Unravelling the Influence of Surface Modification on the Ultimate Performance of Carbon Fiber/Epoxy Composites

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ABSTRACT: The overall performance of polymer composites depends on not only the intrinsic properties of the polymer matrix and inorganic filler but also the quality of interfacial adhesion. Although many reported approaches have been focused on the chemical treatment for improving interfacial adhesion, the examination of ultimate mechanical performance and long-term properties of polymer composites has been rarely investigated. Herein, we report carbon fiber (CF)/epoxy composites with improved interfacial adhesion by covalent bonding between CFs and the epoxy matrix. This leads to the improved ultimate mechanical properties and enhanced thermal aging performance. Raman mapping demonstrates the formation of an interphase region derived from the covalent bonding between CFs and the epoxy matrix, which enables the uniform fiber distribution and eliminates phase separation during thermal cycling. The covalent attachment of the CF to the epoxy matrix suppresses its migration during temperature fluctuations, preserving the mechanical performance of resulting composites under the thermal aging process. Furthermore, the finite elemental analysis reveals the effectiveness of the chemical treatment of CFs in improving the interfacial strength and toughness of silane-treated CF/epoxy composites. The insight into the mechanical improvement of CF/epoxy composites suggests the high potential of surface modification of inorganic fillers toward polymer composites with tunable properties for different applications.

KEYWORDS: surface modification, carbon fibers, polymer composites, interfacial adhesion, mechanical property

1. INTRODUCTION

Inorganic-polymer composites have been widely used in various industrial fields (i.e., aerospace and automotive industry, construction materials, and daily goods) and advanced technologies (i.e., solid-state batteries, sensors, and actuators) attributed to their high mechanical strength and stiffness while maintaining their lightweight.1−9 The ultimate performance of the composite depends on several factors including the type of reinforcement, the polymer matrix, and the interface layer.10−12 Among different fillers, carbon fibers (CFs) are especially interesting because of their superior mechanical properties, high thermal stability, low density, and scalability.13−17 Currently, around 90% of commercial CFs are produced from polyacrylonitrile via a well-established process delivering an extremely strong material with a superior strength-to-weight ratio.18 Utilization of CFs in reinforcing epoxy resin is one of the current research focuses due to the versatility of both materials and the outstanding combination to deliver high-performance structural materials.19,20 Commonly, the fabrication of CF/epoxy composites is performed by the physical blending of two components at high shear to ensure good dispersion of CFs in the polymer matrix followed by curing under specific conditions.21,22 However, aside from the exceptional mechanical properties of CFs, the resultant CF-reinforced composites usually have unsatisfactory performance caused by their poor compatibility between the inorganic filler and epoxy matrix. The weak interfacial adhesion between the CFs and epoxy matrix prevents them from their performance with theoretical strength. Their interfacial adhesion can significantly influence the effectiveness of load transfer from the weak-part polymer matrix to the substantial-part CF.23,24

The interfacial adhesion between CFs and epoxy resin, measured by the micro-rheological flow of the epoxy over the surface of CFs, determines the inorganic−organic interface, local stresses, defects at the interface, and so forth.25 Different approaches have been utilized to modify CFs, including oxidation, coating with sizing agents, nanomaterial deposition,
or chemical grafting, to facilitate the interfacial adhesion via chemical bonding, van der Waals interactions, surface wetting, and mechanical interlocking. In this aspect, modification of the CF surface with minimal damages is essential and challenging to enable high-performance properties and resistance to various physical and chemical stimuli. Among established methods of CF modification, chemical treatment is an effective approach to diminish the phase separation and improve interfacial adhesion between the CFs and polymer matrix. Without excessive deterioration of the CF surface, chemical modifications enable the introduction of new moieties on the CF surface that can be effectively interlocked with the matrix via covalent bonding. For example, Yuan and coworkers reported the improvement of interfacial shear strength of the CF/epoxy composite through oxidative etching of CFs via microplasma initiated by microwave irradiation. However, the overall tensile properties of resulting composites decreased slightly due to the defects and irregularities rendered by significant oxidation of the CF surface. Amino-functionalization of carbon-based fillers which in some cases achieves an improvement of 50% in the Young’s modulus of epoxy composites. Recently, Zabihi et al. reported effective amino-functionalization of CFs, which allowed an improvement in fracture strength and the modulus of epoxy composites by 19 and 10%, respectively. A multi-step approach was used to graft hyperbranched polyurethane on an electrochemically oxidized CF to introduce multiple amino groups that facilitated covalent attachment to the epoxy matrix, improving interfacial laminar shear strength via the formation of the continuous network at the interphase layer. Another study claimed an advanced approach by introducing polyamide grafting and deposition of carbon nanotubes/graphene oxide to combine covalent bonding with mechanical interlocking while controlling the thickness and grafting sequence on the CF surface. Until now, most of the studies have been focused on determining the effect of chemical treatment on interfacial adhesion. Along with experimental studies, molecular dynamics simulations are also integrated to study the effect of interfacial interaction between the treated carbon fillers and polymer matrix. However, its influence on the long-term mechanical performance of CF/epoxy composites, especially under thermal aging conditions, has been rarely investigated.

Figure 1. Chemical structures of (a) curing agent Jeffamine T-403 and (b) epoxy precursor bisphenol A diglycidyl ether for epoxy composite synthesis. (c) Optical image of a 50 μm milled CF. (d) Process of functionalization of the milled CF via chemical treatment to improve interfacial interactions with the epoxy matrix.
Herein, we report a direct pathway to enhance the ultimate mechanical performance of CF/epoxy composites by chemical functionalization of CFs that can react with the polymer matrix. Unlike previously reported approaches applied to fabricating CF/epoxy composites that normally use multi-stage energy-consuming approaches, the one-batch chemical approach is applied to functionalize the CFs and improve their miscibility and interfacial bonding strength. The designed step-wise curing of CF/epoxy composites improves CF dispersibility in the epoxy matrix while diminishing composite defects. Raman mapping combined with machine learning (ML) is utilized to study the effect of surface modification of CFs on interfacial adhesion that contributes to the thermal properties and overall mechanical performance. Moreover, a unique approach has been demonstrated to evaluate the long-term mechanical performance of CF/epoxy composites via exposure to a thermal cycle of temperature variations. The finite element analysis (FEA) is applied to unveil the effect of CF functionalization on the interfacial strength and toughness between the CF and epoxy followed by examining the relationship between the orientation state and mechanical performance of designed CF/epoxy composites.

2. RESULTS AND DISCUSSION

2.1. Fabrication of CF/Epoxy Composites. Fabrication of high-performance CF composites requires a good combination of the reinforcement agent and polymer matrix and effective interfacial interactions to provide a desirable transition of stress across the filler–matrix interface. The polymeric matrix typically consists of a thermoset, such as epoxy resin, and its mechanical properties determine the overall performance of resulting composites. Herein, the stoichiometric ratio of amine-based curing agent, that is, Jeffamine T-403, to epoxy precursor, that is, bisphenol A diglycidyl ether, is tuned to formulate an epoxy matrix with feasible mechanical properties. As illustrated in Figure 1a,b, the selected epoxy precursor and curing agent are mixed at 3:1, 2.5:1, 2:1, and 1.5:1 molar ratios and cured at elevated temperatures.

![Figure 2](https://example.com/figure2.png)

**Figure 2.** (a) XPS spectra of treated CFs. (b) N1s XPS spectra for the a-CF and s-CF. (c) Phase separation phenomena in CF/epoxy composites using a conventional curing regime: a cross-section of the 5 wt % p-CF/epoxy composite. (d) SEM images of the phase-separated 5 wt % p-CF/epoxy composite. Shear stress–strain curves of pure epoxy, p-CF/, a-CF/, and s-CF/epoxy mixtures at 25 (e) and 75 °C (f).
temperatures with a determined dogbone geometry. The impact of epoxide/amine ratios and curing temperatures on the tensile properties of resulting epoxy thermosets is evaluated using an Instron universal testing machine. Increasing the molar ratio of the precursor and curing agent (from 1.5:1 to 3:1) leads to enhanced tensile strength due to higher cross-linking density. The mechanical strength of polymer resin improves when the curing temperature rises from 80 to 100 °C, which is similar to that at 120 °C (Figure S1). The epoxy thermosets with a molar ratio of 3:1 show the highest mechanical strength among different feeding ratios regardless of curing temperature. However, considering the amine oxidation at high temperatures evidenced by the yellowness of resulting epoxy thermosets cured at 120 °C, the curing condition at 100 °C for 3 h is selected for the following fabrication process.

As illustrated in Figure 1c,d, the milled CFs with a length of 50 μm are chemically functionalized with the amino-terminal group through a one-pot process including chemical oxidation followed by silane treatment to introduce amino groups on the surface. The amino-functionalized CFs (s-CFs) act as additional cross-linkers in the fabrication of epoxy composites, which is expected to increase interfacial adhesion via covalent bonding with the polymer matrix. After acid treatment, the scanning electron microscopy (SEM) images show some minor irregularities on the acid-treated CF (a-CF) surface. According to the X-ray photoelectron spectroscopy (XPS) results, the a-CF has 10% of oxygen, significantly higher than that of a pristine CF (p-CF) (3%), indicating the presence of hydroxyl and carboxyl groups (Table S1). The s-CF surface appears neat and smooth, confirming that no further defects are formed after silane treatment (Figure S2). The appearance and morphology of the s-CF surface after the final treatment are similar to those of p-CF, confirming the robustness of the used treatment for effective CF surface functionalization. The XPS deconvolution spectra of the s-CF show two new binding energy peaks at 103 and 402 eV corresponding to N 1s and Si 2p, respectively, confirming the amino-functionalization of the CF surface (Figure 2a,b). Moreover, the surface roughness, as a critical parameter determining the extent of interfacial adhesion, has been examined via atomic force microscopy (AFM). It is found that the surface roughness increases obviously during the chemical treatment process, that is, p-CF < a-CF < s-CF = 5.7 < 12.7 < 22.1 nm, demonstrating successful treatment including acid etching and chemical attachment on the CF surface (Figure S3). The incorporation of reactive sites could enable the chemical cross-linking of CFs with the polymer matrix.

CF/epoxy composites were initially fabricated by incorporating different amounts of CFs (1, 5, 10, and 20 wt %) into the epoxy matrix (3:1 epoxy/amine ratio) and cured via the conventional method at 100 °C for 3 h. However, noticeable phase separation occurs as observed via SEM, which can be explained by the poor compatibility and different densities of the CF and epoxy resin, along with reduced viscosity of the polymer matrix at high temperature which results in rapid settling down of CFs (Figure 2c,d). To achieve uniform impregnation of CFs in epoxy resin, the effective dispersion of CFs in the resin and pre-fixing before the gel point are essential. Herein, as illustrated by the advanced curing stepwise protocol shown in Figure S4a, the epoxy matrix is
Preheated at 50 °C for 60 min to allow initial curing followed by adding a specific amount of milled CFs. The mixture is then mixed for an additional hour at 50 °C to enable uniform distribution of CFs, followed by a stepwise cure at 50, 75, and 100 °C. The precise curing protocol helps initiate cross-linking to a certain curing extent at each temperature step, thus allowing us to maintain a high level of viscosity to avoid settling down of fibers. Moreover, the applied curing regime allows us to achieve a fully cured product with a final gel content of 95–98.5% (see Table S2). Such a rational stepwise curing process can efficiently preserve their uniform impregnation in a polymer matrix (Figure S4b). Aside from the applied stepwise curing protocol, the surface functionalization of the CF surface has also shown a significant contribution to the dispersibility of CFs in the epoxy medium. The p-CF exhibits poor dispersibility in the polymer matrix due to its low surface energy and poor wettability.

Comparatively, the presence of amino groups allows enhanced interaction with the polymer matrix, resulting in the uniform dispersion of s-CFs in the medium as determined by the SEM imaging (Figure S5).

The comparative rheological behavior of pure epoxy resin and CF/epoxy mixtures is evaluated at different temperatures to examine the effect of CF incorporation on their ultimate viscoelastic properties. Commonly, pure epoxy exhibits Newtonian fluid behavior where the viscosity is equal to the shear stress/shear rate, as shown in Figure 2e,f.47 The viscosity of epoxy increases with the presence of CFs (~37% increase: 6.9 vs 9.6 Pa·s) at 25 °C and exhibits a linear behavior with the rise of the shear rate. It is worth pointing out that the presence of s-CFs in the epoxy matrix results in noticeable enhancement of viscosity compared to that in a-CF and p-CF/epoxy mixtures (>10%) (Figure 2e). This can be explained by the uniform dispersion of s-CFs and improved interaction between s-CFs and epoxy precursors. The same trend is observed for the viscosity of CF/epoxy mixtures measured at 75 °C (Figure 2f). At a higher shear rate, the CF/epoxy mixtures show a distinct deviation from the pure epoxy in terms of viscosity. This suggests that chemical treatment intrinsically promotes the miscibility and interactions between the CFs and epoxy matrix.

2.2. Thermal and Mechanical Performance of CF/Epoxy Composites. To evaluate the effect of impregnation of CFs on the thermal properties of CF/epoxy composites and their interactions with the epoxy matrix, the composites with the 5 wt % p-CF, a-CF, and s-CF are examined using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The maximum decomposition temperature of the neat epoxy resin is 392.7 °C. In contrast, incorporating 5 wt % of p-CFs slightly increases the decomposition temperature, demonstrating the enhanced thermal stability of the resulting composite (Figure S8). In addition, the different char yield measured by TGA between neat epoxy and s-CF/epoxy composites is 3.9–4.1%, which is consistent with theoretical CF loading. The acid treatment of CFs increases the amount of oxygen-containing functional groups on the a-CF surface, which is prone to degradation. Therefore, the char yield in a-CF/epoxy composites determined by TGA is lower (close to 3.1%). As illustrated by DSC measurement, CF/epoxy composites show slightly lower $T_g$ values (79–82.2 °C) compared to the neat epoxy resin (83.3 °C) (Figure 3a). It could be explained that the formation of micro-gaps between the CFs and epoxy affords more free volume at the interface, thus enhancing the mobility of polymer chains.48 With the same loading amount, the a-CF/epoxy composites have noticeably lower $T_g$ than CF/epoxy composites and s-CF/epoxy composites due to cavities and high surface roughness of...
a-CFs, which may lead to even higher free volume and enhanced chain mobility.49

The viscoelastic properties of CF/epoxy composites with 5 wt % CF loading are explored by dynamic mechanical analysis (DMA) in the temperature range from 40 to 175 °C. As shown in Figure 3b, the higher storage modulus of epoxy composites compared to that of neat epoxy in the glassy region (<70 °C) can be explained by the increased stiffness of CFs enhancing the rigidity of the epoxy matrix.48,50,51 Moreover, it is worth noting that the existence of covalent bonds between the s-CFs and polymer matrix enables even higher $E'$ values in the range.48 On comparing the loss modulus in the glass transition region (80−90 °C), it is seen that $E''$ of s-CF/epoxy composites is significantly higher than that of neat epoxy (390 vs 260 MPa), which confirms the higher heterogeneity of the system and enhanced energy dissipation caused by the incorporation of CFs (Figure 3c). Higher $E''$ values are explained by higher heat generated during damping under the dynamic condition in CF/epoxy composites due to the high associating interaction between CFs and polymer chains.52

The enhanced mobility of polymer chains and interfacial friction with CFs in the epoxy matrix lead to lower $T_g$ as determined by the maximum tan δ peak (Figure 3d). The performed creep testing shows that the fabricated CF/epoxy composites are resistant to creep rupture at 30 °C. The long-term creep resistance of the epoxy composites can be significantly enhanced with reduced creep deformation by introducing s-CFs to the epoxy matrix. Moreover, the creep deformation for s-CF/epoxy composites compared to that of p-CF and a-CF/epoxy composites has been considerably reduced because the intimate s-CF/epoxy interface allows the effective load transfer between the s-CF and epoxy matrix (Figure 5a).

To evaluate the effect of surface modification of CFs on the ultimate mechanical performance, the tensile tests of neat epoxy and CF/epoxy composites are performed. The s-CF is expected to enhance interfacial adhesion between the CF and epoxy matrix via the formation of permanent covalent cross-links, therefore facilitating improved fiber–matrix stress transfer under loading. The filler dimension is also a key parameter affecting the distribution of CFs in the polymer matrix and its mechanical performance. Herein, aside from using CFs with 50 μm length ahead, we also chemically modify the CF with 200 μm length here to evaluate the effect of filler dimension and CF loadings on the mechanical properties of CF/epoxy composites. As illustrated in Figure 4, the ultimate tensile strength for 50 μm CF/epoxy composites has improved considerably compared to that of neat epoxy (60.8 MPa) with the highest value for 1 wt % CF loading (73.9−75.3 MPa). However, a further increased amount of CFs in the epoxy matrix does not enhance material strength, perhaps due to poor distribution of CFs into the matrix with higher loading and lack of effective fiber–matrix stress transfer. Upon introduction of amino groups, the covalent attachment of s-CFs to the epoxy matrix effectively facilitates the successful load transfer from the polymer to the filler, thus maintaining the stiffness of the composite. The effect of surface treatment of CFs is observed in Figure 4a−c, where at the same CF loadings, the tensile strength of s-CF/composites has noticeable improvements. Moreover, with the same amount of CFs, the 5 wt % s-CF/epoxy composites significantly increased tensile strength (72.5 MPa) compared to the 5 wt % p-CF/epoxy composite (62.6 MPa). This could be explained via covalent bonding and improved interfacial interaction.53

Figure 5. (a) Schematic representation of the thermal aging process in CF/epoxy composites. (b) Thermal cycling protocol for CF/epoxy composites during the aging process. (c) Extent of deterioration of tensile strength of epoxy composites after thermal cycling.

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by the better dispersity of s-CFs and effective covalent reinforcement of the epoxy composite. The low surface energy and inertness of p-CFs lead to poor dispersibility and decay of composite mechanical performance, especially at higher loading percentages. Considering epoxy composites with incorporated 200 μm CFs, no significant improvement of tensile strength is observed, which could be explained by the poor dispersibility of CFs that led to the deficiency of desired stress transfer at the fiber–matrix interface. The deficiency in uniform distribution of 200 μm CFs in the polymer matrix plays a significant role in the mechanical performance of resulting CF composites. Therefore, the surface treatment of such CFs has a negligible effect on their ultimate tensile strength (Figure S10a,b).

Temperature variation occurs in many application fields of CF-based composites including automotive, aerospace, and so forth. At the same time, different thermal expansion between the hard filler and soft matrix will interfere with their intimate contact and hence mechanical performance afterward. Therefore, it is crucial to evaluate the properties of CF/epoxy composites during thermal aging to predict their performance during service. Herein, the mechanical performance of original fabricated and thermal cycling exposure CF/epoxy composites with 1 wt % CF loading is studied. The thermal cycling of CF/epoxy composites is conducted by heating a range of composites at 80 °C for 24 h and then cooling down to 4 °C while holding at this temperature for the next 24 h (Figure Sb). Their tensile properties are evaluated after thermal exposure of composites to 12 thermal cycles (24 days). As illustrated in Figure 5c, the overall decay in mechanical properties of CF/epoxy composites could be attributed to the aging and degradation of the epoxy matrix. This is consistent with a recent study where the ultimate tensile strength of epoxy materials decreases with increased thermal aging time because the embrittlement of epoxy resin during such a process results in the growth of microcracks. The deterioration of mechanical properties is also caused by the residual thermal stress in the polymer matrix due to the difference in the coefficient of thermal expansion (CTE) between the CF and epoxy polymer (CF: from −1.04 × 10⁻⁶/°C; epoxy polymer: 44–55 × 10⁻⁶/°C). The existence of CTE mismatch in composite components also leads to the stress concentration at the interface, the creation of cracks, and potential delamination in that region (Figure 5a). As it is known, the decrease in free volume in the epoxy polymer during thermal aging leads to the formation of a highly dense-packed structure that has a lower extent to withstand the applied force, leading to microcrack formation, which subsequently leads to polymer failure at lower loads (lower tensile strength). Therefore, the formation of a robust interface layer between the s-CF and epoxy matrix helps prevent excessive packing of polymer chains, thus affording limited polymer mobility and enhanced capability to withstand applied loads. On the contrary, due to the natural immiscibility and poor distribution of CFs in the epoxy matrix, the highest decay in mechanical properties is observed in the p-CF/epoxy composites. On the other hand, a noticeable improvement in the tensile strength of s-CF/epoxy composites after thermal treatment is observed. The chemical attachment serves as a bridge domain in the polymer matrix during thermal cycling, preserving its mechanical performance. As expected, the s-CF/epoxy composite has the lowest decay of ultimate tensile strength among different composites because the covalent reinforcement of the epoxy matrix prevents the reduction of free volume during the thermal cycling.

2.3. Unveiling the Effect of Surface Treatment of CFs on the Mechanical Performance. Evaluation of mechanical properties of treated CF/epoxy composites and their performance during thermal aging provides an insight into the effect of CF treatment on the interface between the nanofiller and epoxy matrix. The enhanced tensile strength and storage modulus in a glass region for s-CF/epoxy composites could be attributed to the improved interfacial adhesion of s-CFs to the epoxy polymer via permanent covalent bonding that facilitates better stress transfer across the composite matrix. The performed thermal aging study also suggests that the permanent attachment moderately preserves its mechanical properties during thermal cycling and partially releases the stress concentration at the interface of the epoxy composite, which is commonly presented in regular physically blended CF/epoxy composites.

With the capability to explore the interfacial heterogeneity, Raman mapping with clustering analysis is employed to study the effect of chemical treatment of CFs toward examining the interfacial region CF/epoxy composites. Mapping scaled by the intensity of an individual Raman signal allows estimating the distribution of representative species. For example, the Raman mapping based on the C–H stretching, vC–H at 2968 cm⁻¹ shown in Figure S6, indicates the epoxy distribution on a scanned area. This peak only shows up in the epoxy reference (Figure S6). Notably, the s-CF has two bands centered at 1349 and 1593 cm⁻¹, ascribed to the carbon D and G bands, respectively. These two bands convolute with the Raman peaks from the epoxy in the same region. Combined with the low weight ratio of CFs (<1 wt %) in each composite, distinguishing the carbon distribution in each sample using the D and G bands becomes quite challenging. The s-CF, however, has a band centered at 2697 cm⁻¹ (Figure S6), which is overlapped with the 2D band of the CF and becomes more intense after silane treatment. Despite its capability of estimating the distribution of a given species, the Raman mapping based on individual Raman peak intensity fails to unveil the heterogeneity of chemical information statistically. In addition, critical information on the spatial structural difference is missing. Herein, the structural heterogeneity can be distilled by the K-means clustering analysis. Briefly, the K-means clustering algorithm is to partition the total number of Raman spectra (denoted n), \( \{x_1, x_2, x_3, ..., x_n\} \) within the Raman mapping into K sets (K ≤ n), to minimize the within-cluster sum of squares, defined by the objective function J as

\[
J = \arg\min_{\{c_i\}} \sum_{i=1}^{K} \sum_{x \in S_i} ||x - c_i||^2
\]

(1)

Here, \( c_i \) is the mean of points (or centroid). It serves as the cluster spectrum in the K set \( S_i \). The value of the centroid is updated to a new one \( c_i^{new} \) based on the following equation

\[
c_i^{new} = \frac{1}{|S_i|} \sum_{x \in S_i} x_j
\]

(2)

The algorithm experiences iterative refinement until it is converged. Consequently, the total number of m spectra can be grouped into several clusters with similarities. The centroid spectrum of that cluster can then represent the standard features of all spectra in each category.
As shown in Figure 6a, the Raman mapping of CF/epoxy composite spectra can be categorized into three clusters (color-coded for three regions, green, blue, and red). While the red zone has an average spectrum bearing mostly the noise (cluster 3 in Figure 6a), the other two clusters exhibit meaningful Raman bands, with Cluster 1 (green) representing the epoxy and Cluster 2 (blue) representing the mixture of the CF and the epoxy (due to the existence of the 2D band at 2700 cm$^{-1}$). However, there is no distinguished interfacial region between the CF zone (blue) and the epoxy zone (green). For the a-CF/epoxy composite, we assume the $K$ value to be 5. However, based on Figure 6b, there is no appreciable difference among all centroid spectra from different clusters. The vanished 2D band of the a-CF may indicate a less favorable interaction between the a-CF and the epoxy matrix. Intriguingly, the s-CF/epoxy composite exhibits several zones with distinguished structures (Figure 6c). The green zone (Cluster 3) reveals the centroid spectrum identical to that of the epoxy, suggesting that the green-colored region was filled by epoxy. The brown zone (Cluster 4) and blue zone (Cluster 2) exhibit a transition from the bulk epoxy to the red and cyan zones. In this region, the peak intensity at 2700 cm$^{-1}$ is noticeably higher than that of the bulk epoxy. Such a transition region may serve as a third phase that bears structural information stemming from the interaction between the s-CF and epoxy. The transition region observed from the s-CF/epoxy composite is not seen in the other two counterparts. It manifests the preferable interfacial interactions between the s-CF and epoxy matrix. The presence
of an interfacial region between the s-CF and epoxy matrix confirmed by Raman mapping has improved the mechanical performance of CF/epoxy composites.

After tensile tests, SEM imaging of CF/epoxy composites is primarily conducted to reveal the effect of surface treatment of CF on the interface. SEM images show that the contact area between the p-CF and epoxy matrix after tensile testing appears to be very smooth attributed to a lack of friction and ease of pulling out p-CFs from the polymer matrix due to their poor interfacial adhesion. On the other hand, the interface between s-CFs and the epoxy matrix is relatively rough with cavities, indicating the effective bonding with the polymer while reinforcing tensile properties.

The simultaneous breakage of the s-CF and epoxy matrix after tensile measurement confirms their strong interfacial bonding where the interfaces almost remained intact even after failure. Hence, the enhanced interface holds the s-CF and epoxy matrix together, which is mainly responsible for the transition in the failure mode from interfacial debonding to transverse fracture (Figure 4d–f).

Covalent bonding between the s-CF and polymer matrix allows a high-strength interface region and improves mechanical strength even after the thermal process. SEM imaging is also used to study the process of potential migration of CFS in the polymer matrix during the thermal cycling, while the elevated temperature reaches the glass transition region. The difference in the CTE and enhanced mobility of polymer chains close to the \( T_g \) region could directly impact the final distribution of CFs after thermal aging. The results show a slight change in the distribution of p-CFs in the p-CF/epoxy composite after thermal aging, suggesting that during the heating/cooling cycle, p-CFs can migrate within the polymer matrix forming some aggregations shown in Figure S11a. On the other hand, the covalent attachment of s-CFs to the epoxy matrix suppresses the s-CF movement during the thermal aging process, preserving its distribution on the s-CF/epoxy composite. Moreover, such efficient bonding retains its
intimate contact after the thermal process on materials with different CTEs. Thus, the improved adhesion between the s-CF and epoxy matrix leads to effective stress transfer along the fiber–matrix interface during the tensile tension as shown in Figure S11b, therefore enhancing the stiffness of the composite.

To further confirm the effect of the surface modification of CFs on final composite performance, we also extracted the interfacial properties and studied their mechanical performance using FEA simulations. The FEA models are established via a Python-Abaqus customized program (Figure S12), and the interfacial strength and toughness are fitted with experimental data. Figure 7a compares the stress–strain curves of 5 wt% p-CF, a-CF, and s-CF/epoxy composites under tensile loads. By fitting the interfacial properties, the FEA results match the initial stress–strain curves, stiffness, and the ultimate strength of the experimental data. Divergences between FEA and experimental curves are observed at large strains. This can be explained by the fact that the interfaces of each fiber and the surrounding matrix are identical in FEA; however, inevitable random defects may exist in experimental cases. Therefore, when larger strain is applied, these defects make experimental data deviate more from the theoretical modeling cases. The s-CF/epoxy composite enhances interfacial strength over the p-CF and the a-CF interfaces by 25 and 56%, respectively. In addition, the silane treatment of CFs results in a substantial increase (>1.6 times higher) in interfacial toughness compared with p-CF (Figure 7b). Under tensile loading, the contours of the first-principals stress and strain distributions are shown in Figure 7c,d for s-CF interfaces and Figure S13 for p-CF and a-CF interfaces. The maximum stress occurs around the ends of the transversely oriented fibers (90°), which causes the stress concentration and leads to interface failure, failing the whole composite. In short, performed simulation studies also confirm the effectiveness of CF surface treatment in enhancing the final performance of CF/epoxy composites via a detailed analysis of the mechanical properties of the CF/epoxy interface.55,66

The fabrication of CF/epoxy composites with strong interfacial interactions allows significantly enhanced mechanical performance and long-term stability which is vital for practical applications including automotive and aerospace industries. Thus, the rational design of the CF surface by the introduction of sites for covalent bonding provides opportunities for the development of high-performance composite materials.

3. CONCLUSIONS

In summary, we investigate the effect of interfacial adhesion on the ultimate mechanical performance and long-term properties of CF-reinforced polymer composites via the efficient chemical treatment of milled CFs. The one-batch silane treatment of CFs results in a robust interphase between the s-CF and epoxy matrix, which achieves improved physical performance. Among all tested compositions, 1 wt% 50 μm CF loading has shown promising thermal and mechanical properties, for example, tensile strength. The unique thermal aging test reveals the positive effect of surface modification of CFs for long-term applications where 1 wt% of the s-CF epoxy composite can effectively preserve its mechanical performance over 12 thermal cycles, that is, 24 days, superior to that of p-CF epoxy composites. Raman mapping results confirm the presence of a notable interphase area between the s-CF and epoxy, establishing the presence of strong interfacial interaction between the matrix and surface-modified carbon filler. SEM imaging shows cavities and the rough area around the s-CF/epoxy interface, suggesting the presence of strong interactions due to permanent covalent bonding. FEA also confirms the effect of chemical treatment of CFs toward the formation of a strong s-CF/epoxy interface with higher toughness that withstands higher loadings and provides better stress distribution across the composite. The insight into the relationship between the inorganic/organic interface and mechanical/thermal aging performance of silane-treated CF/epoxy composites will shed light on the rational design of high-performance filler-reinforced polymer composites for various applications.

4. EXPERIMENTAL SECTION

4.1. Materials. Pitch-based CFs used in this study were DIALEAD CARBON FIBER: K223HM distributed by Mitsubishi Chemicals, Inc., with a density of 2.2 g/cm³, an average length of 50–200 μm, a tensile modulus of 900 MPa, and a tensile strength of 3.8 GPa. The epoxy precursor bisphenol A diglycidyl ether with a purity of 100% and trimethylolpropane tri[poly(propylene glycol), amine terminated] ether (T-403) with an average Mn of 440 g/mol were supplied by MilliporeSigma and used as received. Sulfuric acid (ACS reagent, 95.0–98.0%), nitric acid (ACS reagent, ≥90.0%), ethanol (ACS reagent, >95% pure), and (3-aminopropyl) trimethoxy silane (97%) were supplied by MilliporeSigma.

4.2. Functionalization of Milled CFs. The pure milled CF (3 g) was dispersed in the mixture (300 mL) of sulfuric/nitric acids in a volume ratio of H₂SO₄/HNO₃ = 3:1, respectively. The acid treatment of milled CFs was carried out at 60 °C for 1 h. Then, the a-CF was purified using distilled water and dried in a vacuum oven for 24 h at 80 °C. Silane treatment was conducted using a-CFs (2 g) dispersed in ethanol (100 mL) and mixed with 23 mL of the silane agent (3-aminopropyl) trimethoxy silane at 300 r.p.m. and heated at 60 °C overnight. The modified CF (s-CF) was washed with distilled water three times and dried in the vacuum oven at elevated temperature to constant weight.

4.3. Fabrication of CF/Epoxy Composites. CF/epoxy composites were fabricated by mixing the epoxy binder with milled CFs in 0.5–20 wt%. The epoxy binder was prepared in various epoxy/amine ratios 3:1, 2.5:1, 2:1, and 1.5:1 by mixing the epoxy precursor bisphenol A diglycidyl ether with the curing agent trimethylolpropane tri[poly(propylene glycol), amine terminated] ether at 50 °C till the mixture became homogeneous. Then, a specific amount (0.5–20 wt %) of milled CFs was added to the binder mixture and mixed for 30 min. The CF/epoxy mixture was poured into Teflon dogbone molds (200 × 50 × 10 mm) and cured according to the curing protocol. The conventional curing was performed at elevated temperatures (80, 100, or 120 °C) for 3 h. Herein, the samples were step-wise cured at 50, 75, and 100 °C for 1 h at each temperature.

4.4. Characterization of Treated CF and CF/Epoxy Composites. SEM was applied to evaluate the surface morphology of the p-CF, a-CF, and s-CF, and the fracture morphology of CF/epoxy composites was observed using a scanning electron microscope (Zeiss Auriga focused ion beam–SEM system, Carl Zeiss Microscopy GmbH, Germany), with an acceleration voltage of 5 kV. The non-conductive samples were sputter-coated with gold for 10 s before testing using a high-vacuum turbo evaporator.

XPS of pristine and treated CFs was carried out using a Thermo Scientific instrument (Waltham, MA, USA) to detect the elemental composition of the CF surface. The XPS data were obtained using an Al Kα X-ray source operated at 15 kV for an applied power of 300 W. AFM measurements in a tapping mode were performed using the instrument AIST-NT, Novato, USA. An OTESPA-R3 tip from Bruker with a resource frequency at 550 kHz and with a radius of < 10 nm was used. The phase and topography of the CF surface were measured. The surface roughness was obtained from topography images using instrument software. The CF samples were prepared by
dispersing each type of CF in DI water at a 10 mg/mL concentration. The silica wafers were cleaned with various solvents and dried using a nitrogen gas. 0.2 mL of solution with CFs was drop-cast on the wafer followed by the solvent evaporation under ambient conditions for 24 h. In order to prevent uneven solvent evaporation, a lid was placed over a Petri dish with the sample, and initially, a few drops of water were placed next to the sample. After 24 h of drying, the samples were purged with nitrogen gas to remove all water.

Raman spectroscopy experiments were conducted on a confocal Raman spectrometer (WITec, GmbH 532 nm, objective = 100 ×, a grating with 600 grooves/mm, numerical aperture (N.A.) = 0.9, local power < 300 μW). The laser spot diameter was estimated to be 0.7 μm. The scan region was set at 30 × 30 μm², with a 600 nm/pixel step size. The integration time was set to 3 s for each point. All Raman mappings were analyzed using Witec Project Plus software and the K-means clustering algorithm integrated into the Scikit-learn platform with a previously reported similar method.56,67

TGA of the CF/epoxy composites was done by using the TA TGA Q50. For the TGA test, the composite samples (10–15 mg) were heated from room temperature to 800 °C at a heating rate of 20 °C/min using a nitrogen flow of 50 mL/min. The glass transition temperature of CF/epoxy composites was analyzed using DSC (TA Instruments DSC 2500) in the heating/cooling/heating regime in the temperature range (0–180 °C) with dry nitrogen purging of the sample at a 50 mL/min flow rate. The composite samples (10–20 mg) were heated/cooled at a 10 °C/min rate. Using the temperature ramp test, the mechanical properties of the CF/epoxy composite were determined using DMA 850 (TA Instruments) in the temperature range of 20–150 °C. The rectangular-shape sample specimens were loaded between clamps and soaked at starting temperature for 5 min before testing.

Creep tests for CF/epoxy composites were conducted on the DMA 850 (TA Instruments) at a temperature of 30 °C (below glass transition temperature). Static stresses of 1 and 2 MPa were applied at the center point of the long side of the sample through the sample thickness for 1000 s.

Thermal aging of CF/epoxy composites was conducted by applying thermal cycling using low-/high-temperature variations to CF/epoxy composites (4 °C for 24 h/80 °C for 24 h) over 12 thermal cycles. The tensile testing of cured CF/epoxy composites was performed before and after thermal aging. Tensile properties of CF/epoxy composites were determined according to ASTM D1708 using an Instron universal testing machine 3343 with 1 kN cell capacity at a cross-head speed of 1 mm/s. At least five samples were tested from each composition, and the average data of tensile strength, elongation at break, and moduli were calculated.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.2c11281.

Stress–strain curves of epoxy thermosets cured at various temperatures; element composition of the CF surface before and after treatments determined by XPS; SEM images of the p-CF, a-CF, and s-CF with the length of 50–200 μm; advanced curing protocol for CF/epoxy composite fabrication and the SEM image of the 10 wt % p-CF/epoxy composite cured using a stepwise heating protocol; Raman mapping and spectra of p-CF/and s-CF/epoxy composites; TGA curves of CF/epoxy composites; stress–strain curves of 200 μm CF/epoxy composites; and FEA model of CF/epoxy composites (PDF)

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**Notes**

The authors declare no competing financial interest.

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