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Title: Interfacial Properties of Hybrid Cellulose Nanocrystal/Carbonaceous Nanomaterial Composites for Proceedings of the **American Society for Composites—Thirty-sixth Technical Conference**

Authors: Ozge Kaynan
Lisa Perez
Amir Asadi

ABSTRACT

Cellulose nanocrystal (CNCs) assisted carbon nanotubes (CNTs) and graphene nanoplatelets (GnP) were used to modify the interfacial region of carbon fiber (CF) and polymer matrix to strengthen the properties of carbon fiber-reinforced polymer (CFRP). Before transferring CNC-CNTs and CNC-GnPs on the CF surface by an immersion coating method, the nanomaterials were dispersed in DI water homogeneously by using probe sonication technique without additives. The results showed that the addition of CNC-CNT and CNC-GnP adjusted the interfacial chemistry of CFRP with the formation of polar groups. Furthermore, according to the single fiber fragmentation test (SFFT), the interfacial shear strength (IFSS) of CNC-GnP 6:1 and CNC-CNT 10:1 added CFRP increased to 55 MPa and 64 MPa due to modified interfacial chemistry by the incorporation of the nanomaterials. This processing technique also resulted in improvement in interlaminar shear strength (ILSS) in CFRPs from 35 MPa (neat composite) to 45 (CNC-GnP 6:1) MPa and 52 MPa (CNC-CNT 10:1).

INTRODUCTION

Carbon fiber reinforced polymer composites (CFRPs) have been highly used in applications such as aerospace and automotive areas due to their high strength to weight ratios[1, 2]. Yet, the main disadvantage of CFRPs (especially epoxy composites) is their brittle fracture behavior and their nature of low resistance to impact loads. These drawbacks can be mitigated by enhancing the interfacial properties between the components. An effective interfacial bonding between the components depends on the stress transfer from the polymer matrix through the reinforcing fibers. Hence, a well-architectured interface in CFRP is desired to achieve improvements in the comprehensive mechanical performance of the composites[3, 4].

Ozge Kaynan, Department of Materials Science and Engineering, Texas A&M University, College Station, Texas 77843, United States
Lisa Perez, High-Performance Research Computing, Texas A&M University, MS 3361 College Station, Texas 77843-3361, United States
Amir Asadi, Department of Engineering Technology and Industrial Distribution, Texas A&M University, College Station, Texas 77843-3367, United States

Various strategies have been proposed to increase the interfacial bonding between the fiber and the polymer matrix including surface treatment[5], polymer sizing[6], and the incorporation of nanomaterials at the interface[2, 3, 7, 8]. The latter strategy provides a great potential to enhance fiber-matrix bonding and to increase the toughness of CFRPs. It has several advantages such as the ability to be directly applied at the interface of CFRPs and easy manufacturing, which makes them suitable for industrial applications. For this purpose, cellulose-based nanomaterials have been used at the interface of CFRP for improving the interfacial bonding of the components[9]. The rod-like cellulose nanomaterials, which are called cellulose nanocrystals (CNC), offer relatively strong mechanical properties, low density (1.5 g/cm^3), high aspect ratio (10-100), and availability in nature, which make them potential candidates to modify the interface of CFRPs [1, 7]. A way to further enhance CNCs mechanical properties at the interface is to combine them with highly strong nanomaterials such as carbon nanotubes (CNTs) and graphene nanoplatelets (GnPs). In the literature, the researchers showed that cellulose nanomaterials create an interaction such as electrostatic attraction[10] when combined with carbon nanomaterials including CNTs and GnPs. Our previous paper[7] showed the potential use of CNC-CNT in CFRP, yet the interfacial performance of these composites remained unclear.

In this study, we investigated and compared the interfacial properties of CRRPs enhanced by CNC-CNT and CNC-GnP. The CNC-CNT and CNC-GnP suspensions were prepared by a probe sonication technique in which CNCs were used to assist the dispersion of pristine CNTs and GnPs in DI water. The CNC-CNT and CNC-GnP nanomaterials were transferred to the CFRP interface by immersion coating technique. Then, the nanomaterial incorporated CFs were used to manufacture composites by vacuum-assisted resin transfer molding (VaRTM). The surface chemistry of CFs and interfacial chemistry of CFRPs were correlated with the interfacial and interlaminar properties of CFRPs. The results showed that the incorporation of CNC-CNT and CNC-GnP into CFRPs resulted in the formation of polar groups at the interface, which helped to enhance the interfacial shear strength (IFSS) and interlaminar shear strength (ILSS) of CFRP composites.

MATERIALS AND METHODS

CNCs (2.3-4.5 nm diameter and, 44-108 nm length) were supplied from CelluForce, QC, Canada. The pristine multi-walled CNTs (USNano, USA) with the diameter of 5-15 nm and length of 10 µm and GnP (Celtig, USA) with 2-5 µm dimensions were used as received. Furthermore, the unidirectional Hexcel IM7 Intermediate Modulus CFs and Pro Set epoxy INF-114 and INF-211 were used.

The aqueous suspensions with 0.2 wt % CNC, CNC-CNT, and CNC-GnP were prepared using probe sonication at 20 kHz frequency with 75 % intensity. These suspensions were used for immersion coating of CFs, where the fabrics were immersed in a bath of suspension for 20 minutes, and followed by drying overnight and then in the oven at 60°C.

After the coating process, the composites for the ILSS test were prepared by VaRTM with a stacking sequence of $[0_2,90_2,0_2]_s$. The composites were cured at 60°C for 8 hours. The ILSS test was conducted according to ASTM D2344. Furthermore, to evaluate the IFSS, the single fiber fragmentation (SFFT) samples were prepared by inserting a single filament from the coated CF row into a dog-bone shape mold by taping

down two of its ends and followed by pouring epoxy into the mold. The same curing process with the hybrid composites was followed for ILSS composite curing. Kelly and Tyson's method[11] was adopted for shear lag analysis, and Weibull distribution was applied.

The suspension quality for coating was conducted by zeta potential measurements and dynamic light scattering (DLS) at room temperature. X-ray photoelectron spectroscopy (XPS) was used to reveal the coating effect on CF surface features. Nano-IR was used to investigate the chemistry at the interface of nanomaterial incorporated CFRP composites. Furthermore, both IFSS and interlaminar shear strength (ILSS) revealed the nanomaterial effect on macroscopic properties of CFRPs.

RESULTS AND DISCUSSION

Suspension Quality by Zeta-Potential Measurements

The dispersion quality of the suspension is a critical parameter because the nanomaterials are transferred to CFs by using the suspensions. Hence, the homogeneously dispersed suspension is an indication for homogeneously distributed nanomaterials on CF surface. Zeta potential measurement is a good method to understand the suspension quality as the high values indicate well-dispersed nanomaterials in solution. Hence, the dispersion quality of CNC, CNC-CNT, and CNC-GnP suspensions were investigated by zeta potential measurements as presented in **Fig.1**. CNCs form a well-dispersed aqueous suspension, which was seen in the literature [3, 7], and its zeta potential value was 53 mV. The addition of GnP in CNC led to reducing the zeta potential value to 45 mV at CNC-GnP 2:1. Once the ratio was changed to CNC-GnP 6:1 the value reacted at 58 mV. This indicates that CNC-GnP 6:1 ratio was sufficient to obtain a homogeneous suspension. Furthermore, the zeta potential of CNC-CNT increases from 0 (4:1) to 52 mV (10:1). These outcomes suggested the CNC-CNTs and CNC-GnPs were well dispersed in DI water.

The hydrodynamic diameter of the nanomaterials by DLS was also displayed in **Fig. 1**. The average hydrodynamic diameter of CNCs was 75 nm. In CNC-GnP suspensions, the diameter was 1338 nm for a 4:1 ratio and by further addition of CNCs, it remained almost the same with 1330 nm for 1:6. The formation of hybrid CNC-CNT increased the hydrodynamic diameter of CNCs to 275 nm. Interestingly, increasing the ratio of CNCs did not change hydrodynamic diameter significantly.

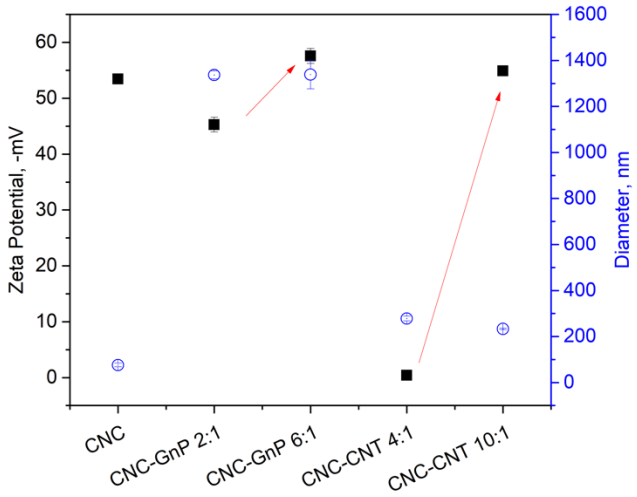

Figure **1**. Zeta-Potential and DLS of CNC, CNC-GnP, and CNC-CNT with different ratios. The red arrows indicate the rise in the zeta potential of CNC-GnP and CNC-CNT, respectively.

Surface Properties of Carbon Fibers

The presence of polar groups (O=C) on the CF surface is one important parameter to achieve a robust bonding between CF and epoxy because the epoxy reacts with the polar groups of the surface. As the CF surface has insufficient polar groups, the surface is required to be modified to enhance the interfacial properties. **Fig. 2** presented the XPS survey spectra of neat CF, CNC, CNC-CNT, and CNC-GnP added CF surfaces, where the major peaks were C1s (at 284.4 eV) and O1s (at 532 eV). The O1s ratio of neat CF (31%) was remarkably increased up to 42 % with the addition of CNCs. As expected, the addition of CNT and GnP resulted in a decrease in O1s ratio (35 % for GnP and 36 % for GnP), 12 % and 16 % increase in O1s was reported due to the presence of CNCs. The XPS survey spectra suggested that the addition of nanomaterials increased the surface affinity for chemical reactions of CFs.

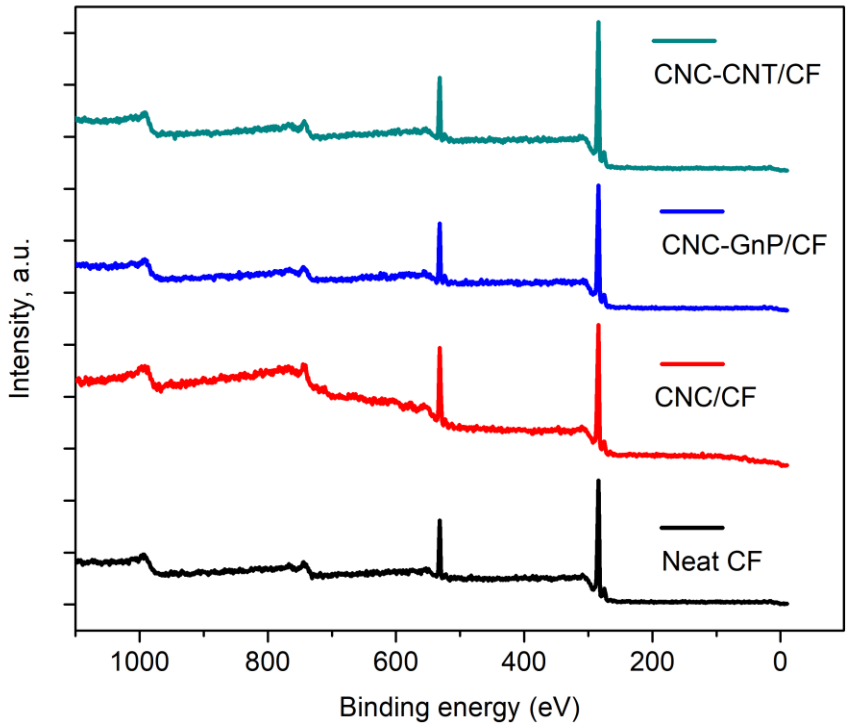

Figure 2**.** The XPS survey spectra of neat, CNC, CNC-CNT, and CNC-GnP coated CF. The peaks at 284.4 eV and 532 eV correspond to C1s and O1s.

Interfacial Chemistry of Nanomaterial Incorporated CFRP by Nano-IR Measurements

The Nano-IR reveals the nanoscale IR spectra of the materials. In this paper, the Nano-IR was used to understand the chemical effect of nanomaterials at the interface. **Fig. 3** showed a polished Nano-IR sample. The encircled area demonstrated the Nano-IR measurements. From the epoxy region to the CF region, 5 points (2 µm) between the epoxy region and CF region were investigated for each sample to reveal the chemistry change at the interface. The C-O peak at 1040 cm^{-1} was primarily investigated to understand the interfacial interactions between CF and epoxy. The neat CFRP (**Fig. 3 b**) displayed a slight change in the C-O peak from the epoxy to the CF region. The CNC addition (**Fig. 3 c**) increased the C-O peak at the interface (IF) 1, IF2, IF 3, and the CF region. Similarly, CNC-GnP coated CF/epoxy in **Fig. 3 d** showed a slight rise C-O peak at the interface (IF1 IF2, IF 3). In the case of CNC-CNT, the peaks showed a significant increase at the interface regions. The broad C-O at the epoxy region became sharper and stronger at IF1, IF2, and IF3, which denotes the increased interaction of CF with epoxy with the help of CNC-CNT. In conjunction with the XPS results, the Nano-IR outcomes showed that corresponding C-O peak increase occurred in the CNC, CNC-GnP, and CNC-CNT added CF/epoxy. This might be because of the increase in polar groups with the addition of nanomaterials at the interface as discussed in **Fig. 2**. The analysis of the Nano-IR spectra at discrete points away from the fiber demonstrates that the

nanomaterials deposited directly on the CF surface migrate away to activate the interface region.

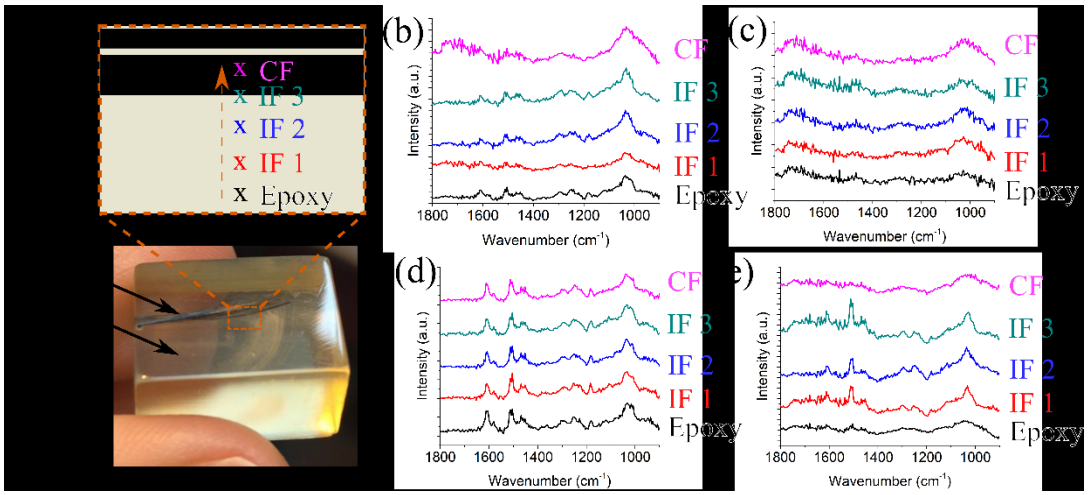

Figure 3. (a) The Nano-IR CFRP sample encircled the CF. The Nano-IR spectra of (b) neat, (c) CNC, (d) CNC-GnP, (e) CNC-CNT incorporated CFRP in the range of 1800-900 cm^{-1}, respectively.

The Interfacial and Interlaminar Properties of Nanomaterial Incorporated CFRP Composites

The effect of CNC, CNC-GnP, and CNC-CNT addition in CFRP composites was revealed by IFSS and ILSS as displayed in **Table I**. The IFSS of the neat composite was 36 MPa. With the addition of CNC, the IFSS value raised to 45 MPa. Further enhancements in IFSS were achieved in CNC-GnP (6:1) and CNC-CNT (10:1) to 55 MPa and 64 MPa. As the macroscopic properties of composites are related to interfacial performance, an ILSS test was conducted to understand the coating effect on interlaminar properties of the composites. The ILSS of CNC-GnP 6:1 and CNC-CNT 10:1 enhanced to 45 MPa and 52 MPa, respectively, compared to neat composite (35 MPa) as shown in **Fig. 3**. The addition of nanomaterials at the interface affects the interfacial chemistry. Although both IFSS and ILSS results showed enhancements compared to neat CFRP composite in **Table I**, a significant improvement was noted in CNC-CNT added CFRP.

Table I. IFSS AND ILSS RESULTS OF NEAT, CNC, CNC-GNP, AND CNC-CNT INCORPORATED CFRP.

CFRP	IFSS (MPa)	ILSS (MPa)
Neat	36.2±3	35.5±0.6
CNC	45.4±4	33.9±1.6
CNC-GnP 6:1	55.3±2.7	45.0±0.9
CNC-CNT 10:1	64.1±2.8	52.1±1.3

CONCLUSION

In this study, we focused on the interfacial properties of CF/epoxy composites enhanced by CNC, CNC-CNT, and CNC-GnP. The zeta-potential and DLS results showed that CNC, CNC-CNT, and CNC-GnP formed homogeneous suspension in DI water. Furthermore, the addition of nanomaterials increased the polar groups on the CF surface as revealed by XPS survey spectra. Also, the Nano-IR showed that the chemistry from epoxy to CF surface was altered by the addition of nanomaterials Moreover, the maximum IFSS enhancements were noted in CNC-GnP 6:1 and CNC-CNT 10:1 incorporated CFRPs, which were 55 MPa and 64 MPa, respectively. Also, in comparison to neat CFRP (35 MPa), the ILSS values of CNC-GnP 6:1 and CNC-CNT 10:1 added CFRPs were improved 45 MPa and 52 MPa, respectively due to the modified interfacial chemistry by the incorporation of the nanomaterials. The overall results showed that interfacial and interlaminar properties of CFRP composites can be engineered by the addition of nanomaterials at the interface.

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