

CNT-INITIATED PATTERNING OF POLY(URETHANE-UREA) IN ULTRAHIGH DENSITY FORESTS

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Abstract

The present work seeks to understand how increasing CNT volume fraction affects the molecular and morphological behavior of PUU synthesized *in situ* in densely-packed aligned-CNT forests. To this end, CNT forests have been biaxially densified and wetted with a poly(urethane-urea) (PUU) matrix to form ultrahigh volume fraction (V_f) PUU polymer nanocomposites (PNCs), with CNT V_f 's of 1, 10, and 20%. DSC showed progressively greater kinetic restriction of the chains with greater CNT V_f . ATR revealed fewer instances of N-H and C-H stretching, indicative of reduced chain mobility during the polymerization process. AFM images reveal that 10% CNTs give rise to significant ordering of the PUU by the CNTs, though greater CNT V_f 's do not see this influence. This supports the conclusions from DSC and ATR that greater CNT volume fraction leads to reduced chain mobility and greater phase-mixing. The observed effects of CNT V_f on PUU matrix morphology suggests that CNTs can be used to control PUU phase size and capitalize on the mechanical properties which arise from such anisotropic morphology.

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 [1], [2]. One method for fabricating such materials is to grow a conformal coating of carbon nanotubes (CNTs) off of the surfaces of advanced woven microfibers such as carbon fiber, etc. [3]. This level of architectural complexity brings with it potentially confounding effects when endeavoring to study fundamental interactions between the matrix material and CNTs. One method of circumventing these

complications is to employ CNT forests (also termed vertically-aligned CNTs, CNT arrays, etc.), which can be directly infused with the matrix material of interest [4], [5].

Poly(urethane-urea) (PUU) is of particular interest due to its quasi-static and dynamic mechanical properties [6], [7], as well as the degree to which it can be tuned to suit the desired application [8], [9]. It has also been found that the modulation of these stoichiometries and soft-segment molecular weight can give rise to preferential microphase mixing [10].

Previous work has revealed that PUU polymerized *in situ* in 1% V_f CNT forests leads to unusual morphology, which is driven by CNT-matrix preferential patterning [11]. In order to dive deeper into the mechanisms governing this observed phenomenon, this work looks at PUU polymerized in CNT forests of greater CNT V_f .

2. Methods

2.1 Poly(Urethane-Urea) Polymer Nanocomposite Fabrication

PUU PNCs at high CNT V_f were produced by first growing CNT forests in a chemical vapor deposition furnace on a catalyst-coated silicon wafer according to previously-developed methods [4]. Once grown, the CNT forests were biaxially densified according to Wardle's method [12]. The densified forests were then enclosed in appropriately-sized silicone chambers, and then covered with a steel mesh. This confinement prevented buckling of the forests during matrix wetting. The PUU prepolymer with 5:4:1 ratios of HMDI:DETA:PTMO (PUU541) was mixed, degassed, and poured over the entrapped densified forests, and wetting occurred *via* capillary forces. The wetted CNT forests were cured at 130°C for 24 hours [13].

2.2 Molecular & Morphological Characterization

Differential scanning calorimetry was performed using a TA Instruments Discovery DSC. ATR was performed using a Thermo Scientific Nicolet iS50R FT-IR. Atomic force microscopy (AFM) was conducted using a Cypher Scanning Probe Microscope. A silicon tip with a natural frequency of 70kHz and stiffness of 2Nm was used to perform alternating contact mode scans at a scan rate of 0.6Hz.

3. Results & Discussion

Differential scanning calorimetry (DSC) PUU541 at all CNT V_f 's has been recorded in Figure 1, and reveals an exotherm at ~240°C, which increases in magnitude with increasing CNT V_f . Similar exotherms have previously been linked to irreversible chain rearrangement [14]. The fact that these exotherms are not present at low CNT V_f 's suggests that the PUU in these materials have already achieved a state of thermodynamic favorability, while PUU in greater CNT V_f PNCs require additional heat to permit such rearrangement. This trend can be explained by the increasing restriction of PUU chains with greater CNT V_f , intensifying kinetic entrapment in the as-cured state. In instances where this prevails, i.e. high CNT V_f 's, additional heat must be added to liberate the chains which have been frozen in a thermodynamically unfavorable arrangement.

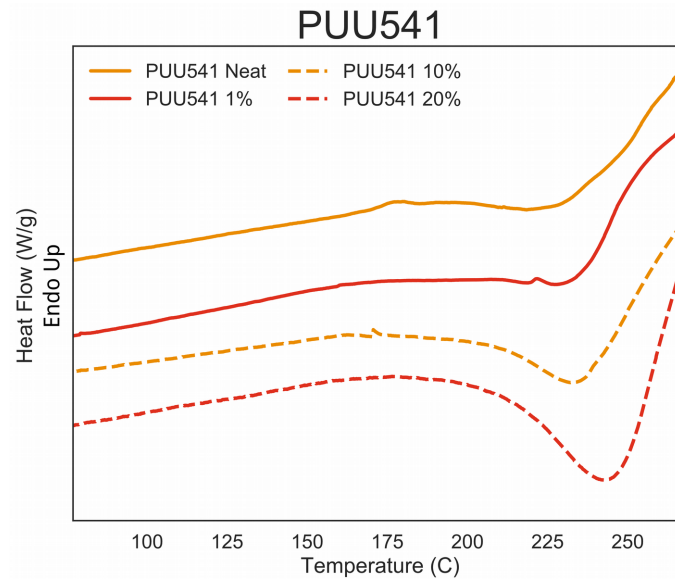


Figure 1: Characteristic DSC graphs for first heating phase of PUU541 materials at all V_f 's.

ATR data confirms the theory that dense CNT forests restrict chain mobility of as-cured PUU. The identification of each feature for ATR results was based on work by others [15]–[18]. Three regions of interest lie within $4000\text{--}1775\text{ cm}^{-1}$, which can be seen in Figure 2 for PUU541 materials. First notice that the peak associated with unreacted diisocyanate at 2324 cm^{-1} is extremely small for all materials, suggesting nominal residual unreacted diisocyanate. This suggests that the cure cycle is suitable to push cure to completion in all materials. The peak at 3315 cm^{-1} is associated with N-H stretch [15]. Sharper peaks in this region are indicative of phase-separation and the formation of N-H bonds. No definitive distinction can be made from the data whether these bonds are ordered, disordered, or free, as only one peak appears. From previous findings [14], however, this feature indicates ordered N-H bonds. Notice that greater CNT V_f leads to reduced prominence of this peak, suggesting fewer N-H bonds present; a sign of reduced mobility and inability of chains to form these preferential arrangements [19]. Finally, C-H stretching is associated with the band at $3000\text{--}2800\text{ cm}^{-1}$ [15]. A similar trend as was seen in the N-H region is reflected in the C-H region, attributed also to the reduced mobility from CNTs and from hard-segments.

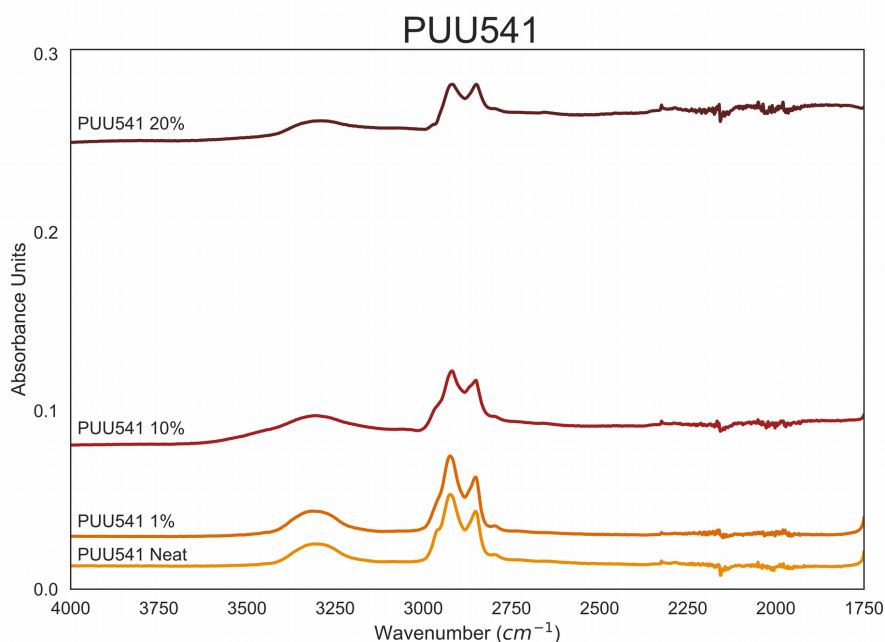


Figure 2: Characteristic ATR graphs from 4000-1750 cm^{-1} for PUU211 materials at all V_f 's.

AFM observations of PUU541-10 revealed significant morphological influence of the PUU matrix by the aligned CNTs, which can be found in Figure 3 (a) and (b). The CNTs have apparently induced overwhelming order in the matrix by producing these columns which surround each CNT. It appears as though this CNT packing has achieved some optimized combination of CNT spacing and chain mobility to permit the PUU organization in this way. Higher CNT V_f 's, however, show only amorphous matrix, which is presumed to arise from a matrix which is kinetically trapped by the tightly-packed CNTs. AFM images of PUU541-20 can be found in Figure 3 (c) and (d). This observation suggests that there is an ideal CNT V_f which is dense enough to drive significant morphological ordering, but low enough to permit the PUU chains from arranging freely. This amorphous appearance is consistent with small phase-size due to the prevention of free phase mixing by the presence of dense CNT forests.

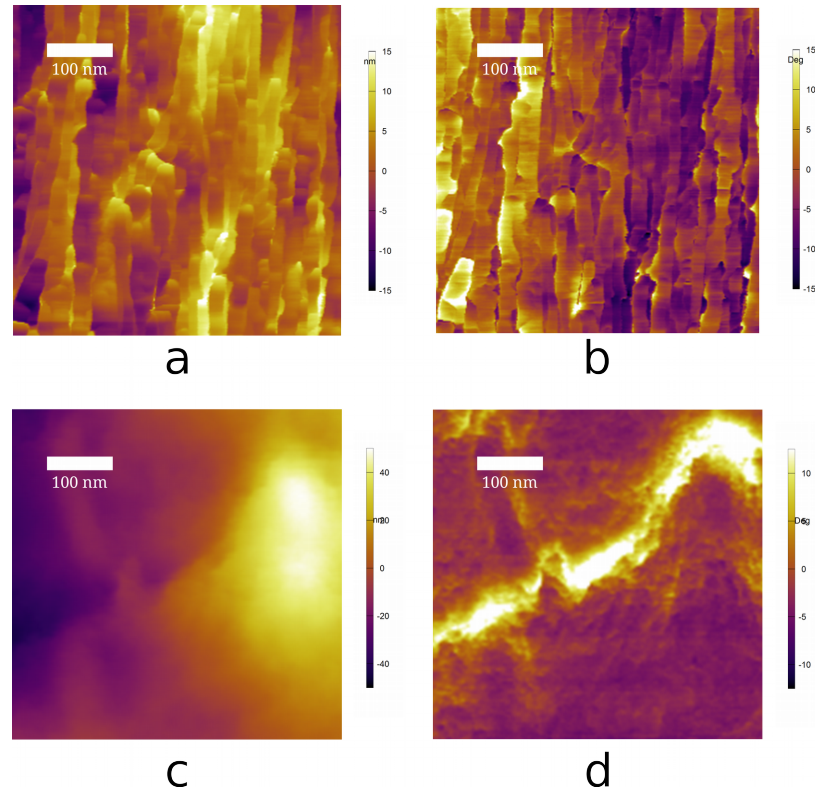


Figure 3: Characteristic AFM: (a) height and (b) phase maps for transversely-oriented PUU541 with 10% CNTs. (c) height and (d) phase maps for longitudinally-oriented PUU541 with 20% CNT. In each, the CNTs are oriented top-to-bottom.

Conclusions

Aligned-CNT forests at 1, 10, and 20% have been infused with poly(urethane-urea) (PUU). Increasing CNT density has been found to give rise to kinetic entrapment of the PUU chains during the cure cycle. This results in a greater degree of phase mixing, and thus, smaller phase size of the biphasic PUU. Additionally, 10% CNT V_f PUU PNCs exhibited significant ordering by arranging the phases into a columnar morphology. This effect was seen to a lesser extent in the 1% CNT PNCs, and not at all in PNCs with 20-30% CNTs. This is due to greater restriction of chain mobility at these CNT densities. By modulating the CNT V_f , PUU phase size and microphase morphology can both be controlled.

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