

Effect of curing condition on the piezoresistivity of multi-walled carbon nanotube/epoxy nanocomposites

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Abstract

Non-monotonic electrical resistance changes have been observed in multi-walled carbon nanotube (MWNT)/epoxy nanocomposites subjected to tensile loading, but the mechanism is not fully understood. While most previous works investigated the effect of nanofiller content on the piezoresistivity of MWNT/epoxy nanocomposites, this work evaluates the impact of curing condition. The results indicate that the monotony of the piezoresistivity could be enhanced by using a higher curing temperature. It is therefore proposed that when cured under a different temperature, an epoxy matrix would exhibit a different level of spatial heterogeneity in molecular structure and hence in mechanical properties, causing the MWNT network inside the matrix to undergo a different movement trend under tensile loading. This study will facilitate future research on elucidating the underlying mechanism of the non-monotonic piezoresistivity of CNT/epoxy nanocomposites through considering the contribution of the molecular structure of the polymer matrix.

Keywords: Carbon nanotubes; Epoxy nanocomposites; Piezoresistivity; Curing temperature

1. Introduction

Carbon nanomaterial/polymer composites have shown increasingly rapid advances in the last decades, because the mechanical and physical properties of such a nanocomposite could essentially be customized by choosing the right

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nanofiller and matrix [1,2]. Due to their remarkable mechanical, electrical and thermal properties, carbon nanotubes (CNTs) have been used as the nanofillers in many classic works that aimed at enhancing the mechanical properties of the host materials or at developing new multifunctional materials [3,4]. One of the most dominant features of CNT/polymer nanocomposites is that they can achieve electrical percolation at low nanofiller contents, thanks to the high aspect ratio and electrical conductivity of CNTs [5]. In the context of multifunctionality, the piezoresistivity of CNT/polymer nanocomposites, which is enabled by conductive CNT networks, represents a major area of interest, because it is fundamental to strain sensing [6–8]. Moreover, epoxy has received wide recognition as an ideal matrix material for nanocomposites, owing to its outstanding mechanical properties, chemical resistance and versatility [9].

Several studies have reported research on the piezoresistivity of CNT/epoxy nanocomposites under tensile loading. Wichmann et al. [10] observed that the electrical resistance of a MWNT/epoxy nanocomposite would initially increase monotonically and exponentially with tensile strain, but the direction would change from positive to negative when the strain reaches 4%. The critical strain (ε_c) of 4% is common to both the 0.1 wt.% MWNT content sample and the 0.3 wt.% MWNT content sample that were used in their study. The negative resistance change vs. strain relationships were ascribed to molecular-level processes that would take place during the viscoelastic and inelastic deformation of an epoxy matrix in the plastic regime, because beyond 2% strain, the resistance change curves appeared to deviate from the exponential behavior and the gradients of the stress-strain curves began to decline. As inversions in piezoresistivity would lead to undefined responses in strain sensing, i.e., one resistance measurement could correspond to two strain values, several attempts have been made to identify the factors that would affect the trend of the piezoresistivity of MWNT/epoxy nanocomposites. The most extensively discussed factor is nanofiller content. Vadlamani et al. [11] examined the piezoresistive behaviors of MWNT/epoxy nanocomposites that are filled with 0.1 wt.%, 0.3 wt.% and 0.5 wt.% of MWNTs, and found that the critical strains were 1.5%, 1.9% and 3.9%, respectively. Only the 0.5 wt.% MWNT content sample demonstrated a similar critical strain to [10], and the results of the other samples indicated that an inversion in piezoresistivity could occur at an earlier stage under tensile loading and may not coincide with the plastic regime of the epoxy matrix where the stress-strain curve would show a downturn trend. Although in the literature most MWNT/epoxy nanocomposites exhibited non-monotonic piezoresistivity [10–14], contradictory observations have also been made. For instance, Vertuccio et al. [15,16] fabricated MWNT/epoxy nanocomposites with nanofiller contents of 0.025 – 0.5 wt.%, and noticed that the resistance of a sample would

increase monotonically with tensile strain all the way until it fails at 3 – 3.5% strain, despite the fact that the sample would enter the plastic regime at 2% strain.

For MWNT/epoxy nanocomposites, the divergence in their piezoresistivity remains a critical issue that limits their applicability in strain sensing. Haghoo et al. [17,18] investigated analytically how the physical properties of the MWNT nanofillers in a MWNT/polymer nanocomposite would influence the piezoresistive properties of the nanocomposite. However, little attention has been paid to the role of the polymer matrix. In fact, the mechanisms that underpin the electromechanical response of a MWNT/polymer nanocomposite are highly complex and built upon molecular-level phenomena that are related to the physical properties of both the MWNT nanofillers and the polymer matrix, as well as the interactions between the two constituents [19]. Recent studies have recognized that structural heterogeneities could exert significant influence on the electrical, mechanical and piezoresistive properties of MWNT/polymer nanocomposites [20–24]. In the case of a MWNT/epoxy nanocomposite, structural heterogeneities in terms of the local crosslinking densities of the molecular network structure of the matrix, which are critical to the physical properties of the nanocomposite, would be highly sensitive to curing condition [25–27]. Since it has been shown that both the electrical and the mechanical properties of MWNT/epoxy nanocomposites can be modified by adopting different curing conditions [28–32], it is reasonable to speculate that their piezoresistivity, which essentially reflects the coupling between their electrical and mechanical responses, would be influenced by curing condition. However, such correlation has not yet been explicitly demonstrated.

In this study, different curing cycles were employed to fabricate MWNT/epoxy nanocomposite samples. The electromechanical responses of the samples were acquired via quasi-static tensile tests, and the morphologies of the samples were characterized by a field emission scanning electron microscope (FESEM). Based on the experimental results obtained, the effect of curing condition on the piezoresistivity of MWNT/epoxy nanocomposites was preliminarily established. Such dependence was further explained in terms of the differences between the molecular structures of the matrices that would have developed under the different curing cycles employed.

2. Results and Discussion

MWNT/epoxy nanocomposite samples (MWNT purity: >95%, MWNT outer diameter: 50-90 nm, MWNT aspect ratio: >100) were cured under different cycles, as shown in Table 1. Both Cycle A and Cycle B consist of a 24 h or 12 h room temperature curing stage and a 6 h, 60 °C post-curing stage, complying with the curing condition suggested by the manufacturer of the epoxy. On the other hand, direct heat curing was applied in Cycle C (40 – 60 °C), Cycle D

(60 °C) and Cycle E (80 °C). Samples with different MWNT contents (i.e., 0.1 wt.%, 0.2 wt.%, and 0.3 wt.%) were prepared under Cycle A and Cycle D, in order to further evaluate the influence of curing condition on the piezoresistivity of MWNT/epoxy nanocomposites at different nanofiller contents. The samples are labelled as X-MWNT/epoxy-Y, where X indicates the curing cycle adopted, and Y the MWNT content of the sample. The fabrication process of the MWNT/epoxy nanocomposite samples is detailed in the Supplementary Information.

Table 1. Processing conditions of MWNT/epoxy nanocomposites.

Curing cycle	Nanofiller content (wt.%)	Curing temperature and time	Post-curing temperature and time
A	0.1, 0.2, 0.3	Room temperature for 24 h	60 °C for 6 h
B	0.3	Room temperature for 12 h	60 °C for 6 h
C	0.3	40 °C for 2 h, 50 °C for 2 h, 60 °C for 5 h	N/A
D	0.1, 0.2, 0.3	60 °C for 6 h	N/A
E	0.3	80 °C for 6 h	N/A

Fig. 1 compares the electrical conductivities of samples with 0.3 wt.% nanofillers that were cured under different cycles (see the Supplementary Information for the measurement procedure). The results indicate that the electrical conductivity of a sample could be increased by either a reduction in room-temperature curing time (Cycle A and Cycle B) or an increase in curing temperature (Cycle C, Cycle D, and Cycle E). This observation is in line with previous studies [30,31] which showed that a higher curing temperature would enhance the formation of a conductive network due to temperature-induced agglomeration of nanofillers, leading to a higher electrical conductivity in the resultant MWNT/epoxy nanocomposite.

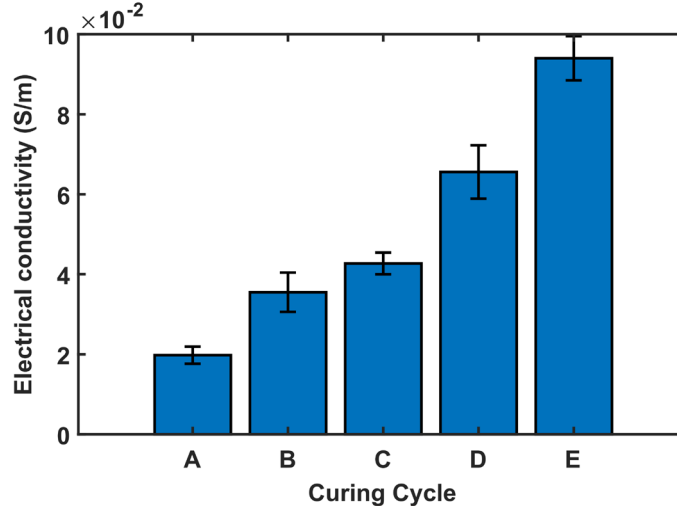


Fig. 1. The electrical conductivities of MWNT/epoxy-0.3 samples that were cured under different cycles (for each sample, three specimens were tested and the mean measurement is plotted (error bar: ± 1 standard deviation)).

Fig. 2 shows the electromechanical responses of samples with 0.3 wt.% nanofillers that were cured under different cycles (see the Supplementary Information for the measurement procedure). The most striking finding that emerged from these results is that samples that are cured under two different cycles could exhibit drastically different electrical resistance change vs. tensile strain relationships. For the Cycle A, Cycle B and Cycle C samples, inversions in piezoresistivity occurred at around 0.28% strain, 0.36% strain and 0.89% strain, respectively. The resistance of each of these samples first increased with strain, reaching its maximum at the respective critical strain, and then decreased until the sample failed. On the other hand, both the Cycle D and Cycle E samples demonstrated a monotonic piezoresistive behavior until failure. For each of these samples, the resistance increased exponentially when the strain was below $\sim 1\%$, most likely because in the early stage of the tensile deformation of a MWNT/epoxy nanocomposite, the quantum tunneling effect is the dominant cause of the resistance change [10,14,33]. For a material that is oriented towards strain sensing, having a monotonic piezoresistive behavior, even if it is nonlinear, would be absolutely crucial [13,16]. The results presented indicate that the piezoresistivity of MWNT/epoxy nanocomposites can be significantly affected by curing condition.

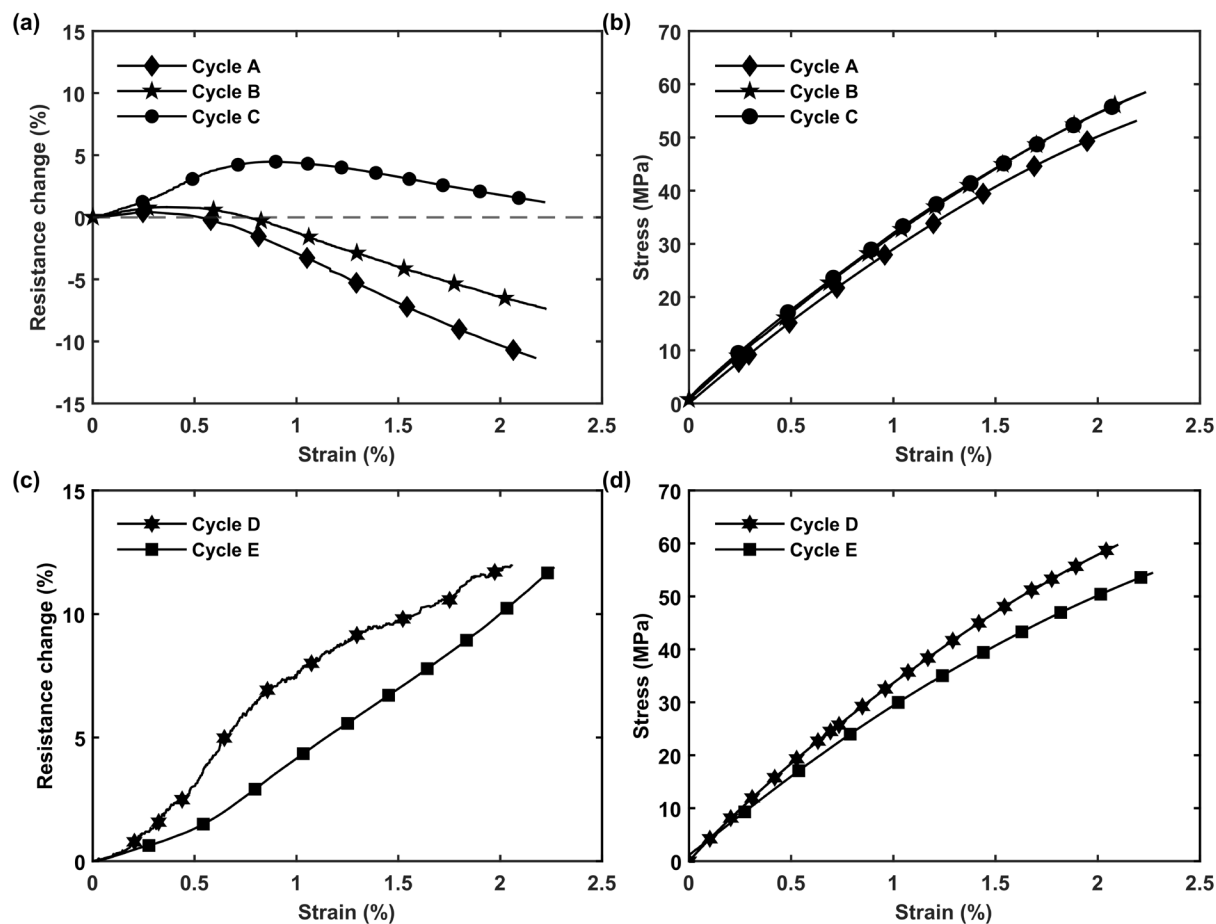


Fig. 2. Piezoresistive behaviors ((a) and (c)) and stress-strain curves ((b) and (d)) of MWNT/epoxy-0.3 samples that were cured under different cycles (for each sample, three specimens were tested and the mean response is plotted).

For the sake of brevity, the electromechanical responses of the Cycle A and Cycle D samples with 0.1 wt.% and 0.2 wt.% nanofillers are presented in Fig. S2 in the Supplementary Information. From the results, it can be seen that while the strain sensitivity (i.e., the gradient of the resistance change vs. strain curve) of a MWNT/epoxy nanocomposite would decrease with nanofiller content (Fig. S2(m), (o) and (q)), nanofiller content would not affect the monotony of the piezoresistive behavior of the nanocomposite nor the critical strain of the nanocomposite (Fig. 2S(g), (i) and (k)).

Fig. 3(a)-(d) show the FESEM images of the tensile fracture surfaces of samples with different piezoresistive behaviors (see the Supplementary Information for the imaging procedure). The Cycle A and Cycle B samples, whose piezoresistive behaviors are non-monotonic, have rough fracture surfaces, indicating that the failures of the samples were accompanied by ductile deformations. On the other hand, the smooth fracture surfaces of the Cycle D and the

Cycle E samples, which have monotonic piezoresistive behaviors, suggest brittle failures [28,29,32]. All in all, it can be seen that curing condition could influence the microscopic deformations and fracture behaviors of MWNT/epoxy nanocomposites. Meanwhile, in all of these samples, MWNTs were generally well dispersed and some micron-level agglomerates were present, meaning the employment of the different curing cycles did not result in a variation in the dispersion of MWNTs. Therefore, nanofiller agglomeration state, despite being recognized as a prominent factor in determining the physical properties of a MWNT/epoxy nanocomposite [34,35], might not be the major cause of the difference in electric conductivity and piezoresistivity between the samples in this work.

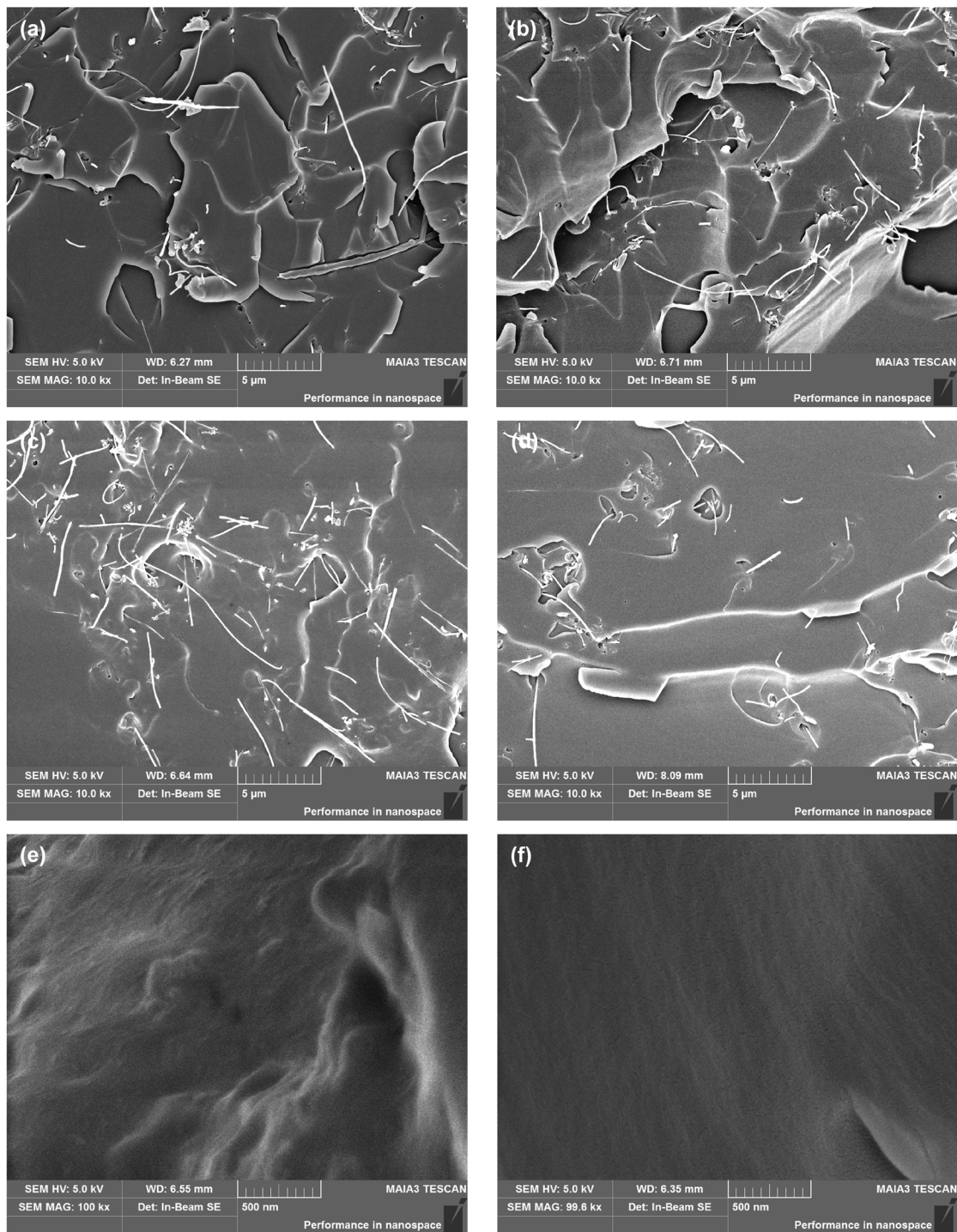


Fig. 3. FESEM images of the tensile fractured surfaces of (a) A-MWNT/epoxy-0.3, (b) B-MWNT/epoxy-0.3, (c) D-MWNT/epoxy-0.3, and (d) E-MWNT/epoxy-0.3, and the cryogenically fractured surfaces of (e) A-MWNT/epoxy-0.3 and (f) D-MWNT/epoxy-0.3.

For an epoxy/amine thermoset, the development process of its highly crosslinked molecular network structure, which determines its physical properties upon curing, has been found to be sensitive to curing condition [25]. The homogeneity of a network structure would vary with curing temperature, because curing temperature would influence the contributions of the different modes of network growth. A relatively homogeneous network structure is expected when the microgels that are formed during the pre-gelation stage are mainly linear segments. At the gel point, these segments become connected to each other, giving rise to a molecular network. Then, the network grows towards vitrification with the formation of crosslinks that are evenly distributed in space. There exists another mode of network growth that produces heterogeneities in network structures. The origin of these nanoscale heterogeneities is the formation of both linear microgel segments and crosslinked microgels during a pre-gelation stage. The presence of crosslinked microgels in the gel structure signifies that crosslinks are formed throughout the entire curing process, instead of mainly from the gel point and onwards, and are concentrated in the regions that are developed from crosslinked microgels. Consequently, the network structure comprises of domains with different crosslinking densities, i.e., heterogeneities. Although the correlation between curing temperature and the homogeneity of a network structure depends on curing kinetics and differs between different types of epoxy/amine thermosets, it is possible to identify the heterogeneities in a network structure by examining cryogenically fractured surfaces using a FESEM [26,36]. Fig. 3(e)-(f) show the FESEM images of the cryogenically fractured surfaces of a Cycle A sample and a Cycle D sample (see the Supplementary Information for the imaging procedure). The nodular morphology of the room temperature cured Cycle A sample implies that heterogeneities had developed in the network structure of the sample [26,36]. In contrast, the morphology of the heat cured Cycle D sample appears to be featureless, suggesting a relatively homogenous network structure. The influence of the heterogeneities in a network structure could manifest in the electrical and the mechanical properties of the cured product as well as its composites.

The difference in electrical conductivity between the samples that were cured under different cycles (Fig. 1) can be explained using an interphase layer model that is based on the different modes of network growth [36]. The model correlates percolation dynamics to the curing-dependent network structure of an epoxy matrix. The lower electrical conductivities of the room temperature cured Cycle A and Cycle B samples could be attributed to the presence of more crosslinked microgels in their gel structures during their pre-gelation stages. By acting as “interphase layers” between MWNTs, domains with higher crosslinking densities would have suppressed the movement of MWNTs during curing and hindered the establishment of conductive paths upon curing. On the other hand, the

thicknesses of the “interphase layers” in a network structure would decrease as the concentration of crosslinked microgels decreases (or as the concentration of linear microgel segments increases). With thinner “interphase layers”, MWNTs would be able to move more freely and the establishment of conductive paths would be more efficient. This could essentially be the physical origin of the temperature-induced agglomeration of nanofillers [30,31] that equipped the heat cured Cycle C, Cycle D, and Cycle E samples with higher electrical conductivities.

A phenomenological description that incorporates the effect of the heterogeneities in a network structure is proposed to explain the correlation between curing condition and the trend of the piezoresistivity of MWNT/epoxy nanocomposites. First of all, it has been widely accepted that the piezoresistivity of MWNT/polymer nanocomposites is mainly driven by deformation-induced construction and destruction of conductive paths [19], which are governed by the distances between adjacent nanofillers. Under a tensile deformation, the MWNTs in a nanocomposite would move away from each other, and as a result, the number of conductive paths in the nanocomposite should decrease and the electrical resistance of the nanocomposite should increase. However, in previous studies as well as this work, negative resistance change vs. strain relationships have been observed in MWNT/epoxy nanocomposites beyond certain strain levels, indicating that there were processes that, under tensile strain, reduced the distances between adjacent nanofillers and/or increased the number of conductive paths [13–16]. These processes were likely to be molecular motions that pertain to the viscoelastic and plastic deformations of the polymer matrices, e.g., plastic flow, alignment of molecular chains, and elongation of entangled molecular chain clusters. Fig. 4 attempts to depict the reason behind the peculiar difference between the monotonic and non-monotonic piezoresistive behaviors of the samples that were cured under different cycles (Fig. 2(a) and (c)). In the more heterogeneous network structures of the Cycle A, Cycle B, and Cycle C samples, both rigid domains with higher crosslinking densities and compliant domains with lower crosslinking densities would have coexisted, resulting in a spatial non-uniformity in mechanical properties [27]. When a tensile loading was applied to one of these samples, viscoelastic and plastic deformations would have been favored in the less crosslinked domains of the network structure, which have complex local strain states and higher local molecular mobility, leading to molecular motions that would have given rise to the construction, as opposed to the destruction, of conductive paths. Since the MWNTs in the sample could have modified the curing kinetics of their surrounding areas [32,37,38], the heterogeneities in the network structure could have also been localized in the vicinity of the MWNTs, pronouncing their influence in causing the MWNTs to move in a way that would lead to a higher number of conductive paths.

Furthermore, in a MWNT/epoxy nanocomposite, the interfacial interactions between the nanofillers and the matrix could modify the physical properties of the matrix regions surrounding the nanofillers, giving rise to so-called interfacial regions whose thicknesses are of a few nanometres [39,40]. An increase in the thicknesses of the interfacial regions, which could result from stronger nanofiller/matrix interfacial interactions, would benefit the viscoelastic behavior of the nanocomposite [34] and the electrical conductivity of the nanocomposite near its percolation threshold [41]. In this work, as curing temperature increases, the electrical conductivities of the MWNT/epoxy nanocomposite samples become greater and the piezoresistive behaviors of the samples change from non-monotonic to monotonic. Therefore, the nanofiller/matrix interfacial interactions in these samples and hence the thicknesses of the interfacial regions in these samples may also exhibit an increasing trend with respect to curing temperature.

A reasonable interpretation of the slight difference in critical strain between the Cycle A and Cycle B samples (0.28% vs. 0.36%) is that for the Cycle B sample, the development of heterogeneities in its network structure would have been halted by the earlier application of post-curing. On the other hand, the noticeably larger critical strain of the Cycle C sample (0.89%) owes to the utilization of a moderately higher temperature from the very beginning of the curing cycle, which would have repressed the development of heterogeneities to a certain extent. In the less heterogeneous / more homogenous network structures of the Cycle D and Cycle E samples, the spatial non-uniformity in mechanical properties would have been much less significant [27]. When a tensile strain was applied to one of these samples, the network structure would have deformed in an elastic manner and the MWNTs in the sample would have mostly moved away from each other. Consequently, the samples always exhibited positive resistance change vs. strain relationships. In summary, it can be inferred that the dependence of the piezoresistivity of a MWNT/epoxy nanocomposite on curing condition would most likely be the consequence of the curing-dependent heterogeneities in the network structure of the matrix. Curing condition could also affect the piezoresistivity of epoxy nanocomposites that are filled with other 1D carbon nanomaterials with high aspect ratios, e.g., single-walled carbon nanotubes and carbon nanofibers, since the deformation-induced topological changes of these nanocomposites would be similar to that of MWNT/epoxy nanocomposites.

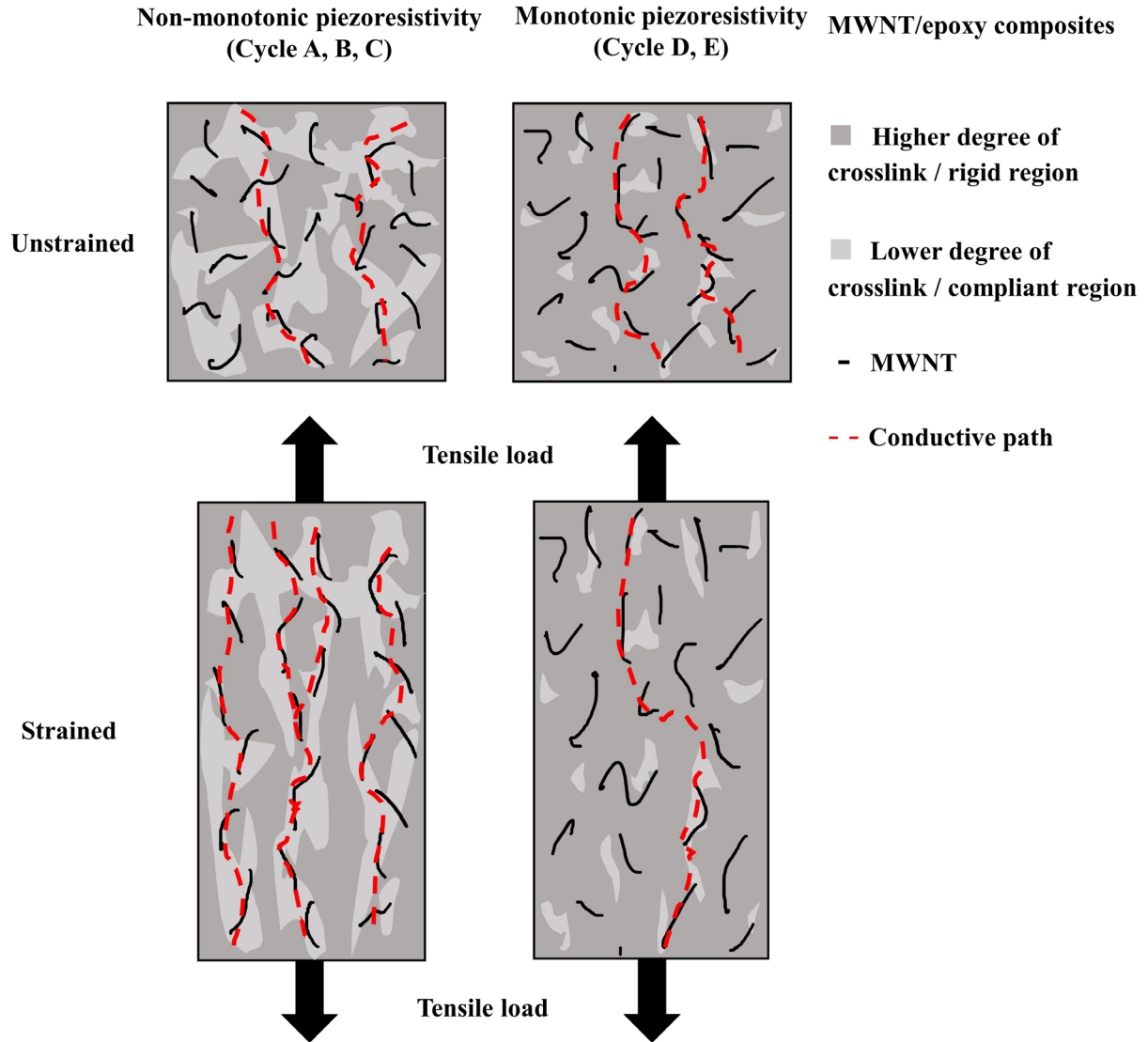


Fig. 4. The effects of curing-dependent spatial heterogeneities in crosslinking density and in mechanical properties on the piezoresistivity of MWNT/epoxy nanocomposites.

3. Conclusion

This study was designed to examine the effect of curing condition on the piezoresistivity of MWNT/epoxy nanocomposites under tensile loading. The results revealed that the piezoresistivity changed from non-monotonic to monotonic when the curing temperature increased from room temperature to 60 °C. With supporting experimental evidence of the differences, in electrical conductivity and in fracture surface morphology, between samples that were cured under different cycles, it is proposed in this work that the piezoresistivity of a MWNT/epoxy nanocomposite

could be a function of the heterogeneities in crosslinking density that would develop in the network structure of the epoxy matrix during the curing process. The findings reported here shed new light on the mechanisms that govern the piezoresistivity of MWNT/epoxy nanocomposites and the dependence of the piezoresistivity on the nature of matrices. The precise association between the piezoresistivity of a MWNT/epoxy nanocomposite and the network structure of the matrix will be elucidated by further molecular dynamic simulations and experimentation.

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