Creep performance of CNT-based nanocomposites: A parametric study

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A R T I C L E   I N F O
Article history:
Received 6 May 2019
Received in revised form 1 July 2019
Accepted 19 July 2019
Available online 22 July 2019

A B S T R A C T
Epoxy materials have been widely applied in various applications ranging from nanoscale structures, such as microelectronic devices, to macroscale components in aerospace and building constructions. The structural stability under constant loadings is a major concern for polymeric materials during long-term service. The incorporation of carbon nanotubes (CNTs) into epoxy matrix has been considered to enhance creep resistance in recent decades. Substantial improvement of CNT-based nanocomposites largely relies on optimized design of material microstructures, and such manipulation requires comprehensive understanding of creep behavior in CNT-epoxy nanocomposites. In addition, effective arrangement of CNTs in epoxy matrix for enhancement in creep resistance needs a systematic study of related parametric effects. In this work, the effects of CNT length, CNT weight fraction and CNT dispersion state on the creep response of nanocomposites are investigated using molecular dynamics simulations. The creep deformation of nanocomposites including creep strain and system dynamics are found to decrease with the increasing length, weight fraction and good dispersion state, showing the contribution of the additional CNTs towards the resistance in time-dependent deformation. These results suggest that the CNT-epoxy nanocomposites with superior creep resistance can be achieved in the design by optimizing the CNT-associated parameters.

1. Introduction

Due to its excellent functions of gap filling and surface protection, epoxy has been widely used as coatings or adhesives for various engineering applications. Triggered by the increasing need for better mechanical performance, the incorporation of nanofillers into polymer matrices has been reported as an advanced approach to develop strengthened composite materials over the past few decades. Among these additives, carbon nanotubes (CNTs) become an attractive candidate because of their high aspect ratio, low density, and exceptional physical properties such as high Young’s modulus, heat conductivity, and electrical conductivity. CNT-reinforced epoxy nanocomposites present many advantages over neat epoxy, and are considered promising composite materials for the new generation, having been employed as bonding adhesives, electronics encapsulation in nano-devices, and structural parts in automobiles and airplanes [1–3]. While the mechanical properties of CNT-reinforced epoxy nanocomposites, including high strength, stiffness and toughness, have been extensively investigated [4–8], the research on creep behaviors showing the long-term performance of these material systems is still limited and not adequately thorough. Due to its inherent viscoelastic nature, the epoxy matrix usually undergoes time-dependent deformation when subjected to continuous stress. The irreversible disentanglement of polymer chains including slippage and stretching, takes place over time. Progressive plastic deformation can lead to failure in epoxy nanocomposites, causing unexpected malfunction or even life threatening hazard in structural components. Therefore, a good description of creep response in these polymeric systems and an optimal addition of CNTs for improved creep resistance are important aspects to be considered for practical engineering applications that require long-term stability and durability.

In the existing literature [9–13], creep experiments on CNT-reinforced epoxy nanocomposites yield inconsistent conclusions on whether the addition of CNTs can greatly improve the creep resistance of nanocomposites. The creep deformation of epoxy nanocomposites in long-term creep tests is found to be reduced with low CNT weight fractions (wt%) in the range from 0.1% to 0.25%, but the creep deformation accelerates when the CNT weight...
fraction reaches 1 wt%, which is attributed to the aggregation of CNTs [9]. The incorporation of CNTs with up to 1 wt% is reported to have a negligible influence on the creep behavior of the epoxy matrix [10]. The reinforcing ability of CNTs in nanocomposites is weaker with higher weight fraction and creep loads as the agglomeration occurs and the adhesion between CNT and epoxy matrix deteriorates [14]. In contrast, increasing CNT weight fraction with good dispersion results in a noticeable decrease of creep displacements [11]. The pronounced improvement in creep resistance of nanocomposites remains even under high temperature and creep loads due to high aspect ratio and interfacial area between CNT and epoxy matrix [12,13,15]. Such a discrepancy in experimental findings is caused by various fabrication factors, indicating the dependency of the creep resistance on CNT size, CNT weight fraction and state of dispersion. Polymer nanocomposites should be designed with emphasis on the CNT-associated parameters in order to obtain optimal creep resistance, which requires the knowledge of the effects of CNT geometry, amounts, and dispersion states on the creep responses. The creep responses of polymer nanocomposites with various volume fractions, diameters and arrangements of CNTs, applied loading levels and conditions have been analyzed using micromechanical modeling, which are found to be in good agreement with experiments [16–18]. In addition to these theoretical results, the understanding of the creep deformation and the reinforcing mechanism of creep resistance in nanocomposites at the atomicistic level is still needed as creep response is fundamentally related to the change of molecular mobility in polymeric systems. The stress-induced segmental dynamics in polymer matrix has been quantitatively measured using an optical photobleaching technique [19], and a quantitative connection between molecular mobility and macroscopic deformation has been established. It is speculated that the addition of CNTs has a hindrance effect on polymer chain mobility of epoxy matrix, as well as the chain slippage and disentanglement [9,12,15]. However, it is insufficient to investigate the effect of individual parameter on the segmental dynamics in epoxy matrix solely by experiments as there are limitations in the precise control of changing variables and the visualization of microstructures. Therefore, the investigation from nanoscale perspective can help to uncover the microstructural interactions and dynamics in the CNT-epoxy nanocomposites, enabling the analysis of the effects from different CNT-associated parameters.

Molecular dynamics (MD) simulations are considered to be an effective tool to elucidate various effects on mechanical performance and connect mechanical response and structural deformation to molecular interactions and motions in nanocomposite systems. MD simulations have been applied to explore the material properties, uncover the mechanical phenomena at the molecular level, and capture the atomic movements in different materials and bonded systems [20–24]. The structures and physical properties of epoxy materials have been predicted using MD simulations [25–28]. The nanoparticles are found to alter the topological constraints and enhance the entanglement under deformation in polymer nanocomposites [29]. In addition, MD simulations have been applied to investigate the effect of interactions between CNT and polymer matrix in the interfacial region on the structural and dynamical properties of nanocomposites [30]. It is reported that the optimization on the mechanical behavior of the CNT-reinforced epoxy nanocomposites highly depends on the interactions between CNTs and epoxy matrix [31–33]. The dispersion state of CNTs has a significant effect on the interfacial interactions between CNTs and epoxy matrix, which changes the interphase, thermal and mechanical properties in nanocomposites [34]. Although MD simulations are employed in measuring and analyzing the mechanical properties of material systems, it is noted that MD approach is inherently limited by the accessible time scales down to the order of nanoseconds. Creep of materials spreads a wide range of time scales, from seconds of microscopic process to years of macroscopic deformation. However, MD simulations can still reproduce trends similar to the experimental observations, even though there are discrepancies in the timescale, as the macroscopic deformation is linked to the microscopic displacement in a consistent manner [35]. The simulation results using extreme settings for surrounding conditions (such as high temperature or external stress) can describe the creep response in different material systems and elucidate the underlying mechanism of creep deformation [36–38] from a relatively short time duration as suitable interactions between molecules in the systems are correctly provided. Moreover, MD simulations are capable of capturing the features of individual segmental movement in material systems corresponding to the creep response observed in the experimental timescales, uncovering the details in molecular interactions that cannot be obtained from bulk measurement.

The objective of this study is to investigate the effects of CNT-associated parameters on the creep responses of CNT-epoxy nanocomposites, and to understand the role of CNT in creep resistance of nanocomposite during the deformation process. In order to characterize the creep response, the time-dependent strains and the microstructural evolutions in different material systems are captured and compared using MD simulations. In addition, the segmental dynamics of the nanocomposite systems are quantified to reveal how CNTs affect the movements of epoxy chains during the creep process. Mechanical insights into the creep-resistant mechanism with the addition of nano-fillers to polymer matrix, as well as guidance for the optimal design of CNT-reinforced polymer nanocomposites with enhanced creep resistance for applications through modulating the CNT-associated parameters, are provided.

2. Simulation methods

2.1. Molecular models

In this study, the cross-linked epoxy matrix of nanocomposites consists of two widely used constituents, diglycidyl ether of bisphenol A (DGEBA) as the epoxy monomer and triethylenetramine (TETA) as the cross-linker. The chemical and atomistic structures of these molecules are shown in Fig. 1(a). To make fair comparison in different cases, the numbers of epoxy monomers and cross-linkers are kept constant, which are 270 and 90 respectively. The pristine single-walled carbon nanotube (SWCNT) of armchair (5,5), one of the well-recognized and typical structures of nanotubes, is prepared as the nano-filler. The end effect of the CNTs including the cap and the hydrogenation is not considered in this study. In order to understand how the addition of CNTs affects the creep performance of nanocomposites, the effects of three parameters associated with the nano-filler, including CNT length, CNT weight fraction, and CNT dispersion (i.e. dispersed and aggregated states) are investigated. The set-up of atomistic models involves two main steps: (1) the strategic placement of the CNTs with variable parameters into the unreacted mixture of epoxy molecules and (2) the cross-linked reaction of epoxy molecules around the CNTs. In step one, different arrangements of CNTs in the systems are carried out by varying one chosen parameter while keeping the remaining parameters fixed to separate the effect from these parameters. To elucidate the effect of the CNT length, the lengths are set in the range of 4–50 Å, corresponding to the aspect ratios of 0.73, 2.18, 3.63 and 7.26 respectively. The selected range contains various CNT shapes from the particle shape to the rod shape. Although the CNT length is several orders of magnitude shorter
than the bulk materials, the mechanical properties and the trends from MD simulations are in good agreement with the experimental results [39] as the models still can represent the interfacial structures between CNT and polymer matrix from atomistic scale. To elucidate the effect of CNT weight fraction, the weight fractions are varied from 2 wt% to 12 wt%, covering the low and high amount cases. This range is selected because the loading of nanofiller in nanocomposite is commonly around 10 wt% in the experiments [40]. The major issue in adding CNTs with high weight fraction (i.e. over 10 wt%) into epoxy matrix is the aggregation of CNTs. Several processing techniques have been applied to overcome this obstacle during fabrication, such as ultrasonic bath, shear mixing, extrusion and chemical purification of CNTs, which are common approaches in lab or for large-scale production [41]. The incorporation of high CNT content has been realized in previous studies [42], showing the reliability of PCFF, which is well correlated to experimental findings. Therefore, PCFF is chosen in this study. The partial charges on different types of atoms are calculated using the

Here, the energy terms consist of the bonded energy terms, the cross-terms and the non-bonded energy terms. The first four terms are bonded interactions, including the covalent bond stretching energy, the bond angle bending energy, the torsion angle rotation energy and the improper energy. The next several cross-coupling terms are for cross interactions, including bond-bond, bond-angle, angle-angle, bond-torsion, angle-torsion, and angle-angle-torsion coupling terms, respectively. The last two terms represent the van der Waals force and the Coulombic force. The predicted physical mechanical and thermal properties of epoxy materials have been found in good agreement with experimental data [25,50], showing the reliability of PCFF. In addition, the properties of CNT [51] and the interfacial interactions between CNT and epoxy [26,52] can be characterized with PCFF, which is well correlated to experimental findings.
QE* method, as the prediction of charges in polymeric systems is in good agreement with experiments and ab initio calculations [53]. The non-bonded interactions, including both Coulombic interactions and van der Waals interactions are calculated with a cutoff distance of 10 Å, which is commonly selected in the study of CNT-epoxy systems [25,34]. The particle-particle particle-mesh (PPPM) algorithm [54] is used to account for the long-range Coulombic interactions. All the simulations are performed under periodic boundary conditions.

2.2. Simulation details and theoretical analysis

The initial configurations are first equilibrated using NVT ensemble (constant number of particles and constant temperature) at the temperature of 300 K for 100 ps. Then, the internal stresses are removed by a further relaxation at the pressure of 1 atm using NPT ensemble (constant number of particles, constant temperature and constant pressure) for another 10 ns. The root mean square displacement (RMSD) of the atoms reaches a constant level before creep simulation. In addition, the changes of con configurations in each case to minimize random errors in the simulation results. The corresponding density of equilibrated structures and the system parameters for nanocomposite systems are summarized in Table 1. The densities are found to be higher than the obtained value of neat epoxy in the previous study [55]. The increase of density in epoxy in the previous study [55]. The increase of density in epoxy during creep deformation during the simulation time. The resulting evolution of the strain is calculated as $\varepsilon(t) = \frac{L(t) - L_0}{L_0} \times 100\%$, where $L$ denotes the instant length of the simulation box parallel to the direction of the applied stress and $L_0$ the initial equilibrium value of this length before creep simulation. In addition, the changes of configurations in the nanocomposite systems during the deformation process are tracked for comparison to analyze the creep response with different CNT-associated parameters.

During creep deformation, the chain reorientation in the polymer matrix is induced by the external stress, and the molecular motion is altered over time. There is a strong correlation between the molecular mobility and the strain rate [19,57–59]. To quantify the local segmental dynamics of polymer chains in the epoxy matrix under constant stress, the bond autocorrelation function is commonly employed [60,61], which is defined as:

$$C_b = \langle P_2[u(0) \cdot u(t)] \rangle$$  \hspace{1cm} (2)

Here, $P_2$ is the second Legendre polynomial. $u(0)$ and $u(t)$ represent the unit vectors aligned along the bonds connecting the end carbon atom to the central carbon atom in DGEBA at the initial state and the running time $t$ respectively, as shown in Fig. 1(c). The angular brackets denote an average over all the bonds in the systems. This function can help to characterize the changed mobility of polymer chains in nanocomposites during creep deformation. The change of dynamics can be further quantified by fitting the bond autocorrelation function to the Kohlrausch-Williams-Watts (KWW) function, which is expressed as [62,63]:

$$C_b(t) = C_0 e^{-(t/\tau_{eff})^{\beta}}$$  \hspace{1cm} (3)

where $C_0$, $\tau_{eff}$ and $\beta$ are fitting parameters, representing the pre-exponential factor that accounts for the relaxation process in very short time scales, the characteristic relaxation time, and the stretching exponent. The polymeric systems experience a range of relaxation times under stress. The different ranges, including the short-time regime that corresponds to the bond and angle vibrations known as $\alpha$ relaxation, and the long-time regime that corresponds to the conformational transitions known as $\beta$ relaxation, are considered in the fitting of the bond autocorrelation function by the KWW function [64,65]. Here, the characteristic relaxation time $\tau_{eff}$ is taken as the measure of the change in dynamics in different time regions instead of the measure of structural relaxation time, which assumes a single relaxation process is dominant over the probed time scales [57]. Moreover, the characteristic relaxation time reflects the relaxation time to the equilibrium state of polymer chains, therefore the larger value of the characteristic relaxation time indicates that a longer time is required to generate the same creep deformation of material systems.

3. Results and discussion

3.1. Effect of CNT length

We first examine the effect of CNT length on the creep response of CNT-epoxy nanocomposites. Fig. 2(a) plots the time evolution of creep strain for the CNT-epoxy nanocomposites containing CNTs with lengths of 4.92 Å, 14.76 Å, 24.60 Å and 49.19 Å. The creep responses of these nanocomposites present two creep stages during the simulation time, including the primary creep and the secondary creep, which are consistent with the trend observed from experiments [66,67]. After applying the stress, the system deforms at a high strain rate at the primary creep stage with an instantaneous

<table>
<thead>
<tr>
<th>System</th>
<th>CNT length (Å)</th>
<th>CNT weight fraction (wt%)</th>
<th>No. of CNT</th>
<th>Total no. of atoms</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanocomposites containing dispersed CNTs with different lengths</td>
<td>4.92</td>
<td>4.4</td>
<td>10</td>
<td>16230</td>
<td>1.156 ± 0.002</td>
</tr>
<tr>
<td></td>
<td>14.76</td>
<td>4</td>
<td>16170</td>
<td>1.157 ± 0.001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>24.60</td>
<td>49.19</td>
<td>16150</td>
<td>1.159 ± 0.002</td>
<td></td>
</tr>
<tr>
<td></td>
<td>49.19</td>
<td>1</td>
<td>16150</td>
<td>1.176 ± 0.003</td>
<td></td>
</tr>
<tr>
<td>Nanocomposites containing dispersed CNTs with different weight fractions</td>
<td>24.60</td>
<td>2.2</td>
<td>1</td>
<td>15950</td>
<td>1.158 ± 0.003</td>
</tr>
<tr>
<td></td>
<td>4.4</td>
<td>2</td>
<td>16150</td>
<td>1.159 ± 0.002</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.4</td>
<td>4</td>
<td>16550</td>
<td>1.173 ± 0.003</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.1</td>
<td>6</td>
<td>16950</td>
<td>1.188 ± 0.001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.1</td>
<td>4</td>
<td>16950</td>
<td>1.202 ± 0.001</td>
<td></td>
</tr>
<tr>
<td>Nanocomposites containing aggregated CNTs with different weight fractions</td>
<td>24.60</td>
<td>4.4</td>
<td>2</td>
<td>16150</td>
<td>1.158 ± 0.002</td>
</tr>
<tr>
<td></td>
<td>8.4</td>
<td>4</td>
<td>16550</td>
<td>1.181 ± 0.003</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.1</td>
<td>6</td>
<td>16950</td>
<td>1.202 ± 0.001</td>
<td></td>
</tr>
</tbody>
</table>
response at the beginning, followed by a slow decrease of strain rate from the initial value. The strain rate then remains constant during the secondary creep stage. The secondary creep stage, as the steady-state creep evolution, generally takes up a relatively large fraction of creep time, and the constant strain rate plays an important role in determining the dimensional stability of material systems. The simulation results show that the longer length leads to less instantaneous strain and creep strain during the deformation process, indicating stronger creep resistance in nanocomposite. This is confirmed with experimental results that longer CNTs induced smaller creep rate than shorter CNTs, which can be attributed to better load transfer efficiency from longer CNTs [68]. A similar trend with the effect of CNT length has also been found in the mechanical modulus under tensile deformation [39,69]. To better quantify the steady-state creep, the constant creep strain rates at the steady stage as a function of different lengths are calculated in Fig. 2(b). The creep strain rate is effectively reduced with the increasing CNT length, showing a high dependence of creep response on the CNT length. Specifically, the creep strain rate at the system with long CNT length (49.19 Å) is about 61.7% lower than the corresponding creep strain rate with short CNT length (4.92 Å).

The energy change during creep deformation is also explored to explain different creep responses during deformation. The changes in potential energy, bonded and non-bonded energies of the nanocomposites with short CNT (4.92 Å) and long CNT (49.19 Å) are shown in Fig. 3(a) and (b), which suggest different deformation mechanisms for different CNT lengths. During the primary creep stage, the bond, bond angle and improper energies change slightly for the short CNT case in Fig. 3(a). The increase in the potential energy is associated with increases in the dihedral angle and the non-bonded interaction energies, which are caused by chain rotation and chain slippage in the epoxy matrix under stress. For the long CNT case in Fig. 3(b), the increase of the potential energy is mainly associated with the non-bonded interaction, while the bond, bond angle, dihedral angle, and improper energies change slightly. During the steady-state creep stage, the dihedral angle and the non-bonded energies contribute to the increase of the potential energy in both systems. The chain rotation starts in the secondary creep for the long CNT case. A close look at microstructural evolution in the nanocomposites with short and long CNT is presented in Fig. 3(c) and (d). For the epoxy chains near the CNTs, the aromatic ring on the DGEBA monomer tends to align parallel to the sidewall of CNT due to the π–π stacking type attraction [31,70]. This orientation of epoxy chain appears less in the short CNT case, while more epoxy chains lie flat on the sidewall of CNT in the long CNT case. This is because the epoxy monomers in the crosslinked network structure are not allowed to interact easily with the CNT to achieve a large amount of aligned aromatic rings, and the long length provides more probability for the reorientation. This also indicates more attraction between CNT and epoxy matrix in the long CNT case.

Before applying the external stress, the molecular sizes of CNT-epoxy nanocomposites in the four cases are similar to each other after equilibrium (see Table 2), and the average of simulation box dimensions is 53.2 Å × 53.9 Å × 54.6 Å with the volume of 156,564.4 Å³. However, the increase in density is evident for the long CNT (49.19 Å) as can be seen from Table 1, as the increase in attraction results in a more packed structure at the interface. The interfacial interaction between CNT and epoxy matrix hinders and slows down the stretching and sliding of epoxy chains towards the direction of the applied load, which leads to smaller creep strain and creep strain rate during the deformation process. Additionally, the short CNT is easily driven by the surrounding epoxy chains and tends to rotate and move during the deformation process, while the long CNT remains almost in its original position. The MSD characterizing the movement of CNT for these two cases are evaluated in Fig. 3(e), which suggests the short CNT provides less enhancement of creep resistance than the long CNT. The change in the creep strain rates in different systems is associated with the polymer chain movement in the epoxy matrix. The local segmental dynamics and the corresponding relaxation time are measured in order to explore quantitatively the chain mobility in nanocomposites during creep deformation as shown in Fig. 3(e). The mobility is significantly lowered with longer CNT length as evidenced by the slower decay of $G_2(t)$ immediately after the stress is applied. The trends of the bond autocorrelation decays also correspond to different creep stages during the deformation process. The fast decay apparently appears in the primary creep stage where the strain rate is high. To further explore the change in creep strain rate in different nanocomposites during steady state creep, the local polymer relaxations are measured by fitting the KWW function. The normalized characteristic relaxation time and the stretching exponent as a function of the CNT length from the KWW fittings are shown in Fig. 4(b) and (c). The epoxy chains exhibit longer.
relaxation time with longer CNT length, resulting in slower chain dynamics in the corresponding nanocomposite during creep deformation. Enhanced mobility and faster relaxation time related to strain rate under stress have been found in previous studies \[^{57-59,65}\]. The stretching exponents increase slightly with increasing CNT length, indicating a narrowing of the relaxation spectrum in the nanocomposite system. These results implicitly reveal that the creep deformation is affected significantly by the change from the short length to the long length.

Fig. 3. The energy changes during creep deformation in the nanocomposites with the CNT lengths of (a) 4.92 Å and (b) 49.19 Å. The snapshots capture the structural evolution during creep deformation in the nanocomposites with the CNT lengths of (c) 4.92 Å and (d) 49.19 Å. The CNTs are colored in black. The epoxy segments aligned parallel to the sidewall of CNT are colored in red, and the stretched and sliding epoxy chains are colored in blue. The single-headed arrow indicates the slippage, and the double-headed arrow indicates the stretching. (e) The mean-squared displacement of the CNTs during deformation in the two cases. (A colour version of this figure can be viewed online.)
3.2. Effect of CNT weight fraction

We next investigate the effect of CNT weight fraction on the creep response of CNT-epoxy nanocomposites. The time-dependent creep strain of different nanocomposites containing CNTs with weight fractions of 2.2%, 4.4%, 8.4%, and 12.1% are plotted in Fig. 5(a). The results show that the creep response becomes less pronounced with the increasing amount of CNTs when CNTs are well dispersed. The enhancement of creep resistance in nanocomposites is more obvious at high CNT weight fraction, i.e., 12.1 wt %. This trend is also found in previous experimental results, which show that the increasing content of CNTs with good dispersion can lead to improved creep resistance [12,14]. The strain rates of different systems at the secondary creep stage are calculated in Fig. 5(b). The strain rate presents a linear descending trend with increasing weight fraction. While the strain rate is altered by a larger range under the effect of CNT length, the reduction in the value of creep strain rate is more pronounced when the CNT weight fraction is increased.

To further investigate the difference in the creep response, the microstructural evolution of the nanocomposites with low (2.2 wt %) and high (12.1 wt%) CNT weight fractions during the deformation are shown in Fig. 6(a) and (b). In the low CNT weight fraction case, fewer epoxy chains are aligned to the CNT sidewall, and the movement of these epoxy chains are restricted. More epoxy chains away from the CNT surface are stretched by the external stress and slide against each other during the deformation process. In the height weight fraction case, more surface area of CNTs with the same aspect ratio is allowed to interact with the epoxy matrix, which induces more confinement in the movement of epoxy chains. The CNTs are surrounded by more epoxy chains, and the stretching in the epoxy matrix is restricted. The epoxy chains slippage mainly appears in the area without CNTs, resulting in the creep deformation smaller than that in the low weight fraction case. However, it should also be noted that the higher CNT weight fraction can cause the aggregation of CNTs due to the van der Waals attractions between them during the dispersion process. Similarly, the tendency for CNTs to move close to their neighbors can be observed in the simulation of the nanocomposite with high CNT weight fraction as shown in Fig. 6(c). The bundle formation of nano-fillers in the polymer matrix has been observed in the previous simulation work [71]. The way the dispersion state affects the creep response will be investigated in the next section.

The dynamics and polymer relaxation in the creep process are measured by the bond autocorrelation function and the characteristic relaxation time from KWW fitting as shown in Fig. 7(a) and (b). The slower decay of the bond autocorrelation function under constant stress appears in the nanocomposite systems with higher CNT weight fraction. In the low weight fraction case, the external

Table 2
Dimension of equilibrated systems with different CNT lengths.

<table>
<thead>
<tr>
<th>CNT length (Å)</th>
<th>x (Å)</th>
<th>y (Å)</th>
<th>z (Å)</th>
<th>Volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.92</td>
<td>53.8</td>
<td>54.3</td>
<td>54.5</td>
<td>159213.0</td>
</tr>
<tr>
<td>14.76</td>
<td>53.2</td>
<td>54.1</td>
<td>54.9</td>
<td>158008.8</td>
</tr>
<tr>
<td>24.60</td>
<td>53.2</td>
<td>53.3</td>
<td>54.3</td>
<td>153970.9</td>
</tr>
<tr>
<td>49.19</td>
<td>52.7</td>
<td>53.7</td>
<td>54.8</td>
<td>155083.5</td>
</tr>
</tbody>
</table>

Fig. 4. (a) The bond autocorrelation decay for nanocomposites with the CNT lengths of 4.92 Å, 14.76 Å, 24.60 Å and 49.19 Å during the creep deformation within the simulation time. (b) The fitted characteristic relaxation time in different nanocomposites as a function of the CNT length, the values are normalized by the relaxation time from the undeformed systems. (c) The corresponding stretching exponent as a function of aspect ratio. The trends indicate the increasing chain mobility with decreasing CNT length. (A colour version of this figure can be viewed online.)

Fig. 5. (a) Creep strain as a function of time during creep deformation of nanocomposites with the CNT weight fractions of 2.2%, 4.4%, 8.4% and 12.1%. (b) The corresponding constant strain rate at the secondary creep stage. The increasing creep response is found with decreasing weight fraction. (A colour version of this figure can be viewed online.)
Fig. 6. The snapshots capture the structural evolution during creep deformation in the nanocomposites with the CNT weight fractions of (a) 2.2% and (b) 12.1%. The CNTs are colored in black. The epoxy segments aligned parallel to the sidewall of CNT are colored in red, and the stretched epoxy chains are colored in blue. The double-headed arrow indicates the stretching. (c) The tendency of aggregation of CNTs in the high CNT weight fraction case. (A colour version of this figure can be viewed online.)

Fig. 7. (a) The bond autocorrelation decay for nanocomposites with the CNT weight fractions of 2.2%, 4.4%, 8.4% and 12.1% during the creep deformation within the simulation time. (b) The fitted characteristic relaxation time during secondary creep stages in different systems as a function of weight fraction, the values are normalized by the relaxation time from the undeformed systems. (c) The corresponding stretching exponent as a function of weight fraction. The trends indicate the increasing chain mobility with decreasing CNT weight fraction. (A colour version of this figure can be viewed online.)
3.3. Effect of CNT dispersion

The previous experimental studies found that the aggregation of nano-fillers in polymer matrix leads to poor mechanical performance, which reduces the efficiency of reinforcement for nanocomposites [72–74]. For the creep responses, the simulation results of time-dependent creep strain in the CNT-epoxy nanocomposites with two different dispersion states, including well dispersion and aggregation are shown in Fig. 8(a). Consistent with the experimental observations [9,74], all sets of results show a considerable decrease in creep strain with dispersed CNTs compared to that with aggregated CNTs. The creep deformation becomes severe with high CNT weight fraction, especially in the case of 8.4 wt% CNTs. The corresponding creep strain rate at the steady stage shown in Fig. 8(b) exhibits opposite trends in these two cases. The strain rate decreases with good dispersion of CNTs, and increases with the aggregation of CNTs. Although there is little difference in the initial creep for the two dispersion states with the same weight fractions, the deviation in the creep strain rate leads to different deformation during creep process. These results suggest that the function of creep resistance is severely impaired in the aggregation state, especially at high CNT weight fraction.

The creep responses of the nanocomposites with 8.4 wt% CNTs in two dispersion states are shown in Fig. 8(a) and (b). In contrast to the well-dispersed state, fewer epoxy chains are aligned parallel to the direction of the CNT sidewall in the aggregated state. The sliding and rotation in the direction of the external stress in the epoxy matrix are more obvious in the aggregated state. This is mainly attributed to the difference in the interfacial area between CNT and epoxy. The well-dispersed state provides more available interfacial area under the same volume fraction condition, maximizing the interfacial attraction between CNT and epoxy and the confinement of epoxy movement.

Accordingly, the local segmental dynamics are measured as shown in Fig. 10(a). The enhancement of dynamics is more significant in the aggregated state with higher CNT weight fraction. The nanocomposites with dispersed CNTs has a better structural network that can provide better creep resistance, as the movement of epoxy chains is uniformly trapped during creep deformation. In contrast, the aggregation of CNTs apparently causes local confinement of chain movement. The dynamics in the nanocomposites presents heterogeneous, and the epoxy chains far from the CNT cluster have higher mobility. Therefore, the addition of aggregated CNTs leads to reduction in the performance of creep resistance. The characteristic relaxation time and the stretching exponent are calculated in Fig. 10(b) and (c). Compared with the dispersed state, the relaxation time is reduced in the aggregation state, resulting in fast chain dynamics and increasing creep response. For the dispersed state, the increases in both the relaxation time and the stretching exponent indicate that more epoxy chains are effectively restricted with high weight fraction. The decreasing stretching exponent in the aggregated state shows that the distribution of bond relaxation time becomes more heterogeneous as the local confinement becomes more apparent high weight fraction. The results indicate that the achievement of better creep resistance in nanocomposites from experiments relies on the state of nanodispersion, where each CNT is individually dispersed in epoxy matrix.

The above simulation results demonstrate that the improvement of creep resistance in epoxy-CNT nanocomposites can be obtained by modulating different CNT-associated parameters including the length, the weight fraction and the dispersion state. The increasing CNT length provides more probability for the interfacial binding, and the increasing CNT weight fraction in the well-dispersed state enlarges the interfacial area for the interactions between CNT and epoxy matrix. Therefore, long CNT length and high CNT weight fraction with a good dispersion state can effectively reduce creep deformation and slow the dynamics of the system, leading to an enhancement in creep resistance. While this work focuses on the three important factors that are commonly
encountered in applications, there are still some other design constraints. The roles of other control parameters such as CNT radius, CNT orientation and CNT/epoxy interactions will be investigated in a future study.

4. Conclusions

In this study, the effects of CNT-associated parameters on the creep responses of nanocomposites are investigated using MD simulations. The simulation results reveal that both the creep strain and the creep strain rate decrease with increasing CNT length and CNT weight fraction. Such enhancement in creep resistance must be achieved alongside a well-dispersed state of CNT in the epoxy matrix. In addition, the dynamics of materials systems are altered with changes in the relaxation time during the creep deformation, which is in line with the changes in the creep strain rate. The molecular simulations provide direct insight into the role played by CNTs in the conformational changes and the interfacial interactions.
between CNT and epoxy that governs the creep response of CNT-epoxy nanocomposites. The sliding and stretching of epoxy chains are effectively confined in the nanocomposites with long CNT length, high CNT weight fraction and good CNT dispersion. The understanding of the effect of different CNT-associated parameters on the creep deformation and the strengthening mechanism in CNT-epoxy nanocomposites is useful for the design of targeted creep-resistant nanocomposites in applications.

Acknowledgment

The authors are grateful to the support from the Research Grants Council (RGC) of the Hong Kong Administrative Region, China [Project No. CityU1255616].

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