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An experimental and numerical study on the mechanical properties of carbon nanotube-latex thin films

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7 **Abstract**
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10 Multi-walled carbon nanotube (MWNT)-latex composite thin films of different MWNT
11 concentrations were fabricated by spraying. Post-fabrication thermal annealing was then
12 conducted on samples sets of different MWNT concentrations, and their microstructure,
13 morphology, and mechanical properties were compared to non-annealed sample sets. The
14 incorporation of up to 3 wt% MWNTs enhanced the mechanical properties of these
15 nanocomposites. In addition, annealing altered the microstructure and morphology of the
16 latex matrix, which enhanced the interactions between MWNTs and the polymer to
17 significantly increasing their ultimate failure strain and tensile strength. Furthermore, the
18 reinforcing effects of MWNTs on the polymer matrix were investigated using numerical
19 simulations. Stress concentrations were found to initiate at MWNT ends, thus giving rise to
20 yielding fronts that tend to coalesce and propagate across the entire film. The enhancement
21 of the mechanical properties of MWNT-latex nanocomposites make them more suitable for
22 field application as multifunctional coatings or sensors.
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26 **Keywords:** annealing; carbon nanotube; mechanical property; nanocomposite; numerical
27 simulation
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31 **1. Introduction**
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34 Carbon nanotubes (CNT) have received significant attention and have been studied
35 extensively since the work by Iijima [1]. Early research has focused on characterizing
36 individual CNTs' intrinsic properties, which include their unique aspect ratios, low density,
37 mechanical [2-4], and electrical [5] properties. In addition, they have been shown to be
38 piezoresistive [6-8] and sensitive to thermal effects [9], among others, which make them
39 prime candidates for multifunctional materials. In fact, their unique properties have been
40 leveraged for developing various CNT-based sensing devices [8, 10]. However, the
41 application of individual CNTs can be challenging due to their small dimension, especially
42 when it comes to large-scale civil, aerospace, and marine structural applications.
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46 On the other hand, CNTs serve as ideal reinforcing materials for engineered composites due
47 to their unique mechanical properties [11-13]. After CNTs are incorporated within
48 materials such as polymer matrices, they can be more readily used as macro-scale
49 nanocomposites for large-scale applications. Examples include using vacuum filtration (for
50 buckypapers) [14], layer-by-layer (LbL) deposition [15], and electrospinning [16], to name
51 a few. Although these methods could successfully fabricate piezoresistive CNT-based thin
52 films, they suffer from limitations, including the use of complicated or time-consuming
53 fabrication procedures, low productivity, and size constraints. In contrast, spray-coating has
54 been investigated as a viable alternative, since it is simple, efficient, low cost, and uses
55 readily available raw materials (e.g., latex) [17, 18]. A previous study by Wang and Loh
56 [19] showed that spray-coated, post-fabrication, thermally annealed MWNT-latex thin
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5 films exhibited improved electromechanical properties; nominal electrical resistance drifts
6 were eliminated or mitigated, which make them more suitable for use as strain sensors for
7 structural health monitoring applications.
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10 The objective of this study was to characterize how nanotube concentrations and post-
11 fabrication thermal annealing affected the bulk mechanical properties of the
12 aforementioned spray-coated MWNT-latex thin films. Monotonic uniaxial tensile tests
13 were conducted so as to not only evaluate the mechanical properties of MWNT-latex
14 composites but to also characterize the effects of MWNT concentrations and annealing on
15 bulk film mechanical properties. The differences observed in mechanical parameters among
16 different sample sets were then correlated with their microstructures. In addition, numerical
17 simulations based on a spring model approach ([20, 21]) were conducted to study the
18 reinforcing and stiffening effects of MWNTs dispersed in a similar polymer matrix. Stress
19 distributions in the films were mapped, and the effect of MWNT distributions on the onset
20 of yielding effects and damage propagation was highlighted.
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26 2. Experimental Details

27 2.1 Materials

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29 The MWNTs used in this study were purchased from SouthWest NanoTechnologies, whose
30 outer diameter and length were 6-9 nm and 5 μm , respectively; their purity exceeded 95%.
31 Poly(sodium 4-styrenesulfonate) (PSS) ($M_w \approx 1\text{M}$) and N-methyl-2-pyrrolidinone (NMP)
32 were from Sigma-Aldrich. The latex solution was from Kynar Aquatec. Other disposable
33 laboratory supplies were from Fisher Scientific. All materials were used as acquired
34 without further purification.
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39 2.2 Thin film preparation

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41 MWNT-latex nanocomposite films were spray-fabricated using an airbrush, following the
42 procedure described in [19]. In short, the fabrication procedure involved two major steps.
43 First, to prepare the spray-able MWNT-latex inks, a mixture of MWNTs, 2 wt% PSS
44 aqueous solution, and trace amounts of NMP was subjected to ultrasonication. Then,
45 appropriate amounts of latex solution and 18 M Ω deionized water were mixed with the
46 sonicated solution. The amount of MWNTs were determined based on the fact that the final
47 sprayed films would possess concentrations of 1, 2, and 3 wt% MWNTs.
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52 Second, the MWNT-latex inks were manually sprayed onto 25 \times 75 mm² glass microscope
53 slides using a Paasche airbrush. The films were air dried in the fume hood for at least 3 h,
54 after which freestanding films were obtained by releasing them from the substrates. In
55 addition, 0 wt% thin films were also fabricated as a control set, following the same
56 procedure, except that no MWNTs were added to the PSS-NMP solution. It should be
57 mentioned that several sets of 1, 2, and 3 wt% annealed MWNT-latex thin films were also
58 prepared. For these sample sets, post-fabrication thermal annealing was conducted using a
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5 StableTemp Model 282A vacuum oven. These freestanding nanocomposite films were
6 subjected to a temperature of 80 °C for 12 h, followed by 150 °C for 3 h in vacuum.
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9 2.3 Thin film characterization

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11 The effects of MWNT concentrations and thermal annealing on the microstructure of the
12 MWNT-latex films were measured by X-ray diffraction (XRD, ScintagXRD). Atomic force
13 microscopy (AFM, Asylum MFP-3D AFM) was utilized for analyzing the films' surface
14 topography. MWNT dispersion, as well as changes in film morphology after annealing,
15 were investigated with scanning electron microscopy (SEM, Philips/FEI XL30 SFEG
16 SEM).
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20 The mechanical properties of MWNT-latex nanocomposites were characterized by
21 conducting monotonic uniaxial tensile tests on freestanding thin films. Here, non-annealed
22 0, 1, 2, and 3 wt% and annealed 1, 2, and 3 wt% thin films were investigated. The
23 freestanding films were cut into smaller specimens of 5×55 mm² and then mounted in a
24 Test Resources 150R load frame for testing. Tensile load was applied using a load rate of
25 1%-min⁻¹ until film failure. During testing, the displacement of the crosshead was measured
26 using an MTI laser displacement transducer connected to an Agilent 34401A digital
27 multimeter (DMM), which was recorded and time-synchronized with load measurements
28 from the load frame using a customized LabVIEW program. It should be mentioned that no
29 detectable relative slippage between the thin film and the crossheads occurred during the
30 tests owing to the use of an appropriate set of rubber-coated grips.
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34 2.4 Numerical simulations model

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36 The numerical model employed for simulating the mechanical behavior of MWNT-latex
37 films was adapted from a recently developed spring model approach. In addition, a non-
38 local lattice formulation was adopted to avoid preferential crack propagation in specific
39 directions due to the regular lattice configuration, therefore providing a more realistic
40 model [22, 23]. As schematically shown in Fig. 1a, a representative material portion was
41 discretized into a set of nodes, each linked to its neighbors through nonlinear “springs”. The
42 constitutive elasto-plastic behavior is shown schematically in Fig. 1b. The non-linearity
43 was introduced in the code through a forward Eulerian incremental procedure ([24]) using
44 a small strain increment (0.1%) at each simulation step. Elastic constants, yield point, and
45 plastic behavior of the latex matrix were obtained from experimental stress-strain curves
46 and average mechanical parameters obtained in this study.
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52 Randomly oriented line inclusions, discretized into a set of equidistant nodes, were
53 introduced into the model to simulate the behavior of the MWNT reinforcements (Fig. 1c).
54 The approach was similar to that adopted in [25], where the reinforcements were treated as
55 1D “anticracks” in a 2D soft matrix. In our approach, it was assumed that no relative
56 displacements are possible between the reinforcement representative nodes, due to the
57 largely superior MWNT stiffness with respect to the matrix. Inclusion nodes are connected
58 to matrix neighboring nodes with “interface” bonds having the same properties as matrix
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5 bonds to simulate a perfect interface. A uniaxial tensile test in displacement control was
6 then simulated on a model sample (Fig. 1d) to obtain the stress-strain behavior of the
7 nanocomposite. Periodic boundary conditions were applied on the lateral boundaries of the
8 sample. Due to the geometry of the problem, a plane stress approximation was adopted.
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10 11 12 13 **3. Results and Discussion**

14 15 **3.1 Microstructure and morphology characterization**

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17 The effects of incorporating MWNTs in latex, as well as annealing, on the microstructure
18 of these nanocomposites were measured using XRD, and representative results are shown
19 in Fig. 2. First, non-annealed 0 wt% thin films (i.e., latex-PSS) showed a broad diffraction
20 peak at $2\theta=16.5^\circ$, which indicates that their microstructure was mainly amorphous. On the
21 other hand, pristine MWNTs exhibited two dominant peaks in their diffraction pattern,
22 which were located at $2\theta=26^\circ$ and 43° , corresponding to (002) and (100) Bragg reflections,
23 respectively [26-28]. The (002) peak indicates the inter-shell spacing of the MWNTs is ~
24 3.4 Å, while the (100) one is due to stacking of nanotubes within MWNTs. It should be
25 noted that other small peaks captured by XRD might due to MWNT impurities. Second, the
26 XRD results of non-annealed films that incorporated MWNTs, which are shown in Fig. 2a
27 (i-iv), possess two peaks at $2\theta=16.5^\circ$ and 26° and are contributed by the polymer
28 matrices and MWNTs, respectively. This means that the incorporation of MWNTs in the polymer
29 matrix did not generate any formation of secondary phases, and MWNTs were randomly
30 oriented. The diffraction peak intensities of MWNTs were also more pronounced in
31 nanocomposites with higher MWNT concentrations. Furthermore, it was found that
32 annealed MWNT-latex films did not show any significant differences than their non-
33 annealed counterparts (Fig. 2b), thereby indicating that post-fabrication thermal treatment
34 did not introduce additional order in the microstructure of these nanocomposites.
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41 The surface topography of MWNT-latex films was investigated using AFM. For the non-
42 annealed films, Figs. 3a (a 0 wt% film) and 3c (a 1 wt% film) highlight spherical latex
43 particles with an average diameter of ~100 nm, forming a closely overlapped and compact
44 matrix. In Fig. 3c, the MWNTs can be observed on the surface of the films and are
45 separately distributed in the latex matrix. In contrast, spherical latex particles in annealed
46 films were hardly discernable, regardless of whether MWNTs were incorporated or not
47 (Figs. 3b and 3d). This result indicates that post-fabrication annealing changed the
48 configuration of latex particles and altered the polymer microstructure. Moreover, one can
49 also observe from the amplitude scale bar in Fig. 3 that the films' surfaces became
50 smoother after annealing.
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55 MWNT dispersion, changes in polymer matrix configurations, and fracture surfaces of
56 MWNT-latex thin films were also characterized by SEM. Several findings can be
57 summarized by comparing the SEM images of non-annealed and annealed 1 wt% thin films
58 as shown in Fig. 4. First, MWNTs were homogeneously distributed and randomly oriented
59 in the polymer matrix, rather than aggregated into bundles. Second, the spherical latex
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6 particles that were present in the polymer matrix in the non-annealed films (Figs. 4a and 4c)
7 disappeared after annealing (Figs. 4b and 4d). Moreover, there were many voids (larger
8 than 300 nm) in non-annealed thin films, which may be due to the slow degassing of the
9 MWNT-latex ink after their deposition, especially when considering the viscosity of the ink
10 solution and trapped air bubbles after spraying. In comparison, the polymer matrices of
11 annealed specimens were more intact, and MWNTs were better integrated with latex.
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14 Furthermore, the fracture surfaces of non-annealed and annealed MWNT-latex thin films
15 were also investigated using SEM. High magnification SEM images of fractured surfaces
16 of representative non-annealed and annealed films are shown in Figs. 4c and 4d,
17 respectively. For both cases, one can observe nanotubes being pulled out of the polymer
18 matrix. However, the diameter of the pulled out fibers for the annealed films (Fig. 4d) were
19 larger than ~150 nm. This suggests that MWNTs were wrapped by polymers, which
20 indicates that the MWNT-polymer interaction forces might be greater in the annealed
21 versus non-annealed ones. In addition, since the melting point of latex generally falls
22 between 120 and 176 °C, depending on its constituents, annealing could soften the latex
23 matrix. The softened latex was able to viscously flow around MWNTs and fill voids while
24 curing defects in the polymer matrix. As a result, annealed films should provide greater
25 resistance to nanotube pull-out and enhanced fracture properties due to stronger MWNT-
26 polymer interactions. Finally, delamination occurred in selected specimens for both non-
27 annealed and annealed films (Figs. 4a and 4b). Since the films were air-dried, the top layers
28 potentially dried faster than the bottom, which affected film integrity in the thickness
29 direction.
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34 3.2 Mechanical characterization 35 36

37 Monotonic uniaxial tensile tests were conducted as mentioned in Section 2.3. Fig. 5 shows
38 representative stress-strain curves of non-annealed 0, 1, 2, and 3 wt% nanocomposite films,
39 in which an initial linear-elastic, followed by a yielding and hardening region, can be
40 identified. The stress-strain profiles of annealed films possessed the same pattern, and thus,
41 are not shown here. To define the yield point, two linear least-squares regression lines were
42 fitted to characterize the initial elastic region and the hardening region. The intersection of
43 the two fitted lines were then assumed to be the yield point, as shown in the inset of Fig. 5.
44 Then, the elastic modulus of the nanocomposites was determined using the slope of the
45 linear best-fit line corresponding to the initial elastic region in the stress-strain curve.
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49 Figs. 6 to 8 summarize the different trends in the mechanical properties of non-annealed
50 and annealed MWNT-latex thin films of different MWNT concentrations. It is obvious that,
51 for both non-annealed and annealed thin films, the dispersion of MWNTs in the polymer
52 matrix should and did improve their tensile strengths and elastic moduli, as shown in Figs.
53 6 and 7a. MWNTs would resist crack formation and bridge micro-cracks in the polymer
54 matrix when the nanocomposites were stretched, thereby improving their strength [29].
55 This was evident from the SEM images of fracture surfaces discussed in Section 3.1 (see
56 Fig. 4). At the same time, due to the MWNT-latex interfacial forces, the nanocomposites
57 required larger external forces to overcome the greater inter-molecular friction to produce
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5 the same deformation as 0 wt% ones, thereby increasing the stiffness of the films. As
6 MWNT concentrations increased, the strengthening and stiffening effects became more
7 prominent, which is consistent with the trend observed in the XRD peaks associated with
8 MWNTs (see Fig. 2). Besides, Fig. 7a shows an approximately linear increasing trend in
9 tensile strength as MWNT concentration increased, again suggesting that at least up to 3
10 wt% MWNTs could be effectively dispersed in the polymer matrix using the spray-
11 fabrication technique employed in this study.
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15 Furthermore, as compared with non-annealed films of the same MWNT concentration,
16 annealed ones exhibited higher tensile strengths but lower elastic moduli, which indicates
17 that thermal treatment could strengthen the thin films while soften the material. Since
18 annealing cured voids in the matrix, MWNTs became better incorporated within the
19 polymer matrix according to the SEM images (see Fig. 4). Annealed films featured higher
20 integrity (i.e., fewer defects), which provided them with higher tensile strengths than their
21 non-annealed counterparts. However, the reduced stiffness could be mainly caused by
22 possible changes in the configuration of the polymer matrix after annealing.
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26 On the other hand, Fig. 7b shows that the ultimate failure strain of non-annealed films
27 decreased as more MWNTs were added. The drop was significant between 0 wt% to 1
28 wt%, and tended to level off beyond that, indicating that thin films with more dispersed
29 MWNTs had less flexibility. This occurred because the MWNT network acts like
30 crosslinks in the polymer matrix, which constrains polymer chains from moving under
31 tensile stress [30]. However, annealed thin films exhibited significantly higher ultimate
32 failure strains than non-annealed ones, especially for the 1 wt% set, whose average strain at
33 failure increased up to ~300%. Therefore, thermal treatment could enhance the flexibility of
34 MWNT-latex thin films, and the improvement was more remarkable on films of lower
35 MWNT concentrations. The effects of annealing on the flexibility could be attributed to the
36 change in the polymer matrix configuration (see Fig. 3). Besides, such enhancements would
37 be more significant in films that possessed higher polymer content, which explains why
38 decreasing MWNT concentration led to an increase in ultimate failure strain after
39 annealing.
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44 Similarly, Figs. 8a and 8b show that the derived yield stress increased as MWNT
45 concentrations increased while yield strain decreased, which was true for both non-
46 annealed and annealed thin films. In addition, thermal treatment consistently increased both
47 the yield stress and yield strain of the films with regard to MWNT concentrations. The
48 aforementioned effects of MWNT concentrations and annealing may also apply here.
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51 3.3 Numerical simulations characterization

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53 Simulations provide numerical predictions for the overall mechanical behavior of the
54 experimentally measured specimens characterized by different MWNT concentrations. The
55 stress-strain curves are presented in Fig. 9. Experimental data for the unreinforced matrix
56 were schematically modeled as an initial linear-elastic phase up to the yield point at 3.1%
57 strain, and a subsequent plastic phase with a 60-fold reduced slope up to failure at a 7%
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5 ultimate strain. These matrix properties were used in simulations for the reinforced
6 composite. The stress-strain curves obtained for increasing reinforcement weight fractions
7 have a similar behavior to that observed experimentally. Increasing MWNT concentrations
8 give rise to a stiffer material with yielding at smaller strain values (i.e., 1.4% for 1 wt%, 1.2
9 % for 2 wt%, and 1% for 3 wt%). This is due to increased stress concentrations in matrix
10 sub-regions where additional load is transferred via the reinforcements. As expected,
11 increasing MWNT concentrations also give rise to greater strength (i.e., 8.4 MPa for 1
12 wt%, 13.4 MPa for 2 wt%, and 17.9 MPa for 3 wt%). It can be seen that stresses are
13 underestimated with respect to experimental values. A probable reason is due to the
14 numerical results being conservative, where higher stress concentrations were imposed by
15 considering CNTs as rigid.
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20 Simulations also allow for mapping stress distributions within the deforming
21 nanocomposite and for highlighting their evolution during applied increasing loading
22 levels. An example is shown in Fig. 10 for a material portion of approximately $9 \times 12 \mu\text{m}^2$.
23 The reinforcements embedded in the softer matrix take up the strains applied on the
24 surrounding zone, and the images show that line inclusions, due to their high aspect ratio,
25 lead to stress concentrations mainly located at their tips. Stress concentrations are initially
26 distributed randomly inside the matrix and act as “seeds” for the onset of yielding, leading
27 to the propagation of plastic fronts. The evolution of plastification is highlighted in Figs.
28 10b and 10c, where plastic zones tend to merge and spread, unless shielded by other
29 MWNTs. This was further highlighted by analyzing the strain distributions in the polymer
30 matrix at different applied strain levels, ε , as shown in Fig. 11. Relative frequency
31 histograms of the strains were provided for the three MWNT concentrations considered in
32 this study, namely, 1 wt% (Fig. 11a), 2 wt% (Fig. 11b), and 3 wt% (Fig. 11c). In each case,
33 a widening of the distributions is observed, especially at high applied strain levels that were
34 well above the yield strain (8%). This indicates that maximum strains most likely first
35 concentrated at MWNT crack ends, where the initial large strain usually occurred. Then,
36 the nanocomposite would evolve to a highly-damaged condition, in which most parts of the
37 polymer matrix would be in a yielded state. Also, it should be noted that both compressive
38 and tensile strains would occur during this process, due to the complex nature of damage
39 propagation in heterogeneous materials. The observed trend was enhanced as MWNT
40 concentrations increased in the specimens.
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48 **4. Conclusions**

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50 In this study, MWNT-latex nanocomposite thin films were fabricated by spraying, and up
51 to 3 wt% MWNTs were homogeneously distributed in the latex polymer matrix. The
52 incorporation of MWNTs in the polymer matrix tended to strengthen and stiffen the
53 nanocomposite, and the effects became more significant as MWNT concentrations
54 increased. This indicates that MWNTs acted effectively as reinforcing fillers in the thin
55 films. In addition, to improve the mechanical properties of MWNT-latex thin films, post-
56 fabrication thermal annealing was carried out. It was found that annealing could enhance
57 flexibility and tensile strength. Such enhancement was mainly caused by changes in the
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5 latex matrix configuration after annealing, which generated stronger interfacial forces
6 between MWNTs and the polymer matrix and formed a more homogeneous microstructure.
7 Based on the numerical simulation results, randomly distributed MWNTs in the polymer
8 matrix could effectively strengthen and stiffen the nanocomposite, which agreed with
9 experimental **results**. Numerical simulations also showed that, upon loading, stresses tended
10 to concentrate at MWNT ends, subsequently leading to local yielding effects that
11 propagated across the entire thin film, thereby explaining the observed elasto-plastic
12 constitutive behavior.
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16 Overall, this work presents a simple, scalable, effective, and low cost fabrication technique
17 suitable for creating MWNT-latex thin films characterized by favorable mechanical and
18 electromechanical properties. Future studies will focus on further developing the spray
19 fabrication technique for two main goals. One is to fabricate MWNT-latex thin films with a
20 broader range of MWNT concentrations so as to investigate whether the findings derived
21 from this study continue to apply. The second is to employ spray coating for fabricating
22 other types of multifunctional nanocomposites.
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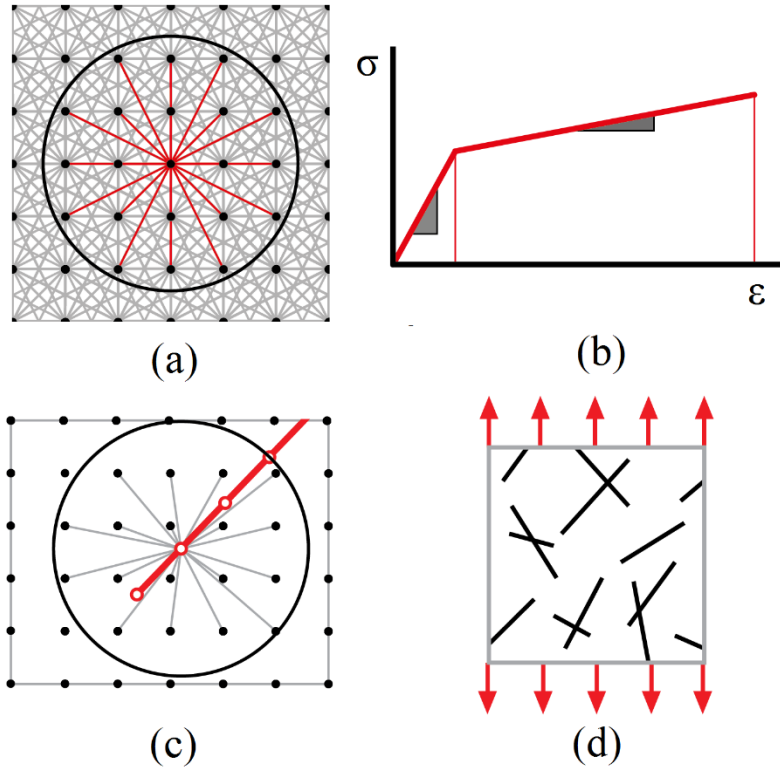


Fig. 1. (a) Non-local bonding between matrix nodes, where the circle represents an effective radius of interaction; (b) the assumed stress-strain behavior of matrix bonds; (c) non-local bonding between rigid line inclusion node and matrix nodes; and (d) schematic of the tensile test of the representative composite sub-domain.

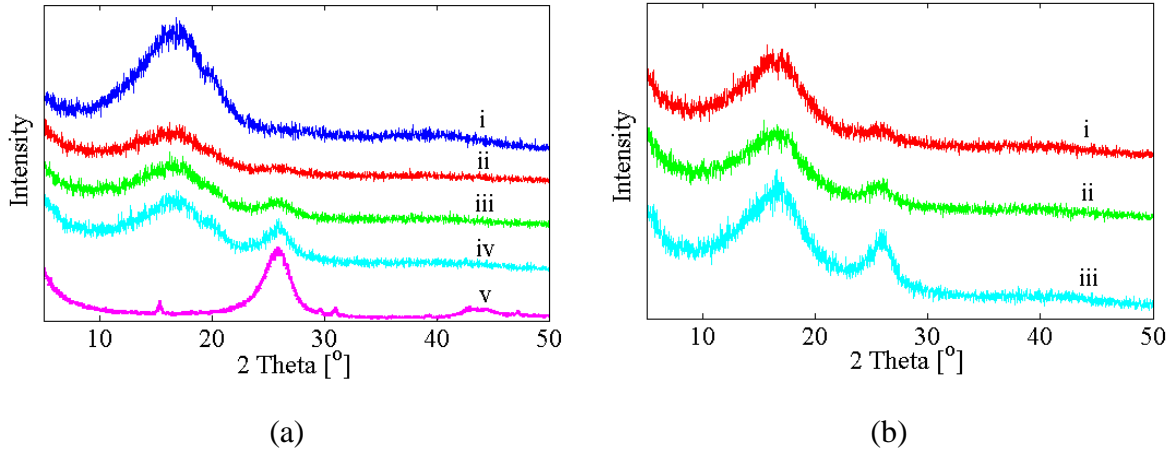


Fig. 2. XRD results for MWNT-latex thin films: (a) 0, 1, 2, and 3 wt% MWNT non-annealed films correspond to i-iv, respectively; v corresponds to pristine MWNTs; and (b) 1, 2, and 3 wt% MWNT annealed films correspond to i-iii, respectively.

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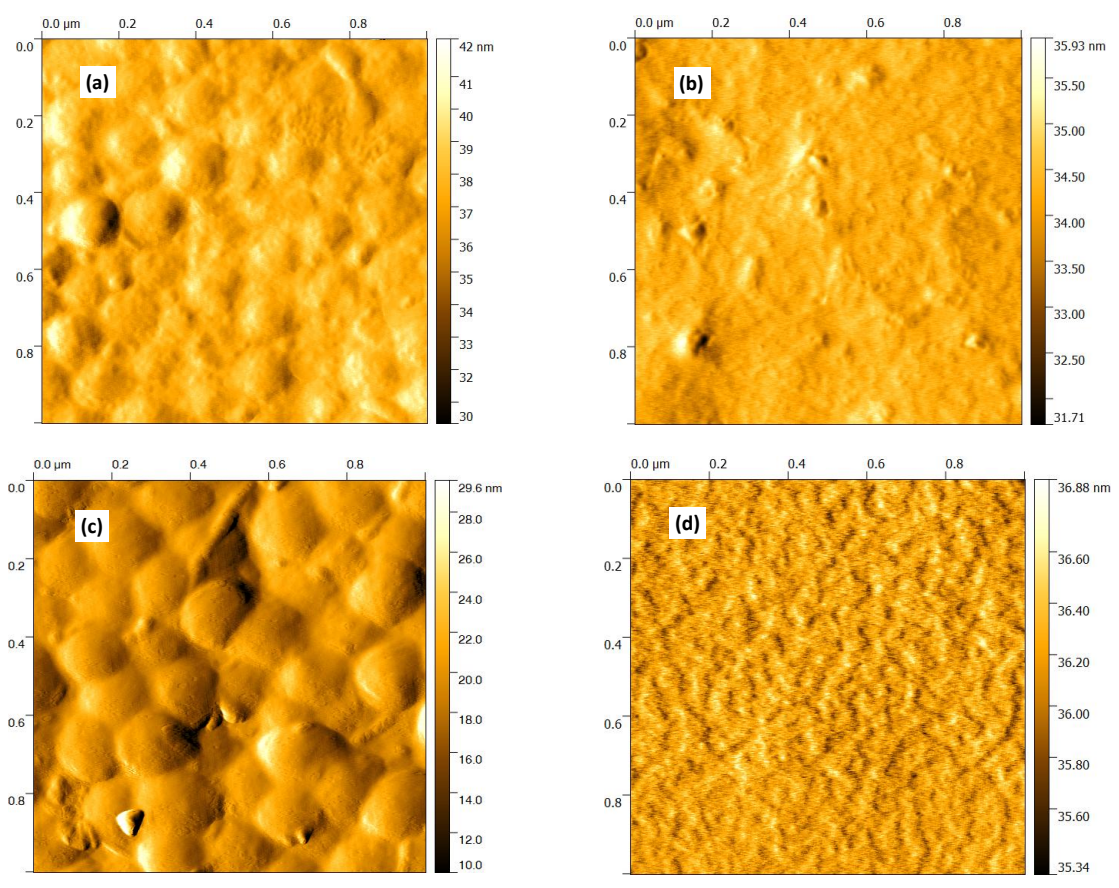


Fig. 3. AFM amplitude images of the surfaces of (a) non-annealed 0 wt%, (b) annealed 0 wt%, (c) non-annealed 1 wt%, and (d) annealed 1 wt% MWNT-latex thin films.

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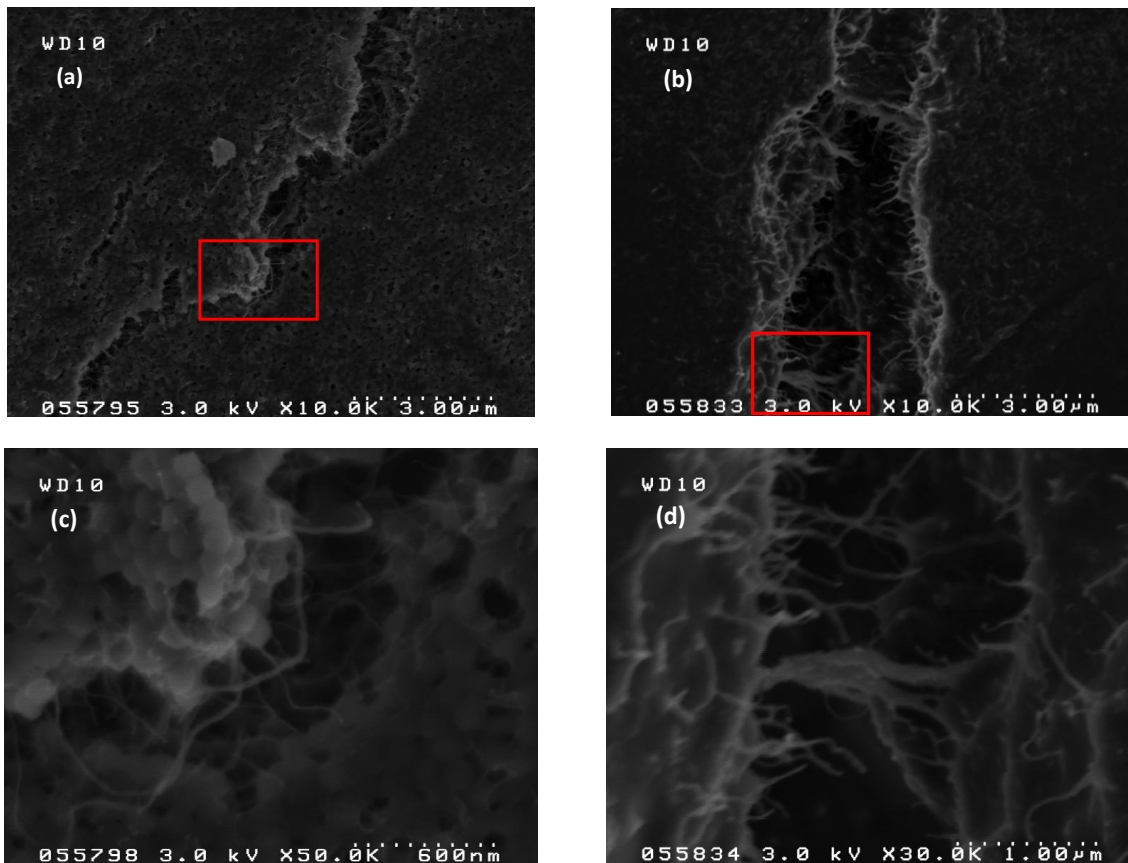


Fig. 4. SEM images of the fracture surfaces of (a) non-annealed and (b) annealed 1 wt% MWNT-latex thin films; (c) and (d) show higher magnifications of the areas marked by squares in (a) and (b), respectively.

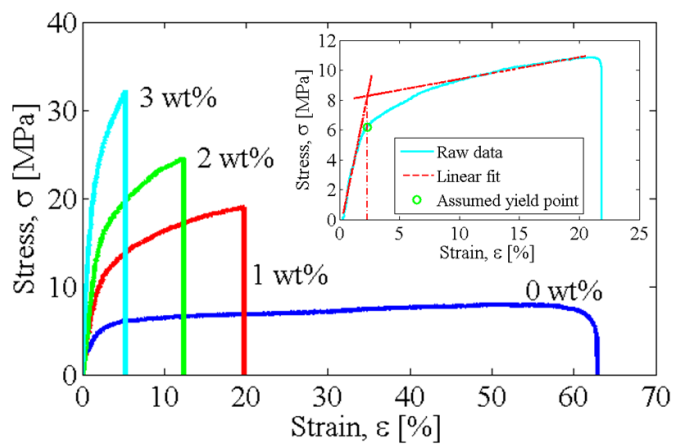


Fig. 5. Representative stress-strain curves of non-annealed 0, 1, 2, and 3 wt% MWNT-latex thin films; the inset shows the technique employed for determining the yield point.

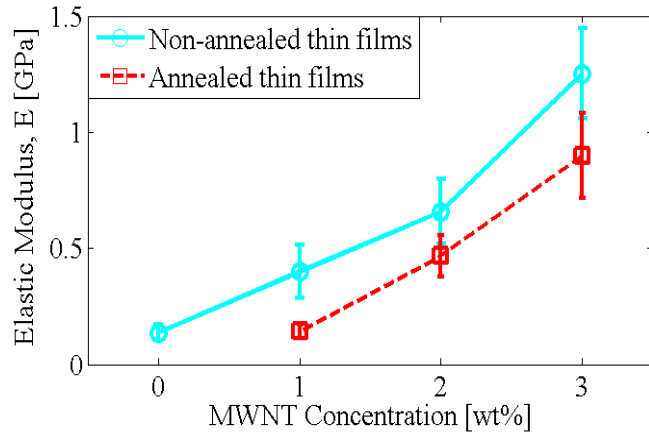
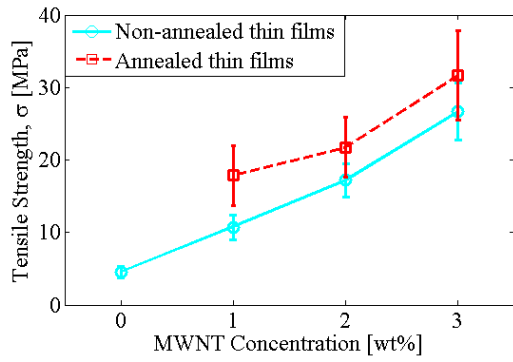
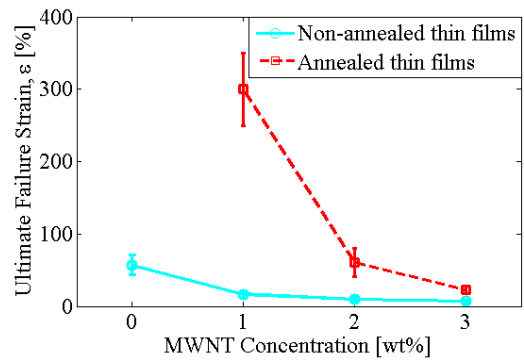


Fig. 6. The average elastic moduli (with standard deviations plotted as error bars) of non-annealed 0, 1, 2, and 3 wt% and annealed 1, 2, and 3 wt% MWNT-latex thin films.

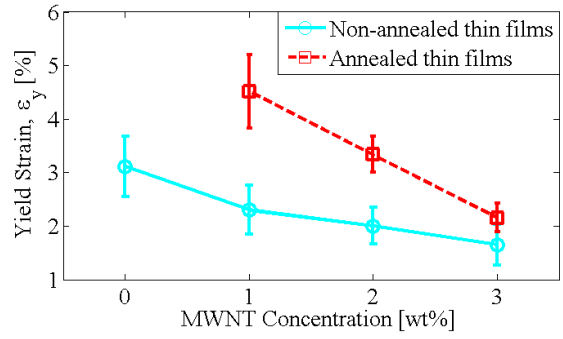
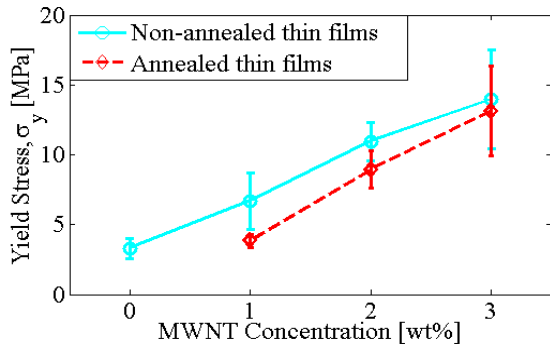


(a)



(b)

Fig. 7. The average (a) tensile strengths and (b) ultimate failure strains (with standard deviations plotted as error bars) of different non-annealed and annealed MWNT-latex film sample sets.



(a) (b)

Fig. 8. The average (a) yield strength and (b) yield strains (with standard deviations plotted as error bars) of both non-annealed and annealed MWNT-latex thin film sample sets.

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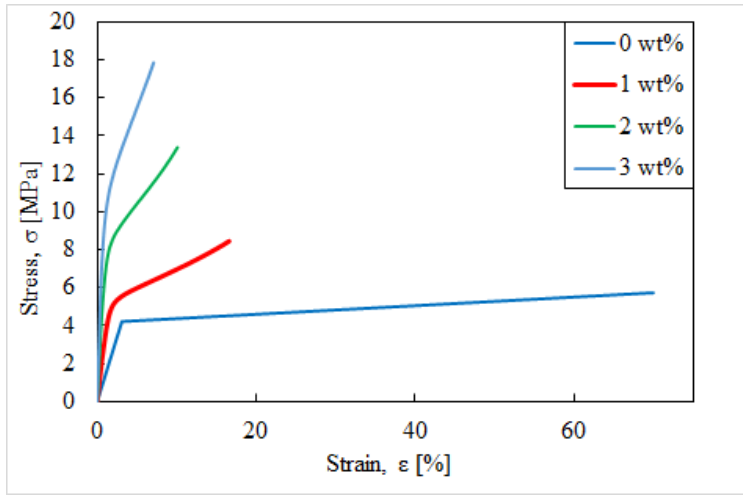


Fig. 9. Simulated stress-strain behavior for MWNT-latex thin films with different MWNT concentrations are shown.

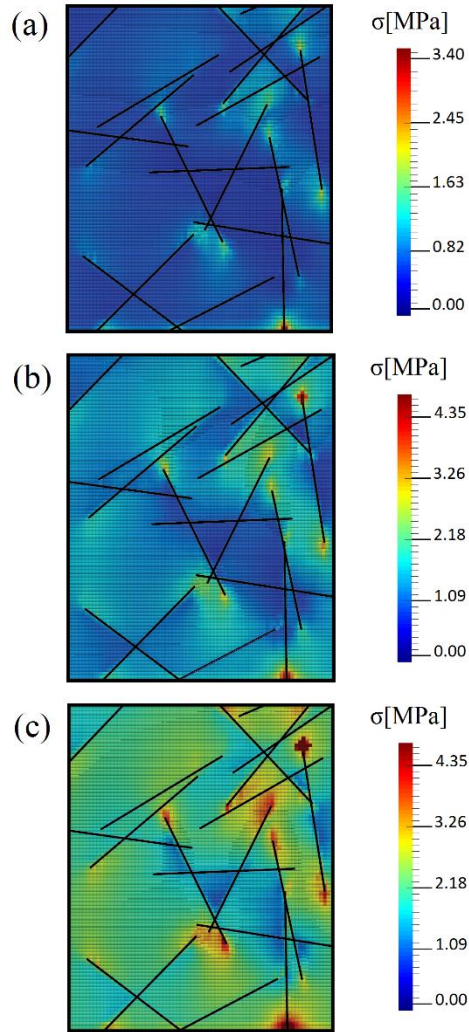
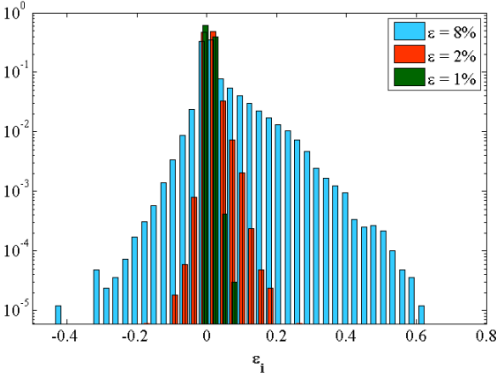
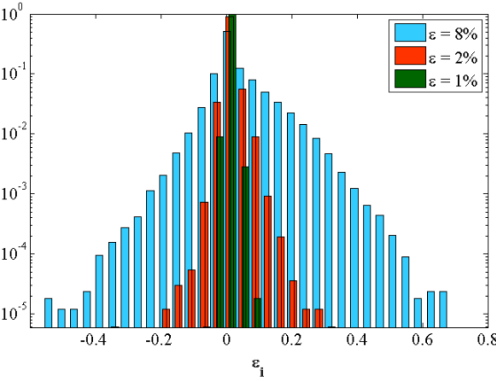


Fig. 10. Evolution of the distribution of stresses in a representative material portion for increasingly applied strains of (a) 1 %, (b) 2 %, and (c) 3 % are presented. Line inclusions represent randomly distributed MWNTs.

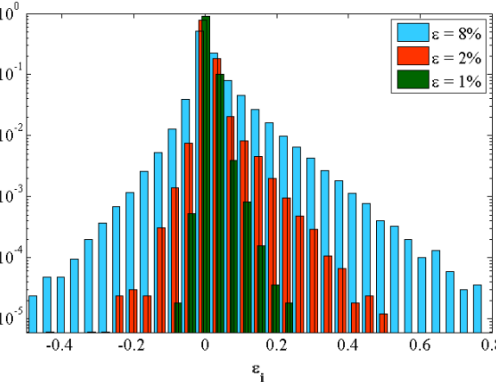
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(a)



(b)



(c)

Fig. 11. Statistical distributions, $p(\epsilon_i)$, of calculated strains, ϵ_i , in MWNT-latex films with (a) 1, (b) 2, and (c) 3 wt% MWNTs are shown. For each plot, distributions at applied external strains of $\epsilon = 1\%$, 2% , and 8% are presented.

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