual mass in the modified samples, which increased with PMHS content, suggests the formation of silica-rich structures (such as silica or silicon oxycarbide) with superior thermal stability during decomposition.

In summary, the TGA/DTG results not only reflect the changes in the curing kinetics of the resol resin in the presence of PMHS (via the shift in the low-temperature mass loss peak, consistent with DSC findings) but also provide robust evidence for the considerable improvement in thermal stability and enhanced char formation of the Resol-PMHS hybrid materials.

3.2. Mechanical Properties of Composites from GF/PMHS-Modified PF composites

To evaluate the role of polymethylhydrosiloxane (PMHS) in enhancing the mechanical properties of resol resin-based composites, the tensile strength, flexural strength, and Izod impact strength of composites containing varying glass fiber (GF) content (30–60 wt%) were determined (Figure 5).

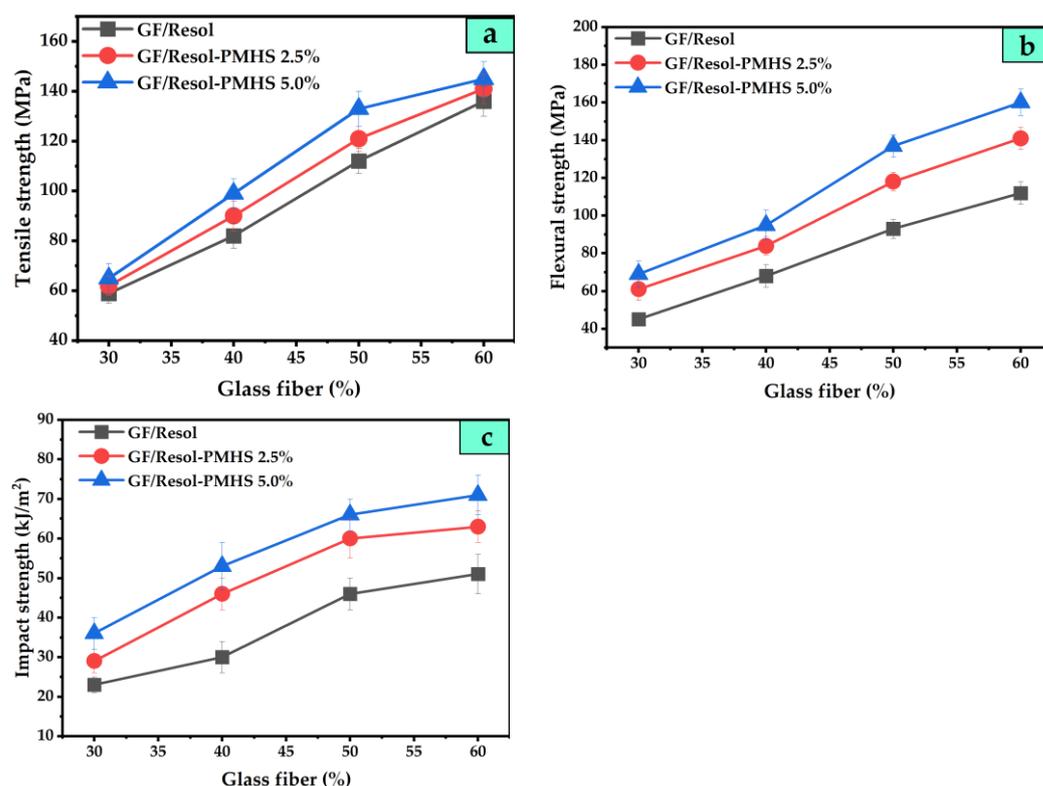


Figure 5. Mechanical properties of glass fiber reinforced resol composites with different PMHS contents in the resol matrix: (a) Tensile strength, (b) Flexural strength, and (c) Impact strength as a function of glass fiber content.

The results (Figure 5a-c) demonstrate, as anticipated, that all mechanical properties improved with increasing GF content, owing to the GF phase acting as the primary load-bearing constituent. More importantly, the modification of resol resin with PMHS led to a significant enhancement in these mechanical characteristics compared to composites fabricated with unmodified resol resin (control samples). Specifically, at all GF loadings investigated, composites based on Resol-PMHS 2.5% and Resol-PMHS 5.0% exhibited higher tensile strength (Figure 5a) than the control. For instance, at 60% GF, the tensile strength of the Resol-PMHS 5.0% sample (145 ± 7 MPa) and the Resol-PMHS 2.5% sample (141 ± 6 MPa) markedly surpassed that of the neat resol composite (136 ± 6 MPa). A similar trend was observed for flexural strength (Figure 5b): at 60% GF, the Resol-PMHS 5.0% sample achieved the highest value (approximately 160 ± 7 MPa), followed by Resol-PMHS 2.5% (141 ± 6 MPa), whereas the control sample reached only 112 ± 6 MPa. This improvement was more pronounced when the PMHS content was increased to 5.0%. Likewise, the Izod impact strength (Figure 5c), a parameter reflecting the material's toughness, was also considerably enhanced by the presence of PMHS. At 60% GF, the Resol-PMHS 5.0% sample achieved an impact strength exceeding 71 ± 5 kJ/m², significantly higher than that of Resol-PMHS 2.5% (63 ± 4 kJ/m²) and the neat resol composite (approximately 51 ± 5 kJ/m²).

This augmentation of mechanical properties can be attributed to several mechanisms. Firstly, PMHS likely improves the wetting of the GF surface by the resin and enhances the interaction and bonding at the fiber-matrix interface. Studies on glass fiber-phenolic composites have demonstrated that the wettability of reinforcing fillers is a significant factor influencing mechanical properties, with proper surface treatment and sizing agents being crucial for achieving optimal fiber-matrix adhesion [37]. Research on interfacial effects in glass fiber/phenolic composites has shown that sizing specially developed for phenolic resin significantly improves resin impregnation into fiber bundles and enhances mechanical properties [38]. The reactive Si-H groups in PMHS can potentially react chemically with hydroxyl groups on the GF surface (often pre-treated with silane coupling agents)

and/or with functional groups in the resol resin, creating covalent or hydrogen bonds. This leads to more effective stress transfer from the matrix to the reinforcing fibers, thereby enhancing the overall load-bearing capacity of the composite. Secondly, the incorporation of PMHS is believed to establish an organic-inorganic hybrid network within the resol matrix. The principle behind this approach is well-supported in the literature; creating nano-ordered hybrid materials from phenolic resins is a known strategy to significantly enhance thermal, mechanical, and film-forming properties [39]. In this context, PMHS serves as an ideal inorganic component, as it is independently recognized for its ability to form complex, three-dimensional networks with enhanced structural integrity [40]. Therefore, the integration of a flexible siloxane backbone into the rigid phenolic framework is expected to yield a synergistic improvement in the material's overall performance. Such a structure could alter the molecular chain mobility or increase energy dissipation capabilities, thereby improving the material's toughness and crack resistance, particularly its impact strength. The previously discussed changes in the matrix resin's structure and thermal stability due to PMHS (as indicated by DSC and TGA/DTG results) might also indirectly contribute to these mechanical improvements.

A comparison between the two PMHS loading levels indicates that increasing the content from 2.5% to 5.0% resulted in more distinct improvements across all measured mechanical properties. This implies that at a concentration of 5.0%, PMHS exerts a more optimal effect in strengthening the interfacial adhesion and/or enhancing the intrinsic properties of the resin matrix.

Analysis of Fracture Surface Morphology

Scanning electron microscopy (SEM) was employed to analyze the fracture surface morphology of composite materials based on unmodified resol resin (GF/Resol) and resol resin modified with 5.0% polymethylhydrosiloxane (PMHS) (GF/Resol-PMHS 5.0%), both containing 60% glass fiber (GF). This investigation aimed to elucidate the influence of PMHS on the microstructure and its correlation with mechanical properties. Figure 6 presents SEM images at various magnifications.

SEM images of the GF/Resol composite (Figures 5a-c) show that while the glass fibers (GF) are relatively uniformly distributed, higher magnifications reveal numerous voids and gaps at the fiber-matrix interface. This poor bonding is further evidenced by extensive fiber pull-out, where the clean and smooth fiber surfaces are tell-tale signs of weak interfacial adhesion [41,42]. This weak adhesion likely stems from a fundamental incompatibility between the hydrophilic surface of the inorganic glass fibers and the more hydrophobic organic resol matrix. Consequently, this flawed interface cannot effectively transfer stress from the matrix to the reinforcing fibers, which compromises the composite's integrity and diminishes its overall mechanical performance.

Conversely, the SEM images of the GF/Resol-PMHS 5.0% composite (Figures 5d-f) demonstrate a marked improvement in the microstructure. At 500 μm magnification, the glass fibers are more tightly encapsulated by the resin matrix, with fewer voids compared to the unmodified sample. At 100 μm and 20 μm magnifications, the fiber-matrix interface appears smoother, with fewer gaps or delaminations. In particular, the 20 μm image reveals a thin resin layer coating the fibers, suggesting that PMHS enhanced the wettability and adhesion at the interface. This microstructural homogeneity signifies a robust interface, capable of enhancing the composite's mechanical performance.

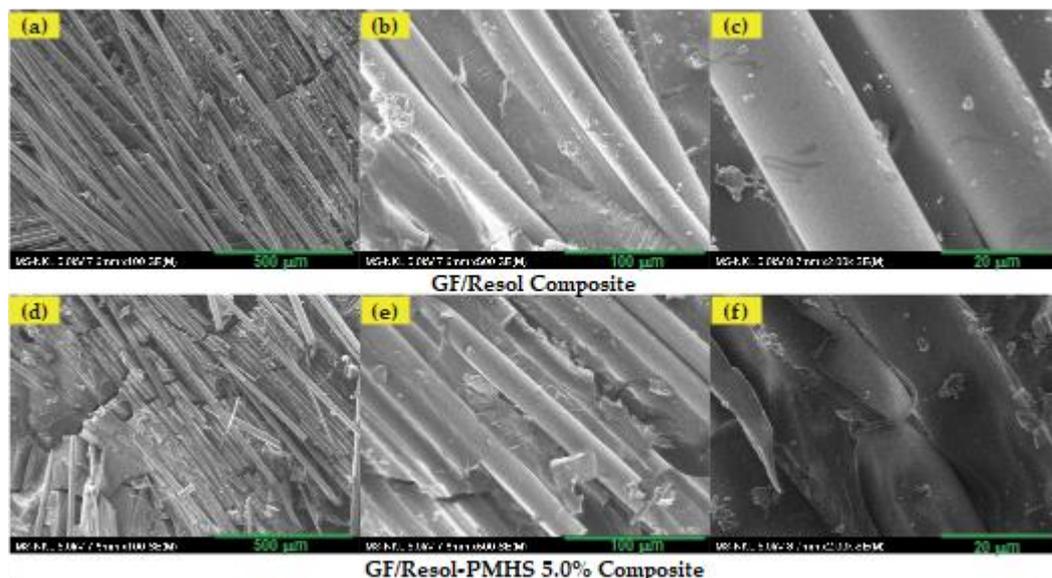


Figure 6. SEM images of GF/Resol (a-c) and GF/Resol-PMHS 5.0% (d-f) composites at 500 μm , 100 μm , and 20 μm .

The superior morphology is attributed to the multifunctional role of PMHS, which acts as a molecular bridge to couple the inorganic glass fibers with the organic resol matrix. On one side, its Si-H groups react with hydroxyls on the glass fiber surface. This mechanism is analogous to that of conventional silane coupling agents, which are known to form robust covalent Si-O-fiber bonds during thermal curing [43]. Simultaneously, the Si-H groups also graft onto the resol resin by reacting with its phenolic hydroxyls to form stable Si-O-C bonds, a reaction confirmed to enhance chemical compatibility in similar phenolic systems [22]. By covalently bonding to both components, PMHS effectively "stitches" the fiber and matrix together. This creates a stronger, more chemically compatible interphase—a finding consistent with the FTIR analysis—and explains the vastly improved adhesion. In performing this function, PMHS acts as a classic coupling agent, which are widely used to enhance the interfacial bonding and mechanical performance of fiber-reinforced composites [44].

The superior mechanical properties of the GF/Resol-PMHS 5.0% composite are a direct result of its improved microstructure. By minimizing defects and creating a stronger fiber-matrix interface, stress is transferred more efficiently from the matrix to the reinforcing fibers. This principle is fundamental to composite mechanics, as efficient load transfer across a robust interface is known to be critical for achieving high strength [45,46]. This mechanism directly explains the substantial improvements observed in the material's static properties, including the increase in tensile strength (from ~130 to 150 MPa) and flexural strength (from ~115 to 170 MPa). Furthermore, the toughened interphase and the more ductile nature of the organic-inorganic hybrid network also contribute to performance by hindering crack initiation and propagation. This additional mechanism is responsible for the observed enhancement in the composite's impact strength.

Thus, SEM analysis provides direct morphological evidence confirming the effectiveness of modifying resol resin with 5.0% PMHS. The formation of a uniform, continuous, and well-bonded fiber-matrix interface is crucial for the substantial improvement in the mechanical properties of the GF/Resol-PMHS composite material. These findings are in complete agreement with and complement the mechanical property data, reinforcing the application potential of this composite material.

4. Conclusions

This study successfully synthesized a PF resol resin modified with 5.0% PMHS, creating an organic-inorganic hybrid network. This modification concurrently enhanced the thermal stability and mechanical properties of the glass fiber (GF) reinforced composite. The improved interfacial adhesion between the fiber and resin optimized performance at a 60% GF content, yielding properties superior to the unmodified sample. These results open potential applications in industries demanding high performance and provide a basis for optimizing production processes. However, further investigation into long-term durability and aging resistance under harsh environmental conditions is warranted.

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Abbreviations

The following abbreviations are used in this manuscript:

PF	Phenol-formaldehyde
PMHS	Polymethylhydrosiloxane
IPA	Isopropanol
GF	Glass Fiber
CNSL	Cashew Nut Shell Liquid
FTIR	Fourier-transform infrared
¹ H NMR	Proton Nuclear Magnetic Resonance
DSC	Differential Scanning Calorimetry
TGA	Thermogravimetric Analysis

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