Ultrahigh Carbon Nanotube Volume Fraction Effects on Micromechanical Quasi-Static & Dynamic Properties of Poly(Urethane-Urea) Filled Nanocomposites†

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Abstract:

Poly(urethane-urea) (PUU) has been infused into ultrahigh volume fraction carbon nanotube (CNT) forests using a heat-curable polymer formula. Polymer nanocomposites with carbon nanotube volume-fractions of 1, 5, 10, 20, and 30% were fabricated by overcoming densification and infusion obstacles. These polymer nanocomposites were nanoindented quasi-statically and dynamically to discern process-structure-(mechanical) property relations of polymerizing PUU in such densely-packed CNT forests. A 100× increase in indentation modulus has been observed, which is attributed not only to CNT reinforcement of the matrix, but also to molecular interactions in the matrix itself. Quasi-static elastic moduli ranging from 10MPa – 4.5GPa have been recorded. Storage modulus for all materials is found to track well at loadings of 200Hz, with little effect observed from increasing CNT volume fraction.

Keywords: carbon nanotubes, polymer nanocomposites, polyurethane urea, self-assembly

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1. Introduction

Hierarchical composites comprising components of multiple length-scales are a promising area of research for the aerospace industry as they offer unparalleled control over material architecture. One method for fabricating such materials is to grow a conformal coating of carbon nanotubes (CNTs) off of the surfaces of advanced woven fabrics such as carbon fiber, aluminum oxide, etc. [1], [2]. An additional level of control can be offered by engineering the interface between the chosen matrix material and the CNTs. This interphase region has been shown to be affected by CNT proximity [3]–[9]. Furthermore, packing and confinement effects which arise from even moderate CNT volume fractions (V_f's) give rise to additional nanostructure [10]. To investigate the phenomena governing this interphase, a model system of vertically aligned CNT forests has been used, which allows for excellent control of CNT V_f and dispersion, while eliminating any potentially confounding effects of more complex hierarchical composites.

The matrix material used here is a poly(urethane-urea) (PUU) which has been investigated previously [11]–[16], and is particularly attractive for its quasi-static and dynamic mechanical tunability. Moderate interactions have been observed previously with this material in the presence of aligned CNTs [17], [18], and so a deeper dive into understanding the nature

of this interaction and the mechanical implications is necessary. Quasi-static and dynamic nanoindentation results will be presented here.

2. Methods

CNT forests were grown at 1% volume fraction on silicon wafers using atmospheric pressure chemical vapor deposition. These CNT forests were biaxially densified down to the requisite dimensions for producing the desired CNT V_f. The densified forests were placed into silicone molds to confine the samples and prevent expansion during polymer infusion. Poly(urethane-urea) (PUU) prepolymer was synthesized using a blocked-isocyanate, diamine, and polyol identical to the method outlined previously [18]. The mixed and degassed prepolymer was poured onto the densified CNT forests and heated at atmospheric pressure to 130°C for 24 hours per the previously prescribed cure cycle [18]. Two stoichiometric variations of PUU were used in the present study: PUU211 and PUU541, where the naming denotes HDMI:DETA:PTMO ratios.

PUU nanocomposites were made with 1, 5, 10, 20, and 30% CNT V_f. Once samples were cured, they were removed from the molds and ultra-cryotomed to reveal smooth surfaces for the purpose of nanoindentation and atomic force microscopy. Sample were prepared so that both the logitudinal (L) and transverse (T) CNT orientations could be tested independently in hopes of elucidating the anisotropy inherent to these ordered structures.

Samples were imaged using a Cypher Scanning Probe Microscope. The silicon tip had a natural frequency of 70kHz and stiffness of 2Nm, and was used to perform alternating contact mode scans at a rate of 0.6Hz.

Nanoindentation tests were performed using a Hysitron TI950 Triboindenter with a Berkovich tip. Quasi-static load functions with a 5 sec. ramp to 200μN, 5 sec. hold, and 5 sec. ramp down were implemented. A 2×2 array of qausi-static indentations was tested resulting in 4 tests per sample. Dynamic load functions with similar times and loads were used, with the addition of a dynamic amplitude of 3μN at frequencies ranging from 1-200Hz. A 1×3 array of dynamic indentations was tested resulting in 3 tests per sample.

3. Results & Discussion

The polymer nanocomposites were found to be highly anisotropic. Indentation modulus and storage modulus data for PUU211 as a function of CNT V_f is found in Figure 1. Similar plots for the PUU541 materials can be found in Figure 2. The longitudinally-oriented CNTs increased the indentation modulus from 60MPa in the neat PUU211 to up to 1900MPa in the 30% CNT V_f PUU211 PNC. The same material with transversely-oriented CNTs exhibited a modulus of only 700MPa. The neat PUU541 was shown to have a modulus of ~1300MPa, while PUU541 with 30% CNT V_f had a modulus of ~4300MPa and 2200MPa in the longitudinal and transverse orientations respectively. All materials were found to behave rate-independently, though with dynamic storage moduli following a similar trend to indentation moduli.
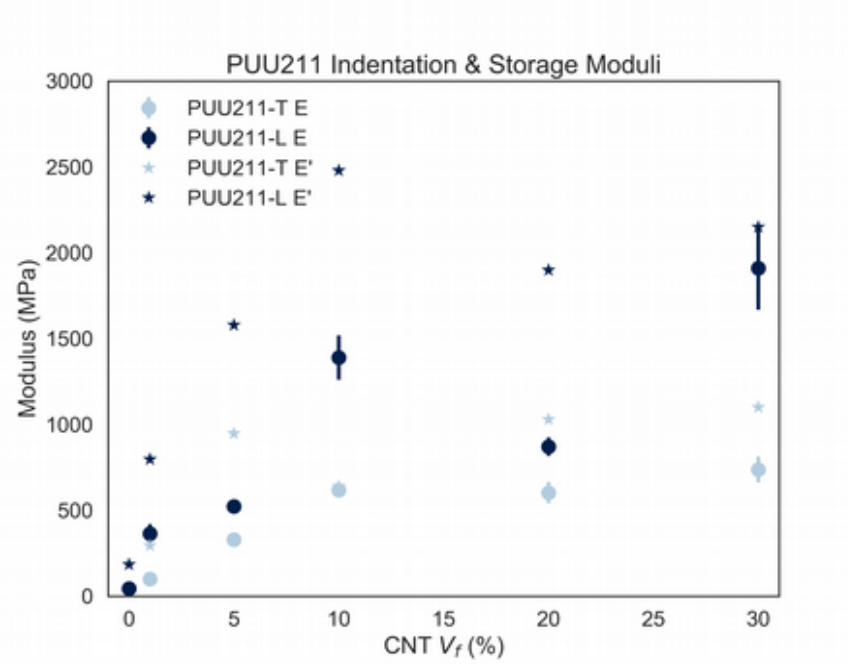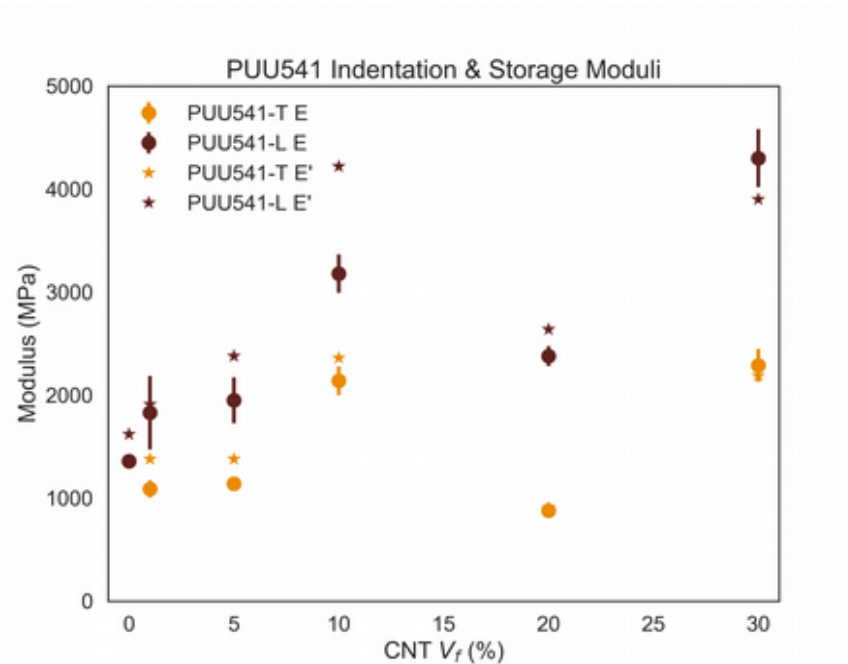
Figure 1: Comparison of quasi-static indentation modulus with average storage modulus (at 1Hz) for each PUU211 material. "T" represents "transverse" tests and "L" represents "longitudinal" tests. "E" is used to designate "indentation modulus," while "E'" is used to designate "storage modulus."

Figure 2: Comparison of quasi-static indentation modulus with average storage modulus (at 1Hz) for each PUU541 material. "T" represents "transverse" tests and "L" represents "longitudinal" tests. "E" is used to designate "indentation modulus," while "E'" is used to designate "storage modulus."

In the case of each polymer, the 10% V_f displayed a local maximum, while the 20% V_f CNTs exhibited a reduction in modulus. The AFM images of 10% CNT V_f PUU541 PNC showed a highly-ordered arrangement of nanophases surrounding the CNTs, while 20% CNT V_f PUU541 PNC was much more amorphous. Examples of these may be found in Figure 3. The ordering found in the 10% CNT V_f PUU541 PNC is thought to be a result of some optimized packing density at this CNT V_f. This appears to be a point which balances the mobility afforded by low CNT V_f and the PUU hard segment ordering initiated by higher density CNT forests. At and above 20% V_f CNTs, the PUU is unable to order itself due to the restriction of such densely-packed CNTs. Though poor ordering and hydrogen-bonding should proliferate at the 30% CNT V_f, the CNTs are so densely packed that their mechanical properties dominate material behavior in these materials.
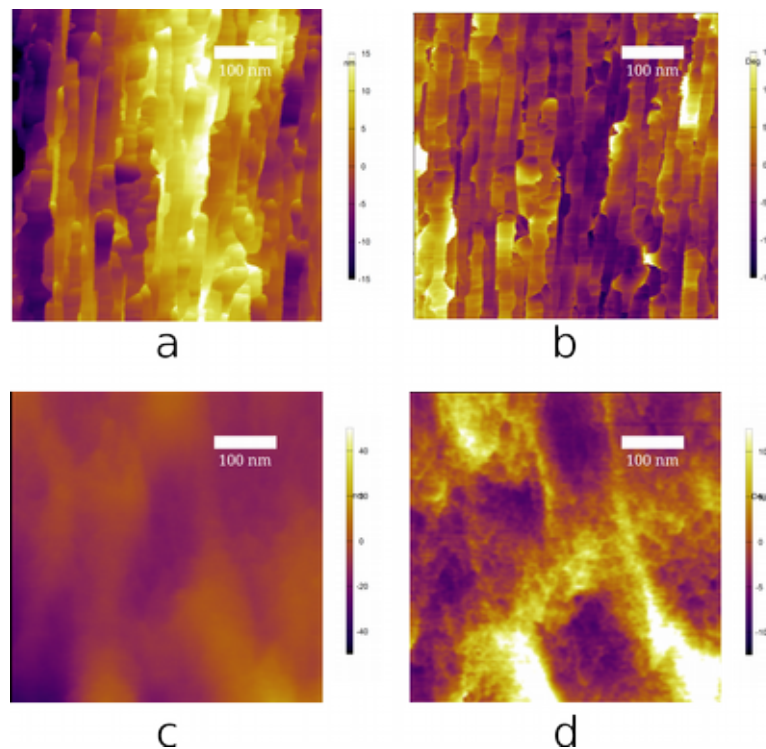

Figure 3: Characteristic AFM: (a) height and (b) phase maps for transversely-oriented PUU541 with 10% CNTs. (c) height and (d) phase maps for longitudinally-oriented PUU541 with 20% CNTs.

4. Conclusions

The CNTs were found to have a profound impact on the microscale mechanical properties of the PUU polymer nanocomposites, with significant anisotropy. An unexpected trend was observed with increasing CNT V_f, which is expected to arise from different polymerization mechanisms governing each regime, giving rise to varied mechanical properties. Mechanical properties below 10% V_f are found to be similar to one another, suggesting that the mechanical properties of these materials is largely matrix-dominated. Around 10% V_f the materials stiffen significantly, which coincides with packed nanophases seen in AFM. This indicates that some ideal packing has occurred for the ordered and oriented hard-segments. Poor polymer chain mobility is thought to cause the reduced stiffness at 20%, and CNT-packing is thought to dominate at 30% V_f.

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Author Contributions

J.G., D.C., and B.W. conceived and designed the experiments. J.G., D.L., and B.W. conceived of and performed fabrication methods. J.G., D.L., and D.C. performed nanoindentation experiments. D.C. performed AFM experiments. All authors contributed to interpreting data and relating findings to a broader body of work. J.G. wrote the paper with input from B.W.

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