

Understanding the effect of functionalization on mechanical properties of carbon nitride reinforced epoxy composites from molecular level

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Abstract. In this work, molecular dynamics (MD) simulations were performed to explore the effects of hydroxyl functionalization on the mechanical properties of carbon nitride (C₃N) reinforced epoxy composites. Pristine C₃N and hydroxy-functionalized carbon nitride (C₃N-OH) reinforced epoxy composites were constructed. Results show that the existence of hydroxyl can significantly improve the tensile and compressive mechanical properties of epoxy/C₃N composites. The tensile yield strength of C₃N-OH reinforced epoxy composite enhanced about 81% compared with that of pristine C₃N reinforced epoxy composite. The root mean square displacement (MSD), interaction energy and free volume distribution of the two models were calculated to understand the reinforcing mechanism. This work promotes the application of two-dimensional C₃N in enhancing the mechanical properties of epoxy.

Keywords: epoxy resin, carbon nitride, hydroxyl functionalization, mechanical property, molecular dynamics.

1. Introduction

Epoxy resin has been widely used in aerospace, coating and electronics fields due to their outstanding mechanical properties and thermostability [1]. However, the crosslinking network structure of epoxy results in its brittleness, weak fatigue resistance and low impact toughness, which limits the application of epoxy in high-end fields [2]. It is urgent to study how to enhance the mechanical properties of epoxy resin to expand its application.

Extensive research have been carried out to improve the mechanical properties of epoxy [3, 4]. It is reported that embedding nanofillers into epoxy is an effectively method. Thereinto, graphene is considered to be an ideal reinforcement because of its superior mechanical properties . Rafiee *et al.* [5]reported that low content of graphene can significantly enhance the tensile strength and fracture toughness of epoxy.

Recently, as a kind of graphene like two-dimensional material, carbon nitride has received considerable attention. From the previous literature one can see that carbon nitride exhibits favourable multifunctional characteristics and is considered to be a promising alternative to graphene [6, 7]. Ji *et al.* confirmed that C₃N exhibits better reinforcement effects on the Young's modulus of epoxy compared with graphene [8]. According to previous findings, surface functionalization can improve the interfacial properties of epoxy composites [9]. However, so far, as we know, the effects of surface functionalization on mechanical properties of C₃N reinforced epoxy composites are still lack of investigation.

Inspired by the above research, this work focuses on the effect of functionalization on the mechanical properties of epoxy/C₃N composites. Pristine C₃N and C₃N-OH were selected to reinforce epoxy composites. The tensile and compressive properties of epoxy/C₃N and epoxy/C₃N-OH systems were studied using MD simulations. The enhancement mechanism was revealed via analyzing the

MSD, interaction energy and free volume distribution of the two systems. It provides a theoretical basis for understanding the mechanical properties of functionalized carbon nitride reinforced epoxy composites.

2. Simulation method

2.1. Atomistic models construction

In this work, the diglycidyl ether of bisphenol A (DGEBA) monomer is crosslinked with triethylenetetramine (TETA) to form the epoxy matrix. The molecular structures of DGEBA and TETA are shown in Fig. 1b. The models of pristine carbon nitride (C_3N) and hydroxy functionalized carbon nitride (C_3N -OH) are shown in Fig. 1a and 1c, respectively. In order to investigate the effect of functionalization on mechanical properties of carbon nitride reinforced epoxy composites from molecular level, C_3N reinforced epoxy composite (referred as epoxy/ C_3N system) and C_3N -OH reinforced epoxy composite (referred as epoxy/ C_3N -OH system) were built respectively. In the modeling process, the C_3N (or C_3N -OH) sheet, whose size was set to be $25 \text{ \AA} \times 25 \text{ \AA}$, was inserted in the simulation cell with a size of $30 \text{ \AA} \times 30 \text{ \AA} \times 30 \text{ \AA}$. Then the DGEBA and TETA molecules were randomly packing in the available place based on the ratio of 3:1. The density of the uncross-linked epoxy was 1.1 g/cm^3 , which is close to the experimental and simulation value [10, 11]. Firstly, conjugate gradient method was used to optimize the uncrossed-linked models and the energy convergence criterion was set to be $0.0001 \text{ kcal mol}^{-1}$. Then the models are equilibrated for 500 ps under isothermal-isobaric (NPT) ensemble at 300 K and 1 atm. Subsequently, the crosslinking reaction was performed by a crosslinking algorithm reported in Lau's research [12]. The cross-linked degree of the two models considered in this work is about 86%.

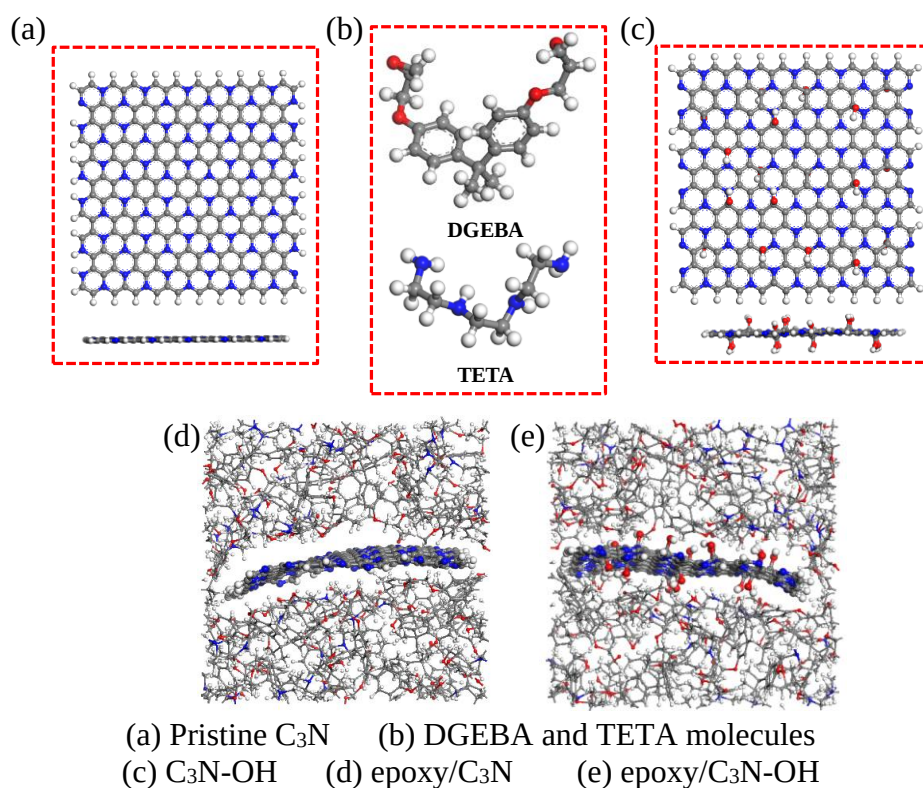


Figure 1. Diagram of the epoxy/ C_3N composite model.

2.2. Simulation details

The crosslinked epoxy/ C_3N system and epoxy/ C_3N -OH system was minimized and relaxed using the large-scale atomic/molecular massively parallel simulator (LAMMPS) package [13]. Polymer consistent force field (PCFF) [14] was adopted to describe the atomistic interactions within the

composite systems. The crosslinked models were relaxed under isothermal-isochoric (NVT) ensemble at 300K for 1ns at first, then under NPT ensemble at 300K for 1ns, and finally under NVT ensemble at 300K for additional 1ns. The integration time step during the relaxation process was set to be 0.25 fs. After the relaxation process, uniaxial tensile and compressive loads were applied along X, Y or Z directions, respectively. The deformation processed were performed under NPT ensemble with a strain rate of $5 \times 10^8 \text{ s}^{-1}$.

3. Results and discussion

3.1. Tensile behavior of C₃N/epoxy composites

In this section, uniaxial tensile tests were performed along X, Y or Z directions for epoxy/C₃N and epoxy/C₃N-OH systems to study the effect of functionalization on the tensile mechanical properties of carbon nitride/epoxy composites. Fig. 2a~c shows the stress-strain curves of epoxy/C₃N and epoxy/C₃N-OH composites along X, Y or Z directions, respectively. According to the stress-strain curves, the yield strength and Young's modulus can be obtained and are collected in Table 1. As shown in Fig. 2a and Table 1, the yield strength and Young's modulus of epoxy/C₃N-OH along X direction are calculated to be 250.86 MPa and 5.70 GPa, corresponding to an improvement of 81.47% and 34.43% compared with epoxy/C₃N, respectively. From Fig. 2b and Table 1 one can see that the yield strength of epoxy/C₃N-OH along Y direction is 165.41 MPa, which is about 45.49% improvement compared with epoxy/C₃N (113.69 MPa). Epoxy/C₃N-OH presents the Young's modulus of 4.52 GPa, *i.e.*, is 9.18% higher than that of epoxy/C₃N. The yield strength and Young's modulus for epoxy/C₃N-OH along Z direction are determined to be 74.49 MPa and 2.23 GPa, which are 68.49% and 64.98% stronger than that of epoxy/C₃N, respectively (see Fig. 2c and Table 1). According to the results above, one can see that the mechanical properties of epoxy/C₃N-OH, including yield strength and Young's modulus, are stronger than those of epoxy/C₃N under uniaxial tensile loads long the X, Y, or Z directions. It indicating that surface hydroxyl modification of two-dimensional C₃N can effectively improve the yield strength and Young's modulus of epoxy/C₃N composites under the tensile loads.

Table 1. Mechanical properties, interaction energy and free volume for the two models.

Direction	Parameters	C ₃ N/Epoxy	C ₃ N-OH/Epoxy
Along X direction	Tensile yield strength [MPa]	138.24	250.86
	Young's modulus [GPa]	4.24	5.70
	Compressive yield strength [MPa]	117.44	164.71
	Compressive modulus [GPa]	2.72	2.86
Along Y direction	Tensile yield strength [MPa]	113.69	165.41
	Young's modulus [GPa]	4.14	4.52
	Compressive yield strength [MPa]	156.95	233.83
	Compressive modulus [GPa]	3.02	3.74
Along Z direction	Tensile yield strength [MPa]	44.21	74.49
	Young's modulus [GPa]	1.36	2.23
	Compressive yield strength [MPa]	240.99	295.23
	Compressive modulus [GPa]	3.96	4.78
Interaction energy [Kcal/mol]		-978	-1789
Free volume distribution [$\text{\AA}^3$]		5664.17	5586.83

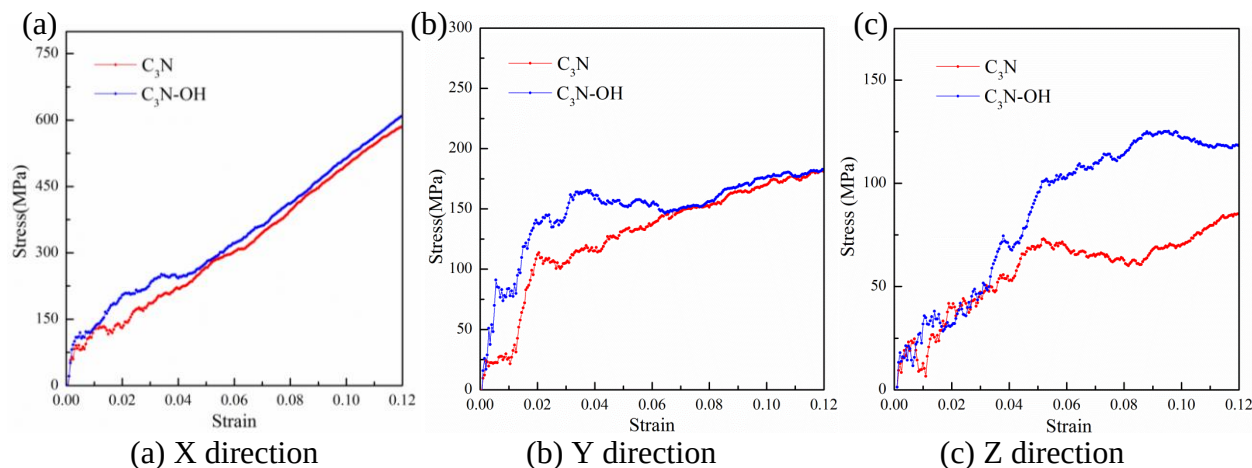


Figure 2. Stress-strain response of two models subjected to uniaxial tensile load.

Fig. 3a,b shows the differences in mechanical properties of epoxy/C₃N and epoxy/C₃N-OH under uniaxial tensile loads along different directions, respectively. As illustrated in Fig. 3a, epoxy/C₃N presents the highest Young's modulus of 4.24 GPa along X direction and the lowest Young's modulus of 1.36 GPa along Z direction. Epoxy/C₃N showcases the strongest yield strength in the X direction, followed by the Y direction, and the weakest in the Z direction. Similar to the epoxy/C₃N, the yield strength and Young's modulus of epoxy/C₃N-OH along X direction is the highest among the three directions (see Fig. 3b). Compared with X and Y directions, Z direction shows significantly weaker yield strength for epoxy/C₃N and epoxy/C₃N-OH systems.

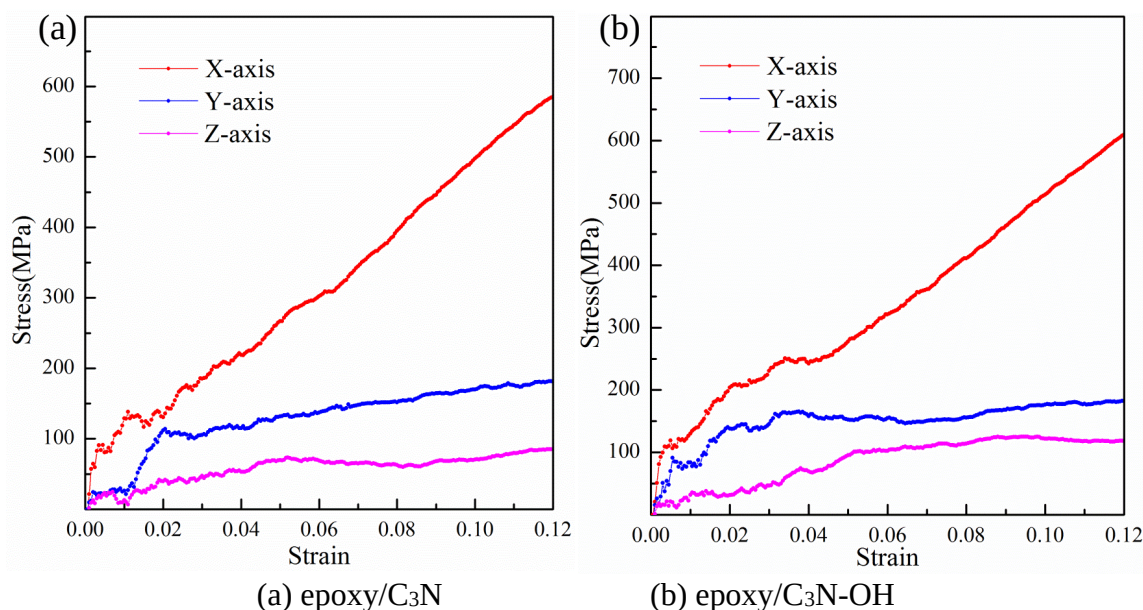


Figure 3. Stress-strain response of two models subjected to uniaxial tensile load along different directions.

3.2. Compressive behavior of C₃N/epoxy composites

To further explore the effect of hydroxyl functionalization on the mechanical properties of epoxy/C₃N composites, uniaxial compression were performed for epoxy/C₃N and epoxy/C₃N-OH composites. Fig. 4a~c plotted the stress-strain response of epoxy/C₃N and epoxy/C₃N-OH composites subjected to uniaxial compressive load along X, Y or Z directions, respectively. The compressive yield strength and compressive modulus are illustrated in Table 1.

As shown in Fig. 4a and Table 1, the compressive yield strength and compressive modulus of epoxy/C₃N-OH along X direction are 164.71 MPa and 2.86 GPa, which are about 40.25% and 5.15% enhancement than that of epoxy/C₃N, respectively. The compressive yield strength and compressive

modulus of epoxy/C₃N-OH along Y direction are calculated to be 233.83 MPa and 3.74 GPa, corresponding to an improvement of 48.98% and 23.84% compared with epoxy/C₃N, respectively (see Fig. 4b and Table 1). From Fig. 4c and Table 1 one can see that compressive yield strength and compressive modulus of epoxy/C₃N-OH along Z direction are 295.23 MPa and 4.78 GPa, *i.e.*, are about 22.5% and 20.71% higher than that of epoxy/C₃N, respectively. Results above indicated that hydroxyl functionalization can significantly enhance the compressive mechanical properties of epoxy/C₃N.

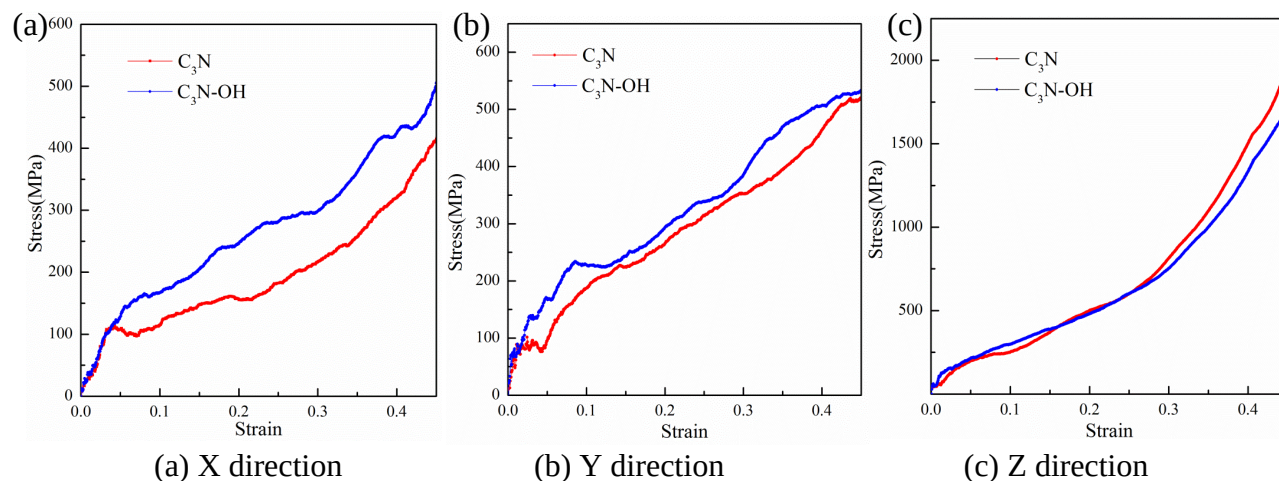


Figure 4. Stress-strain response of two models subjected to uniaxial compressive load.

3.3. Mechanism analysis

In order to further comprehend the enhancement mechanism of hydroxyl functionalization, the MSD, interaction energy and free volume distribution of epoxy/C₃N and epoxy/C₃N-OH systems were calculated as shown in Fig. 5.

MSD is related to the diffusion coefficient of the molecules. A large MSD value represents the higher diffusion coefficient. As shown in Fig. 5a, the MSD value of epoxy/C₃N-OH is higher than that of epoxy/C₃N, indicating that the movements of atoms in epoxy/C₃N-OH are restricted. The phenomenon above maybe caused by the stronger interfacial interaction between C₃N-OH and epoxy. Fig. 5b calculated the interfacial interaction energies of the two models. One can see that the existence of hydroxyl effectively improve the interfacial interaction between C₃N and epoxy. As illustrated in Fig. 5c,d, the free volume of epoxy/C₃N-OH is smaller than that of epoxy/C₃N, suggesting that there are less unoccupied spaces for the translational and rotational motion of epoxy chains in epoxy/C₃N-OH system.

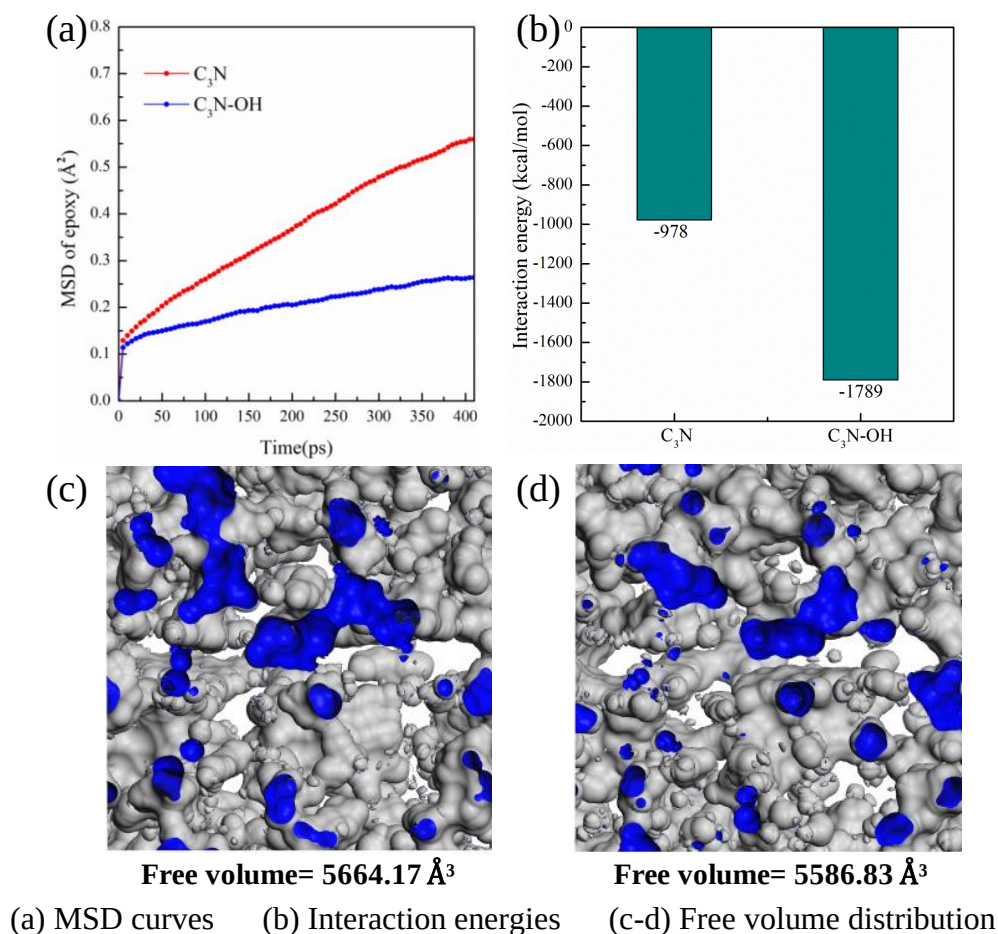


Figure 5. Enhancement mechanism analysis

4. Conclusion

In summary, the effects of hydroxyl functionalization on the mechanical properties of epoxy/C₃N composites were systemically studied using MD method. Results indicates that the tensile and compressive mechanical properties of epoxy/C₃N-OH are much stronger than that of epoxy/C₃N. The enhancement mechanism was explained by analyzing the MSD, interaction energy and free volume distribution of the two models. The smaller MSD value, higher interaction energy and the lower free volume results in the stronger mechanical properties of epoxy/C₃N-OH composite. This paper is helpful to further improve the mechanical properties of epoxy/C₃N composites and expand the application of C₃N.

Acknowledgments

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