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Tensile Characterization of Injection-Molded Fuzzy Glass Fiber/Nylon Composite Material

by Michael A Minnicino and Christopher Goodeaux

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14. ABSTRACT
A carbon nanostructure (CNS) composed of highly branched and entangled carbon nanotubes (CNTs) is grown on a fiber surface and used as a carbon-enhanced reinforcement (CER) in a nylon matrix. A majority of the masterbatch CER material research is focused on electromagnetic shielding applications; however, the CER system, with the CNT network fixed to the host fiber, provides a novel approach of minimizing CNT agglomeration. Tensile specimens are injection molded with varying weight percentages of CER to evaluate effect of the reinforcement on the mechanical properties. Tension testing showed that the introduction of CNS increased the modulus and yield strength of the nanocomposite but reduced its fracture toughness.

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fuzzy fiber, composite, tension test, nanocomposites, short-fiber composites, elastic properties, injection molding

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1. Introduction

Since the discovery of carbon nanotubes (CNTs) by Iijima,[1] considerable research aimed at understanding and processing CNTs has been undertaken due to their outstanding physical properties. CNT properties make them an attractive candidate as a reinforcement in polymer matrix composites. Inclusion of CNTs into the polymer matrix generally increases the composite material stiffness and strength but typically decreases the fracture toughness and strain to failure.[2–8] However, the structural improvement in polymer composites gained through the addition of CNTs is below the expected value as predicted by either the rule of mixtures or the Halpin-Tsai model.[5] The discrepancy between the predictions and experimental results is due to non-uniform dispersion of the CNTs in the polymer matrix. Consequently, a key requirement for realizing improved structural properties is that the CNT reinforcement be uniformly dispersed. Due to their small volumes compared to their large surface areas, CNTs are strongly affected by intermolecular forces that result in the formation of agglomerations of CNTs and thereby make uniform distribution difficult. The formation of aggregates significantly reduces the benefit of adding CNTs to the polymer and makes dispersion difficult.[5, 8–9]

A relatively new CNT system referred to as a carbon nanostructure (CNS) is fabricated by growing multiwalled CNTs on the surface of a fiber to create a network or CNT "forest".[10–12] The fiber has a "fuzzy" appearance due to the CNT forest, and the combination is referred to as a carbon-enhanced reinforcement (CER). Further, the CNT forest of multiple "host" fibers becomes entangled as multiple fibers become proximally close as notionally shown in Fig. 1. These CER systems are subsequently enveloped in a polymer matrix to form a masterbatch CER pellet. In this embodiment, the CNTs are grown from, and therefore fixed to, the host fiber and as a result, CNT agglomeration is largely avoided. The CER material is largely being studied for use in multifunctional applications such as structural-electromagnetic shielding but increases in mechanical properties have been also noted.[12] The CER material used in electromagnetic shielding applications are reported to contain nanotubes in excess of 8 weight percent (wt%).[12] Mechanical testing revealed that polycarbonate (PC) with approximately 4.4 wt% CNS (i.e., CNT network using 30 wt% PC-CER pellet loading) resulted in a tensile modulus increase of approximately 400%, a tensile strength increase of approximately 50%, and the tensile strain to failure reduction of approximately 300% compared to neat PC.[12]

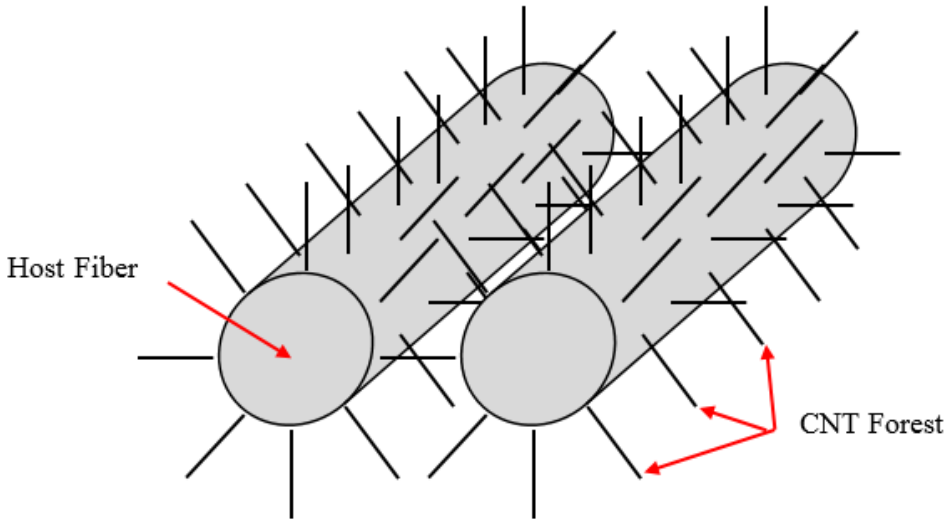


Fig. 1 Fuzzy fiber reinforcement consisting of entangled CNT forest grown from multiple fiber surfaces

In this work, we mechanically evaluate the structural benefit of adding nylon-CER to nylon (PA-6,6) using tension test specimens fabricated by injection molding. The concentration of the CER is varied to determine the relationship between CER wt% and enhanced mechanical properties. The CER/nylon dispersion is characterized using scanning electron microscopy (SEM), and the tensile properties of the prepared composite materials are evaluated.

2. Experimental

2.1 Materials

Both the nylon (PA-6,6) and CER thermoplastic pellet material was supplied by Owens Corning (USA). Two pellets of CER and nylon are shown in Fig. 2. According to the manufacturer, the CER pellet is 59.7 wt% nylon and 40.3 wt% CER, the latter of which is approximately 10.5 wt% CNS and approximately 29.8 wt% glass fiber assuming a ratio of approximately 0.26 wt% CNS per wt% CER for the specified CER pellet loading. The nylon of a few of the CER pellets is dissolved in a gently shaken bath of hexa-fluoro isopropanol to reveal the glass fibers and CNTs; a slide of the dissolved mixture is shown in Fig. 3. From this dissolved mixture it is determined that the glass fiber has an approximate diameter of 10 µm and ranges in length from 0.2 to 0.5 mm. It is also shown in Fig. 3 that the CNT network did not remain attached to the glass fiber surface as we had theorized, but instead had detached from the fiber surface and agglomerated upon dissolving the CER nylon matrix.

Fig. 2 As-received CER pellets (left) and neat nylon pellets (right)

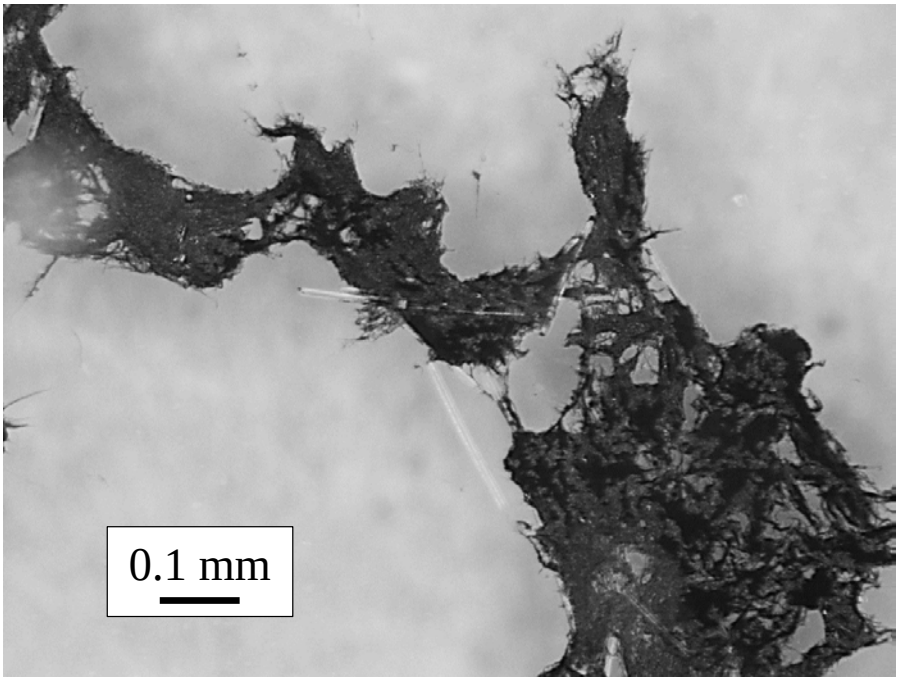


Fig. 3 Optical image of exposed short glass fibers and CNT network resulting from dissolving nylon in acid bath

To view the original orientation of the glass fibers in the CER pellet, the CER pellet is cooled in liquid nitrogen and then carefully fractured by mechanical force. The fracture surface is examined by SEM to evaluate the dispersion and orientation of the glass fibers. The SEM image of the fracture surface shows that the glass fibers are fairly well dispersed and predominantly aligned with the length of the CER pellet as shown in Fig. 4. The presence of numerous exposed glass fiber ends in

Fig. 4 indicates that these fibers were pulled out from the nylon matrix; consequently, it can be inferred that the glass fibers (and possibly the CNTs) do no not adhere well to the nylon matrix. Lau and Hui[13] identify poor adhesion between the matrix and CNT as the critical issue for using nanotubes in advanced structural composites where interfacial bonding of the matrix and CNT is required for maximum strength composites materials.

Fig. 4 SEM image of CER pellet fracture surface

2.2 Fabrication

Before processing the material, the nylon and CER pellet materials were placed in a vacuum oven for 8 h to remove any water absorbed by the pellets. Once dried, all material was kept in a desiccator throughout the fabrication process. Five composite mixtures were chosen, starting with pure nylon and increasing weight percentage of CER pellet material in 25 wt% increments (i.e., 0, 25, 50, 75, and 100 wt% CER pellet). Note that these mixtures correspond to approximate CER concentrations of 0.0, 10.1, 20.2, 30.2, and 40.3 wt%, respectively. The pellets are heated and compounded in a twin-screw microcompounder where the mixture is recirculated at 100 rpm for 3 min. To produce a sufficiently melted mixture with low viscosity for molding purposes, it was necessary to increase the recirculating temperature with increasing concentration of CER as indicated by the following Table.

Table Compounder conditions of CER/nylon composite mix compositions

Mix composition		Mix temperature (°C)
CER (wt%)	Nylon (wt%)	
0.0	100	230
10.1	89.9	235
20.2	79.8	240
30.2	69.8	260
40.3	59.7	275

Once mixed, the composite material was fed into the chamber of a microinjection molder. All material compositions, excluding the 40.3 wt% CER material, were processed with the chamber and mold heated to 150 and 70 °C, respectively, and used a 10 s at 8 bar (0.8 MPa) injection mold process to fabricate the test specimens. For the 40.3 wt% CER material, the chamber and mold were heated to 275 and 150 °C, respectively, and used a 10 s at 12 bar (1.2 MPa) injection molding process due to the higher viscosity of the composite material.

2.3 Characterization

The tensile mechanical properties for the 5 compositions are assessed using the ASTM D-638[14] test standard. Specimens were injection molded to the ASTM D-638[14] Type V geometry as shown in Fig. 5 and subsequently painted with a speckle-pattern for full-field strain measurement using digital image correlation (DIC).[15] Tensile test specimens were secured with pneumatic grips and pulled at a rate of 5 mm/min. The mechanical values reported are the average of 10 samples.

Fig. 5 Injection-molded tensile specimens with DIC speckle pattern applied to gage section (0 wt% CER on left and 40.3 wt% CER on right)

3. Results and Discussion

Typical engineering stress-strain curves for each of the compositions are shown in Fig. 6. The tensile testing results show that the axial strength and modulus generally increase with increasing CER content and that elongation decreases. We report the average tensile elastic modulus and standard deviation as the average slope of 10 engineering stress-strain curves near 0.5%–1.5% strain for each of the 5 CER compositions. The increase in average tensile modulus as a function of CER content is approximately linear as shown in Fig. 7. The tensile modulus of the 40.3 wt% CER composite is 520% greater than the 0 wt% CER composite (i.e., neat nylon) tensile modulus. The average yield strength is set using the 0.2% strain-offset method; the yield strength as a function of CER content is shown in Fig. 8. The yield strength increases nearly linearly with increasing CER content. The tensile yield strength of 40.3 wt% CER composite is 125% greater than the 0 wt% CER composite yield strength. Lastly, as indicated by the engineering stress-strain curves shown in Fig. 9, the fracture strain decreases significantly with the addition of CER. Generally, the drop in elongation to failure is significant between the 0 wt% CER and 10.1 wt% CER compositions as shown in Fig. 9 where the fracture strain for 0 wt% CER is over 100% and the fracture strain for 10.1 wt% CER is approximately 3%. However, the reduction in elongation at failure is less sensitive

to further increases in CER content in the compositional range of 10.1–40.3 wt% CER as the fracture strain is shown in Fig. 9 to decrease from approximately 3% for the 10.1 wt% CER to approximately 1.4% for the 40.3 wt% CER.

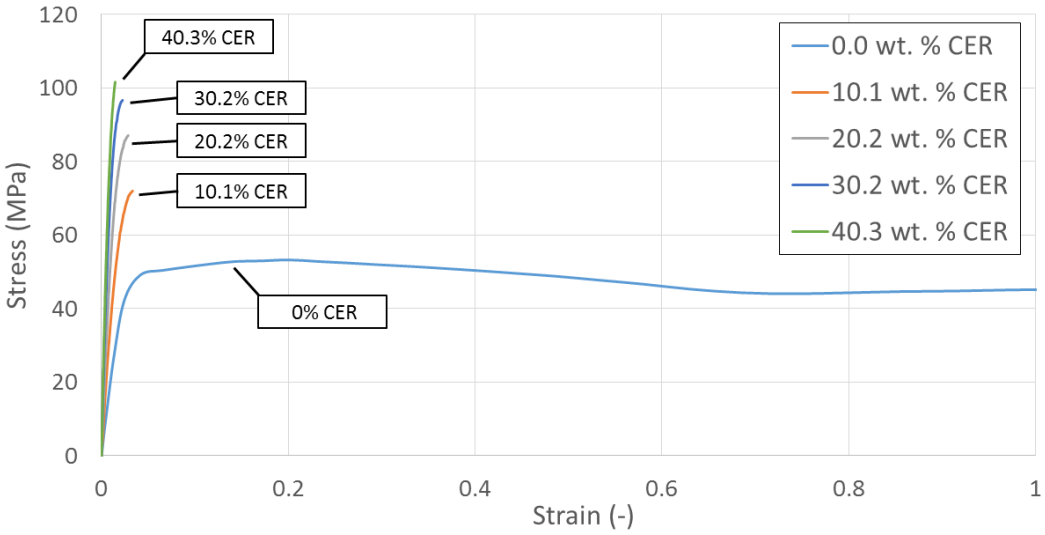


Fig. 6 Tensile stress-strain relation for the 5 compositions of CER/nylon

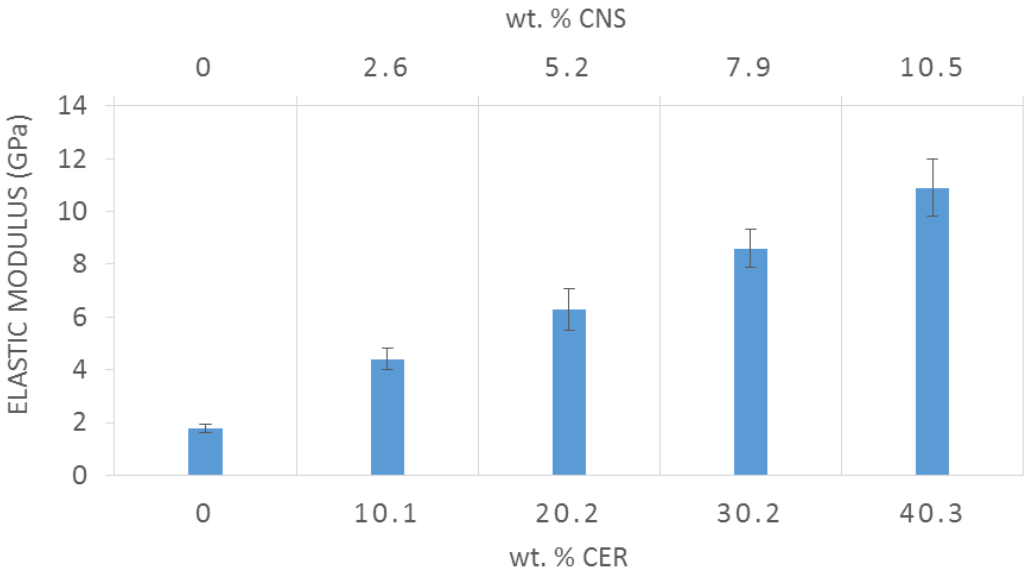


Fig. 7 Average and standard deviation in elastic modulus as a function of composition

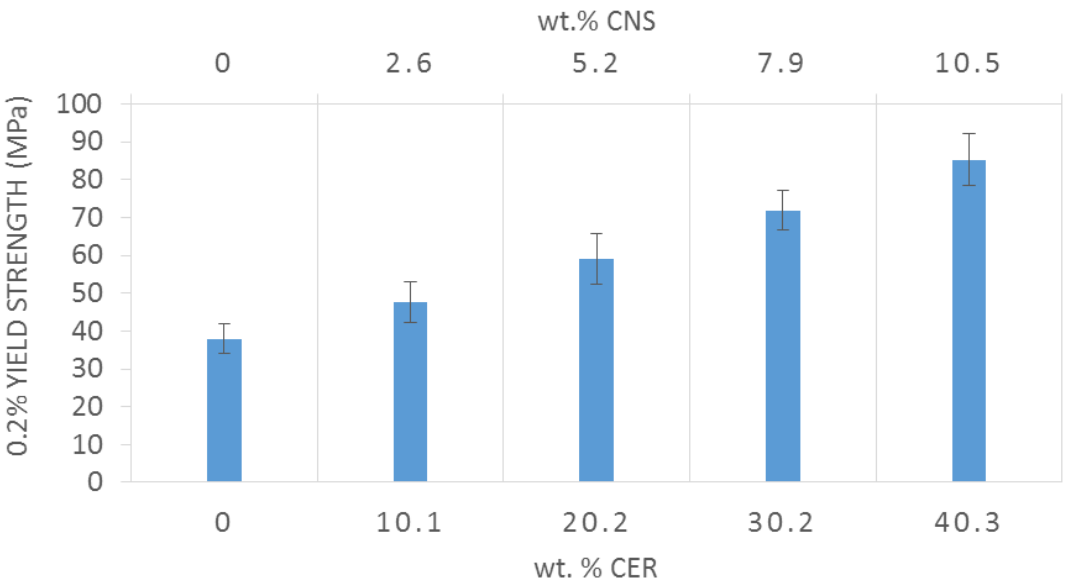


Fig. 8 Average and standard deviation in yield strength as a function of CER composition

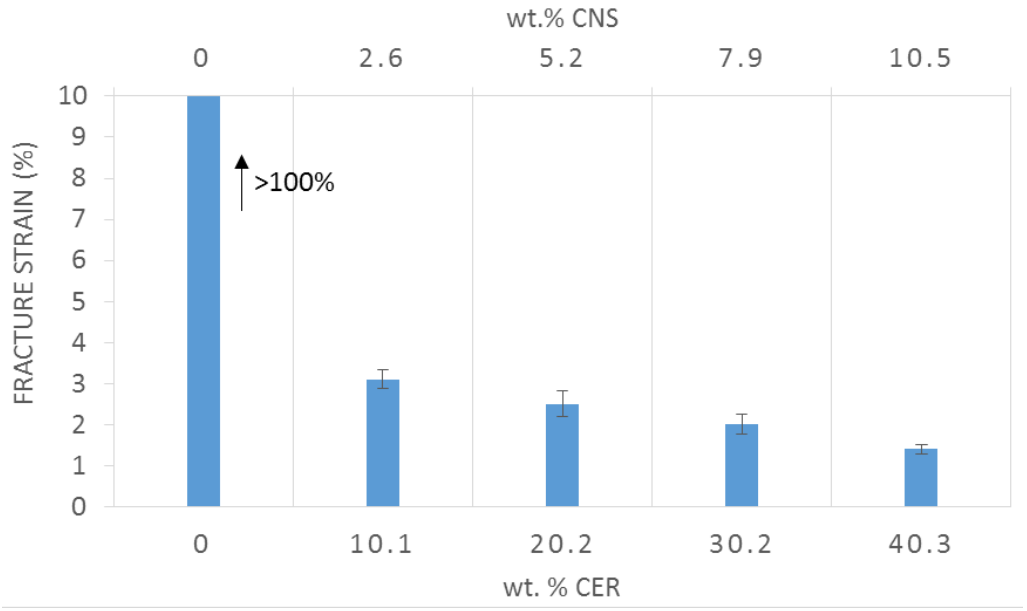
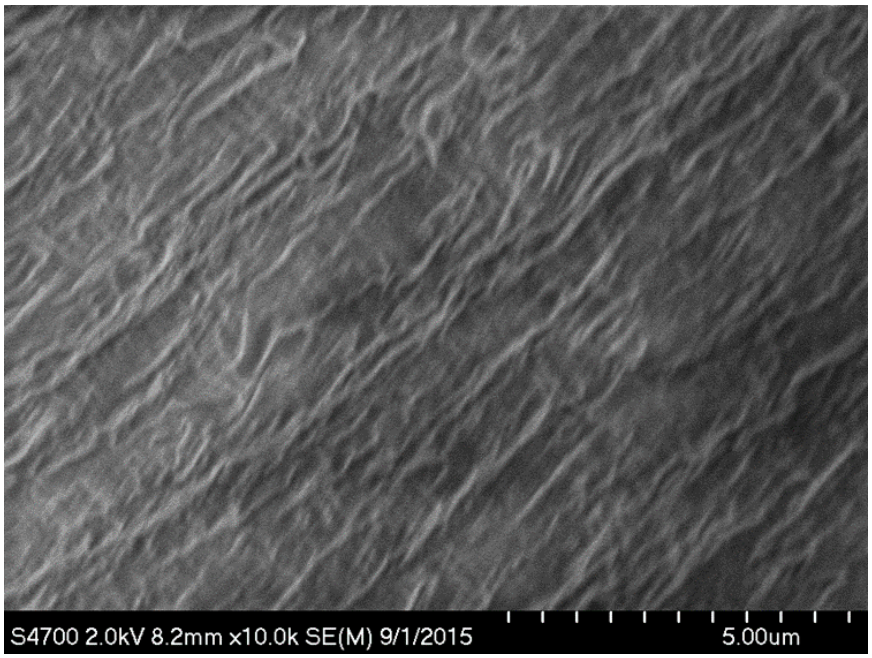
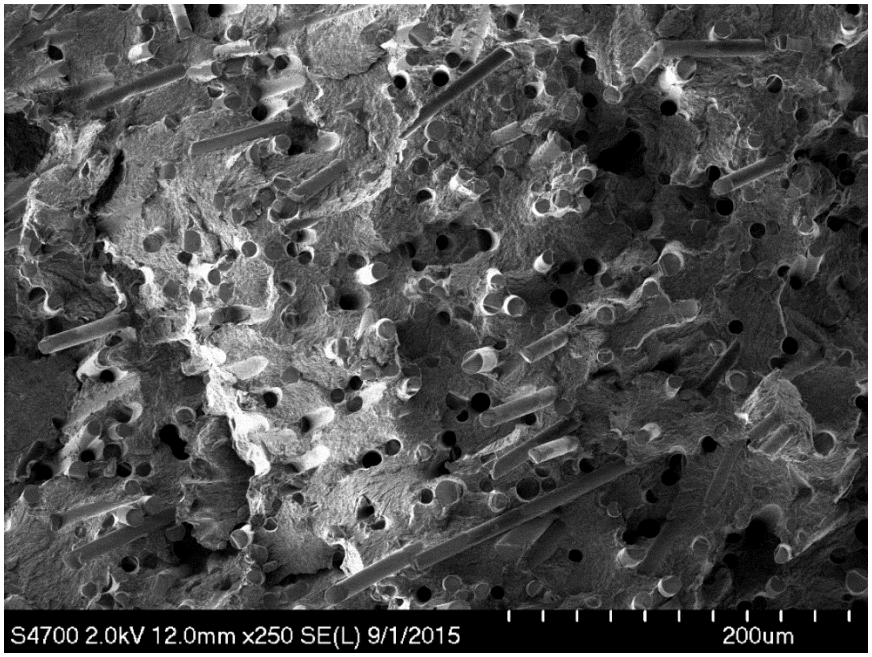


Fig. 9 Average strain and standard deviation in failure strain as a function of composition

SEM images of the tensile fracture surfaces belonging to the 40.3 wt% CER and a neat nylon test specimens are shown in Fig. 10. The fracture surface of the 40.3 wt% CER specimen is much rougher than the neat nylon specimen is and is an indication of embrittlement of the material with increasing amounts of the glass fiber and CNS. Fig. 10b shows that the glass fibers are well aligned with the test specimen gauge axis and are also well dispersed due to the effectively one-dimensional flow of the injection modeling process. Additionally, glass fiber pullout is observed in the CER specimens as shown in Fig. 10b so it may be concluded that the adhesion is not significant between the nylon matrix and glass fiber. Yet, the CNS network remains embedded in the nylon matrix and is pulled from the glass fiber surface during the tension test as shown in the magnified view of the glass fiber and nylon matrix in Fig. 11. This is evidence that the effective bond strength (due to adhesion, thermal expansion coefficient mismatch, entanglement, etc.) between the nylon matrix and CNS is greater than the bond strength of the glass fiber and CNS attachment site.



(a)



(b)

Fig. 10 SEM images of test specimen fracture surface: a) neat nylon and b) 100% CER

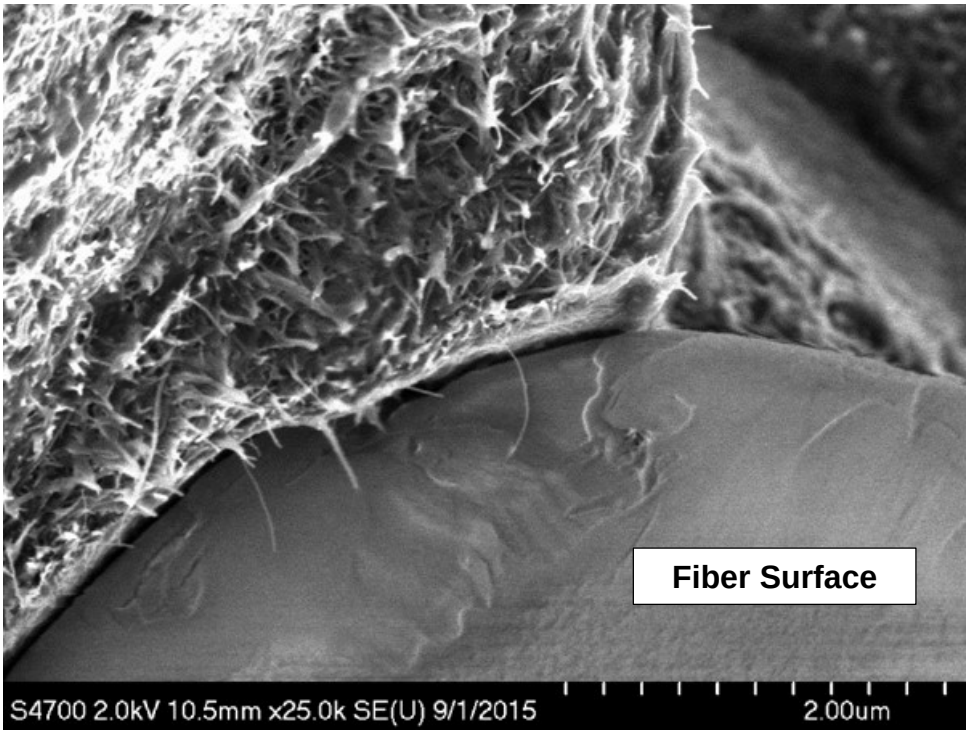


Fig. 11 Close-up SEM image of glass fiber–nylon matrix interface in 100 wt% CER test specimen

4. Conclusions

The primary objective of this research was to determine the increased mechanical properties of nylon resin when blended with a CER. An obvious follow-on to this work is to evaluate the same compositions without CNS (i.e., short glass-fiber-reinforced nylon) and compare the results to these findings. This work shows that the tensile elastic modulus and yield strength of materials with 40.3 wt% CER content were on average 520% and 125% higher, respectively, than those of neat PA-6,6 nylon. Additionally, the increase in tensile elastic modulus and yield strength increases nearly linearly with CER content. This increased elastic modulus and yield strength are accompanied by a reduction in failure strain, which drops by over 100% with the introduction of 10.1 wt% of CER material. The reduction in failure strain is nonlinear with a large reduction in failure strain occurring between the 0 wt% CER and the 10.1 wt% CER compositions. Also, the bonding of the CNS to the glass fiber appears to be low and may prevent the achievement of superior composite mechanical properties.

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List of Symbols, Abbreviations, and Acronyms

CER	carbon-enhanced reinforcement
CNS	carbon nanostructure
CNT	carbon nanotube
DIC	digital image correlation
PC	polycarbonate
SEM	scanning electron microscopy
wt%	weight percent

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