

TUNING INTERFACE VIA MULTI-SCALE MODELING FOR SUPERIOR CARBON NANOTUBE-POLYMER NANOCOMPOSITES/YARNS

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ABSTRACT

This study is concerned with finding an improved route to achieve superior properties of carbon nanotube (CNT)-reinforced nanocomposites by designing their interface using multi-scale modeling. CNTs, widely used as fillers in nanocomposites, and polymer epoxy matrices, are coarse-grained and simulated via dissipative particle dynamics. Then, reverse-mapping of the coarse-grained models into atomistic detail is implemented. The crosslinking mechanism is simulated at the atomistic detail and thermoset matrices containing EPON 862 and TETA hardener molecules with different crosslinking degrees are reconstructed. The physical and mechanical properties of nanocomposites are studied at the molecular level so that optimum process and materials parameters, which are tuned in the production of CNTs reinforced composites, can be explored in detail. The overall mechanical response of uncrosslinked and crosslinked matrix and nanocomposites generated from reverse-mapped systems when subjected to mechanical loading is provided by the stress-strain relationship (up to 5% strain) is presented.

1 INTRODUCTION

Computer modeling and simulation play important roles in exploring the parameters affecting the macroscopic properties of nanocomposites/yarns due to reinforcement. These composites exhibit many superior properties, including mechanical behavior, which can be tuned by an appropriate matrix-filler interaction. However, poor interactions between the matrix and nanofillers are one of the key limiting factors for conveying excellent mechanical properties. Therefore, finding an improved route to achieve superior properties of carbon nanotube (CNT) reinforced nanocomposites, while designing the interface via multi-scale modeling, is of interest. MD simulations have been successfully applied to polymer-CNTs composite systems by several research groups [1-4]. However, to implement solely MD simulations to predict mechanical properties can be challenging due to the requirement of larger representative simulation boxes and longer simulation times to obtain well-relaxed atomistic structures, particularly in presence of CNTs. Herein, we propose a novel multi-scale numerical simulation method for nanocomposites, which can be applied both to thermoset and thermoplastic matrices. First, a coarse-grained parameterization is developed to study nanocomposites on longer length scales. Next, a reverse-mapping process to project atomistic structure back onto the coarse-

grained system is carried out. Consecutive numerical simulations at different length-scales allow prediction of long-term behavior of polymer matrices where direct MD simulations are not time-effective [5-7]. Moreover, we have also explored this multi-scale approach in thermoplastic matrices such as polyvinyl butyral (PVB) and polystyrene-co-glycidyl methacrylate (PSt-co-GMA) which are experimentally proven as good candidates for CNTs reinforced nanofiber/yarns.

In this study, crosslinking mechanism is also simulated and thermoset matrices containing EPON 862 and TETA hardener molecules with different crosslinking degrees are reconstructed from reverse-mapped structures. Mechanical properties of nanocomposites are studied at the molecular level so that optimum process and materials parameters, which are tuned in the production of CNTs reinforced composites, can be explored in detail.

2 METHODS & MATERIALS

2.1 DPD Parametrization

DPD parameterization of uncrosslinked epoxy consisting EPON 862 and TETA hardener molecules was previously studied and optimized by Ozden-Yenigun [8]. We therefore provide a brief overview of the parameterization methodology used. In a DPD simulation, the chains need to be partitioned into beads made up of chemically distinct units that also have similar sizes. The units we use in the current study are displayed in Figure 1(a) whereby the **A**, **B₁**, **B₂** and **C** units represent epoxy and hardener segments, respectively. Meanwhile, considering the regular pattern of carbon nanotubes, nanostructures were coarse-grained based on motion groups shown in Fig. 1(b). Following the established protocol, Hildebrand solubility parameters (δ) [9] were calculated from successive 1 ps equilibrations step and 100 ps MD simulations on simulation boxes that contain 10 beads of the same type with a density of 1.0 g cm^{-3} at 298 K, using the Amorphous Cell and Forcite modules of Materials Studio 7.0® [10]. For all non-bonded interactions, a cut-off radius, r_c , of 8.5 \AA and periodic boundary conditions were applied in the canonical ensemble (NVT). The molar volume of the beads, V_m , was calculated using the ACDLabs/Chemsketch 5.0 [11].

Solubility parameters were determined according to,

$$\delta = \left(\Delta E_v / V_m \right)^{1/2} = (CED)^{1/2} \quad (1)$$

where ΔE_v and CED correspond to molar energy of vaporization and cohesive energy density, respectively. The Flory-Huggins interaction parameters, χ , of the beads were then calculated from,

$$\chi_{ij} = \frac{V_m}{k_B T} (\delta_i - \delta_j)^2 \quad (2)$$

where V_m is the average molar volume of the beads i and j . The calculated values of δ and χ are displayed in Table 1.

χ , is related to the thermodynamics of mixing, and the DPD interactions parameters, a_{ij} , obtained from χ is a measure of repulsion between the beads. The latter are calculated using the linear relationship put forth by Groot and Warren [12] as $a_{ii} = 25k_bT$ and $a_{ij} \approx a_{ii} + 3.27\chi_{ij}$ for a box density of 3 DPD units (Table 1). Carbon nanotubes were treated as rigid rods with high spring constant and repulsive parameters were assigned to describe the interactions between CNTs – epoxy and hardener molecules. We note that this treatment assumes equal repulsive interactions between like beads, which is strictly true only when the molar volumes of the two components are equal [13].

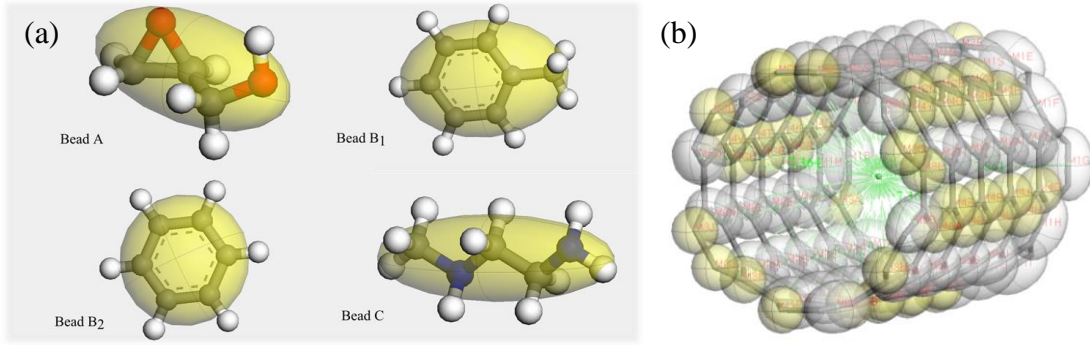


Figure 1: Partitioning of the beads for coarse-grained simulations of a) EPON 862 epoxy and TETA hardener and b) CNTs

In this work, we are interested in the finding long-time evolution of the coordinates of each segment by tracking the centroids of beads. To obtain well-equilibrated crosslinked systems in molecular detail, reverse-mapping was executed at the next stage.

	A	B ₁	B ₂	C	C6
δ (cal cm ⁻³) ^{1/2}	12.46	9.58	9.99	12.66	7.03
V_m (cm ³ mol ⁻¹)	62.8	105.7	89.4	90.5	89.4
A	0.00 25.00	1.18	0.78	0.01	4.59
B₁	25.86	0.00 25.00	0.03	1.57	4.59
B₂	27.56	25.10	0.00 25.00	1.08	4.59
C	25.01	30.14	28.54	0.00 25.00	4.59
C6	40.00	40.00	40.00	40.00	0.00 25.00

Table 1: Properties of beads defined in Fig.1. Solubility parameters, δ , molar volumes V_m , Flory-Huggins interaction parameters, χ_{ij} , (upper diagonal, shown in **bold**) and DPD interaction parameters, a_{ij} (lower diagonal).

2.2 DPD Simulations

For DPD simulations, epoxy, hardener molecules and CNTs were coarse-grained via a pattern document by maintaining initial configuration of each molecule. Different bead names and motion groups were assigned to each structure at this step. Cubic boxes having $30 \times 30 \times 30 u^3$ volume were constructed with a density of 3 DPD, units where u is the cut-off radius. A harmonic spring constant of 200 was chosen for polymer and rigid nanotube beads located consecutively along the structure. The temperature and bead masses were taken as unity and the time step was set 254,117 fs (≈ 0.05 reduced units). The systems were equilibrated for 20,000 DPD time steps, followed by 100,000 DPD time steps for data collection and analysis.

2.3 Reverse-Mapping Methodology

Several methods [14-18, 5-7] have been proposed for reverse-mapping of coarse-grained model into a detailed atomistic model. In this study, a general strategy in line with Marrink *et al.* [18] was adapted to reconstruct low energy atomistic structures. This algorithm significantly reduces data processing times and enables the reconstruction of larger polymer systems. Two consecutive steps have been followed to generate atomistic ensemble that underlies its corresponding well-relaxed coarse-grained system. First, atomistic molecules were positioned close to their reference coarse-grained particles by matching motion groups and centroids. The second step was to relax the

constructed reverse-mapped systems, which follows the successive route of optimization, cooling cycle (from 1500 K to 300 K) at fixed restraint ($100 \text{ kcal mol}^{-1} \text{ \AA}^{-2}$) and short dynamics with the decreasing restraint energy. As the assigned restraints were gradually removed, relaxed reverse-mapped structures were achieved. Later on, crosslinking reaction was simulated both in neat epoxy system and in presence of CNTs under the same conditions. Unreinforced and reinforced epoxy networks were subjected to detailed molecular dynamics simulations for simulation times of up to 5 ns.

2.4 Mechanical Properties Calculation

Stress states associated with loading were obtained from the deformation of the simulation cell. For each strain level, the unit cell was compressed along one dimension (e.g. the y -direction) and the other two dimensions (e.g. x and z -directions) were extended to maintain the constant density; in each compression step, the periodic cell was post-equilibrated (200 ps) with the new dimensions. The stresses were averaged in normal and shear directions over the last half of the equilibration run. Stress tensors (δ_{ij}) of reinforced and unreinforced systems up to 5% strain were obtained and interpreted to calculate elastic modulus and compressive modulus from normal directions.

3 RESULTS AND DISCUSSION

To calculate the mechanical behavior of neat epoxy system and monitor the effects of crosslinking, we utilized reverse-mapped trajectories of both neat and reinforced epoxy systems. The mechanical tests described below were carried out to determine the stress-strain behavior in the normal directions (x, y). Here, we first investigate the change in compressive/tensile strength and modulus during the process of curing reaction in neat epoxy systems. In Fig. 2, it is clear that both compressive/tensile strength and elastic modulus have an apparent dependence on the conversion of reactant. As the curing reaction proceeds, the compressive strength (0.2% strain offset) and modulus (slopes of the stress-strain curves) both increase, as shown in Table 2. The highest compressive strength and elastic moduli are observed in 67% crosslinked epoxy systems (Fig. 3& Table 2). It is predictable that cross-linking plays a significant role in enhancing mechanical properties. As the reaction proceeds, more linkages are formed among epoxy and hardener molecules, thus there would be less chain mobility. Thus, compressive strength and modulus gradually increase with an increasing extent of reaction. Fig. 2(b) reveals stress-strain behavior in another normal direction, x , where is subjected to tensile loading. New linkages in the matrix may lead to anisotropy. There is slight difference between the elastic moduli in the tensile (x and z) directions where at higher conversion rates this becomes much clearer due to the contribution of new linkages.

We next present the results due to the inclusion of CNTs into the system. CNTs are known as stiff and strong materials that would also increase mechanical properties of epoxy. On the other hand, their incorporation into thermoset matrices reduces crosslinking density, which has reverse effect than stiffening. Besides, due to tubular structure and mismatches in elastic modulus in different directions, CNTs would contribute to anisotropy. First, as seen in Fig 4(a) and Fig 4(b), the stress-strain behavior in compressive and tensile loadings indicated enhanced mechanical response within the incorporation of CNTs. Even though CNTs reduce the crosslinking degree, which is effective in increasing mechanical properties, their high strength and stiffness compensate for this effect. Fig 5 shows the yield strength (0.2% strain offset) and elastic modulus of CNTs reinforced epoxy in compression direction. It is clear that embedding CNTs into epoxy systems increase both modulus and strength strengthens the polymer network. However, from experimental point of view, post-curing might be required to alter the effect of CNTs.

	Compressive Strength (GPa)	Elastic Modulus (GPa)
<i>Neat Epoxy Systems</i>		
0% crosslinked	0.68±0.15	3.65±0.29
43% crosslinked	0.96±0.14	4.55±0.18
67% crosslinked	1.21±0.15	5.27±0.65
<i>CNTs Reinforced Systems</i>		
0% crosslinked	0.74±0.05	3.98±0.21
27% crosslinked	0.79±0.27	4.18±0.31
56% crosslinked	1.24±0.17	5.50±0.70

Table 2: Mechanical properties of neat and CNTs reinforced systems at different conversion rates.

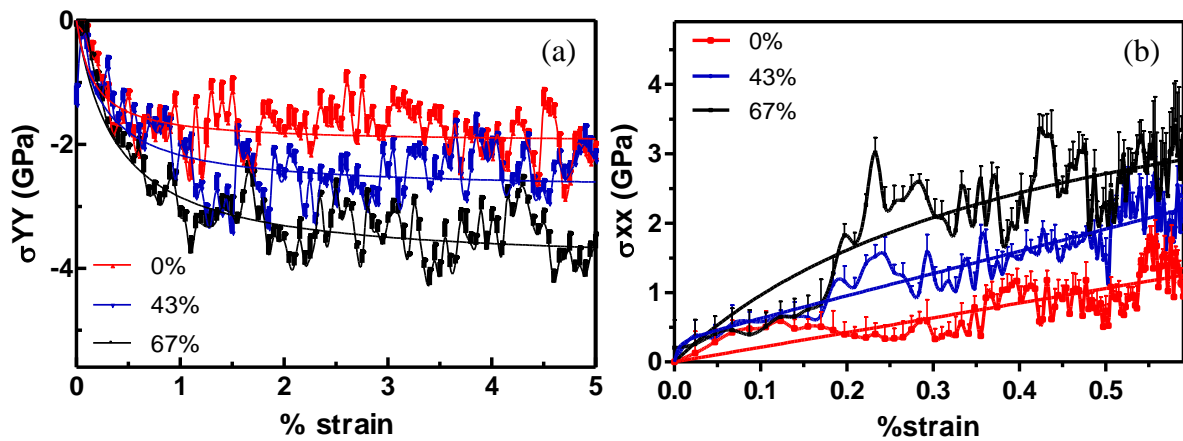


Figure 2: MD simulated (a) σ_{YY} stress-strain curves and (b) σ_{XX} stress-strain curves of neat epoxy resins.

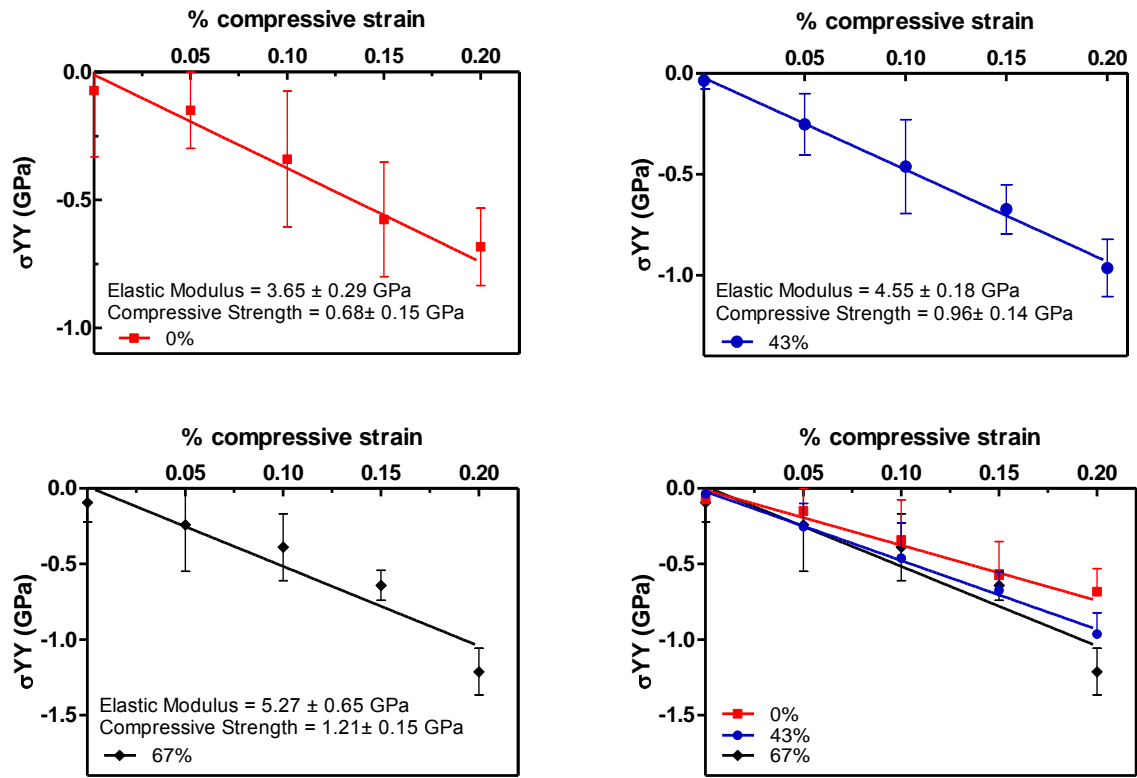


Figure 3: MD simulated σ_{YY} stress-strain curves of neat epoxy resins in elastic regime.

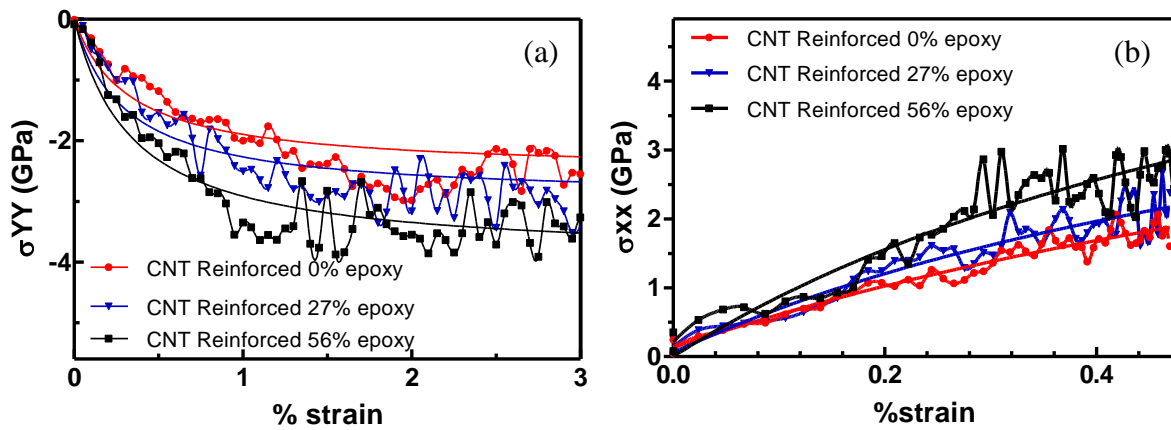


Figure 4: MD simulated (a) σ_{YY} stress-strain curves and (b) σ_{XX} stress-strain curves of CNT reinforced epoxy

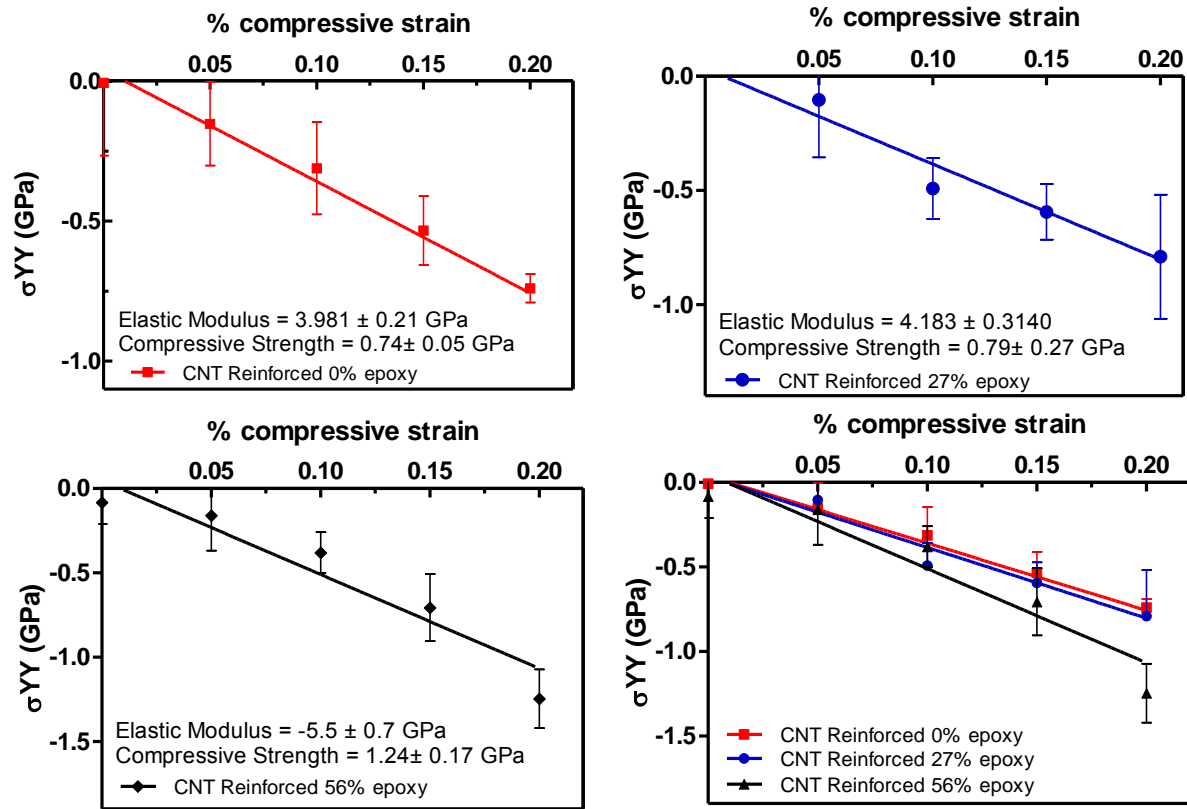


Figure 5: MD simulated σ_{YY} stress-strain curves of CNTs reinforced epoxy resins in elastic regime.

4 CONCLUSION

We have developed a computational strategy for simulating the formation of cross-linked neat and CNTs reinforced polymer networks and predicting their mechanical properties. This methodology based on multiscale simulations involves the following four separate procedures: (i) coarse-graining of epoxy monomers and CNTs, (ii) reverse mapping of the coarse-grained model to a fully atomistic representation and its further equilibration and refinement (iii) cross-linking the monomers (iv) simulation of the atomistic model through classical molecular dynamics (MD) and mechanical testing. Our MD simulated results indicate clearly that, both the elastic moduli (slopes of the stress–strain curves) and compressive strength (at 0.2% offset) of the reinforced composites increases remarkably. Moreover, compressive strength and modulus gradually increase with an increase of conversion, both in neat and reinforced epoxy systems.

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