Effect of graphene oxide doping on anti-/deicing performance of shape memory epoxy resin

Long Chen[a,b,c]*, Yeqin Shen[a,b], Zhanqiang Liu[a,b], Qinghua Song[a,b], Chaozong Liu[d]

([a] Key Laboratory of High Efficiency and Clean Mechanical Manufacture, Ministry of Education, Jinan, China

[b] School of Mechanical Engineering, Shandong University, Jinan, China

[c] Shenzhen Research Institute of Shandong University, Shenzhen, China

[d] Institute of Orthopaedic & Musculoskeletal Science, University College London, London, United Kingdom)

Abstract: Shape memory GO/EP composites with different fractions of GO were prepared by thermal curing. The glass transition temperature was measured and the shape memory performance experiments were performed. The experimental results shows that with the increasing of GO contents, the shape retention ratio of the shape memory GO/EP composites with 1.25 wt% GO content decreased by 8.40%, while the shape recovery ratio increased by 16.26%. The experimental data were analyzed by molecular dynamics (MD) simulation that the chemical bond between the GO layer and the EP molecule is the reason for improving the shape memory performance. In addition, it was found through MD simulation that the agglomeration of GO reduces the recovery performance of the shape memory GO/EP composites. When GO content was 10 wt%, the recovery performance of GO agglomerated composites was 14.38% lower than that of GO uniformly dispersed, and 3.30% lower

than that of pure shape memory EP. Through the combination of experiment and calculation, a new idea for the design of shape memory GO/EP composites was provided.

Key words: Shape memory, Graphene oxide, Polymer, Thermodynamic, Molecular dynamics simulation

1. Introduction

Shape memory material is a special material that can produce shape recovery by external stimulus [1]. Common stimuli are heat [2-3], electric field [4-5], magnetic field [6-7], acid-base [8], and other external stimulus [9-10]. As an emerging polymer material, shape memory polymer has a wide range of applications in aerospace [11], medical [12-13], and industrial manufacturing [14]. Common shape memory polymers include polycaprolactone diol [15], epoxy resin [16], polyurethane [17], etc. These polymers have high glassy-rubbery modulus, thereby producing shape memory effects. Therefore, the shape memory epoxy resin material can be used for the anti-/deicing of the aircraft.

However, pure shape memory polymers also have certain shortcomings and limitations [18], including lower recovery speed and lower recovery ratio [19]. Therefore, different types of carbon nanoparticles, such as carbon nanotubes [20-21], graphene [22], nanoclay

[23], and metals or metal oxides [24] have been employed to improve shape memory performance [25].

GO is a compound composed of graphene and functional groups (such as hydroxyl and carboxyl), and has physical properties similar to graphene [26-27], including high Young's modulus (1.0 TPa) [28] and high thermal conductivity (~5000 /W(m·K)) [29]. GO is widely added as a filler in polymers [30-31]. A tremendous amount of research have shown that introducing GO to polyurethane can significantly increase the elastic modulus and shape recovery rate [32,33,35]. In addition, adding GO filler can effectively improve the thermal response recovery rate of shape memory epoxy resin [34]. Kim et al. [32] introduced 1.5 wt% of GO to acrylate-terminated polyurethane isocyanate and found that the shape memory performance was improved by 1%. Luo et al. [33] added GO to polyurethane and kept it at 80℃ for 4 hours to obtain a Polyurethane/GO composite with self-healing properties and shape memory properties. The modulus was increased by 147.2%, and the shape recovery ratio reached 88.6%. Xu et al. [34] indicated that adding VGCF-GO filler can effectively improve the thermal response recovery ratio of EP with less than about 10% strain during the stretching process. Under the pre-strain was 10%, the maximum thermal response recovery ratio of the GO doped composite increased by 22%. Hhosh et al. [35] added reduced graphene oxide (RGO) to the polyurethane-polystyrene

material, and the samples show that the shape recovery ratio reaches 265~308 % within 33~44 s under microwave stimulation.

In recent years, molecular dynamics simulation has been widely employed to investigate the performance improvement mechanism of shape memory polymers. Molecular dynamics simulation can analyze the effect of GO doping on the shape memory performance of shape memory epoxy resin from the perspective of molecular stretching, intermolecular energy and bonding [36-39]. Wick et al. [36] conducted molecular dynamics simulations on isophorone diamine shape memory EP and the results show that the higher the cross-linking percentage, the higher the bond energy stored by the epoxy resin molecules under the stretching of 50 %. Yang et al. [37] combined a covalent adaptive network with a shape memory polymer for molecular dynamics simulation and found that as the end-to-end distance of the polymer chain decreases, the Diels-Alder network exhibits higher flexibility, which greatly improves the mechanical and shape memory performance. Zhang et al. [38] found that the molecular bonding between GO and EP is the key to enhancing the shape memory performance through molecular dynamics simulation of shape memory GO/EP composites. The reinforcing effect of graphene on the shape memory epoxy from the perspective of molecular entropy and energy was explained by Amini et al. [39]. With the addition of GO, the energy stored in the shape memory epoxy increases, which improves the

recovery performance.

In this paper, the shape memory GO/EP composites with different graphene oxide mass fractions were successfully prepared. The glass transition temperature, shape fixation ratio, and shape recovery ratio were determined. The recovery process curve of shape memory GO/EP material was presented, and the effect of GO on enhancing the shape memory performance was explained. Moreover, the molecular dynamics simulation was established to investigate the influence of the molecular interaction between GO and EP on the shape memory performance, and the influence of the distribution of GO on the shape memory performance of the composites from a microscopic point of view.

2. Experimental section

2.1 Preparation of shape memory GO/EP composites

2.1.1 Materials

The multilayer GO with a purity of 95% and thickness of 3.4~7 nm was provided by Suzhou Hengqiu Technology Co., Ltd., Suzhou, China. The GO has the properties with a layer diameter of 10~50 μm, number of layers 5~10, a specific surface area of 100~300 m^2/g, and a sulfur content of <5 wt%. The manufacturer of epoxy resin E-51 was Shanghai Aotun Chemical Technology Co., Ltd., Shanghai, China. The epoxy value is 184~195 g/mol, the viscosity is 10000~16000 mPa s, the color degree is less than 40 Pt-Co, and the degree of hydrolysis is less than 0.5%. The

curing agent DDM was purchased from Shanghai Zhanyun Chemical Co., Ltd., Shanghai, China, with a molecular weight of 198.26, a melting point range of 89.0~93.2 ℃.

2.1.2 Preparation process

As shown in Figure 1, 6ml ethanol was added to the beaker, and the multilayer GO powder was weighed according to the percentage of the mass of EP as shown in Table 1. The mixture was dispersed ultrasonically for 15 minutes. 30g of epoxy resin was add to another beaker and put into the water bath preheat to 80 ℃ for 10 min, then pour the dispersed GO into the preheated EP. The mixed beaker was placed in an ultrasonic disperser for ultrasonic dispersion for 30 min. The beaker was heated at 90 ℃ for 2 hours in the blast drying oven. After the process, the beaker was moved in a magnetic water bath heating stirrer, which has been preheated to 90 ℃, and the epoxy resin mixture is evenly stirred. In order to have shape memory function after molding, it should not be completely cured that 5.1g curing agent DDM was used. The curing agent was introduced into the beaker containing EP step by step and stirred for 10 minutes until the bubbles disappeared. Finally, the evenly stirred mixtures were poured into the mold, and put it into the blast oven. The curing was at 80 ℃ for 2.5 hours and then 150 ℃ for 2.0 hours.

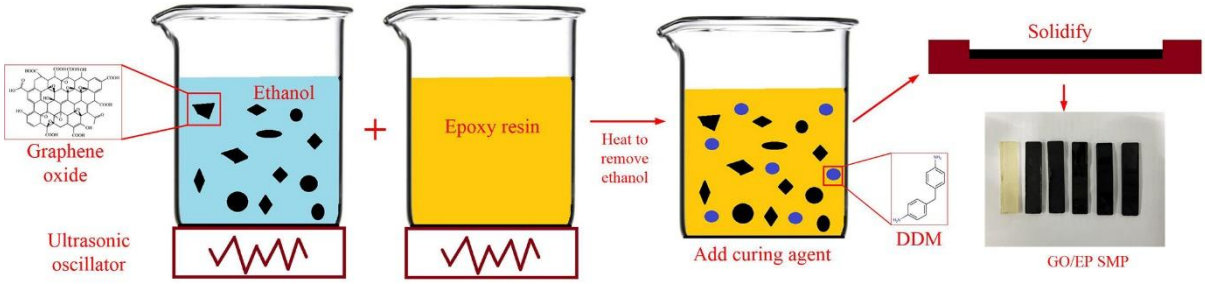


Fig. 1. Preparation of shape memory GO/EP composites.

Table 1. The content of each material in the composite material

	EP (g)	GO (g)	DDM (g)
Shape memory EP	30	0	5.1
GO/EP-0.10 wt%	30	0.03	5.1
GO/EP-0.25 wt%	30	0.075	5.1
GO/EP-0.50 wt%	30	0.150	5.1
GO/EP-1.00 wt%	30	0.300	5.1
GO/EP-1.25 wt%	30	0.375	5.1

2.2 Characterization and measurements

2.2.1 Scanning electron microscope (SEM)

SEM characterization (FEI-QUANTA FEG 250) was performed on the prepared shape memory GO/EP composite samples. The dispersion of GO in EP matrix was observed according to the cross-sectional images of the shape memory GO/EP composites by SEM scanning. Furthermore, SEM images show that there are no visible holes or cracks in the samples, which reflects the adhesion between GO and EP.

2.2.2 Glass transition temperature measurement

The DSC (TA Instrument-DSC 2500) with power compensation was used for the glass transition temperature (T_g) measurement. The supporter of the sample and the reference are independent components. There is a platinum thermistor for heating and a platinum sensor for temperature

measurement at the bottom of the sample and the reference. According to the principle of dynamic zero balance, the temperature of the sample and the reference material should be kept in the dynamic zero balance state whether the sample is endothermic or exothermic. Therefore, the DSC curve was obtained by heating the sample to 200 ℃ and then cooling it at the ratio of 10 ℃/min. The DSC measures the energy difference ($\Delta W=dH/dt$) required to maintain the sample and the reference at the same temperature, which reflects the change of the sample enthalpy. From the point of view of molecular motion, the glass transition is related to the micro-Brownian motion of the molecular segments in the amorphous part of amorphous polymer or crystalline polymer. Below the T_g, the movement of the shape memory EP is basically frozen. After reaching the T_g, the active wave heat capacity of the shape memory EP increases, and the baseline moves to the endothermic side.

2.3 Shape fixity ratio and shape recovery ratio

The prepared shape memory GO/EP composites sample (Size 90×20×4 mm) was placed in a blast drying oven at 150 ℃ for 10 minutes. The sample was taken out and bent in the mold, and kept until the sample cooled to room temperature to record the bending angle. As shown in Figure 2(a), the sample was placed in a water bath heater and heated at 90 ℃. Then the sample was photographed and the bending angle was recorded every 10 s. Figure 2(b) shows the angle change process of the

experimental sample. After the sample was bent and fixed in the mold, the mold was removed and the sample was cooled to room temperature. The sample had a small recovery angle, which was set as θ_0. This state was regarded as the initial state of the experiment. When the sample was placed in the water bath heater, the angle will continue to recover, but it will not recover completely in the end. The sample angle of the final state was set as θ_1. Figure 2(c) shows the recovery process of the shape memory GO/EP composites.

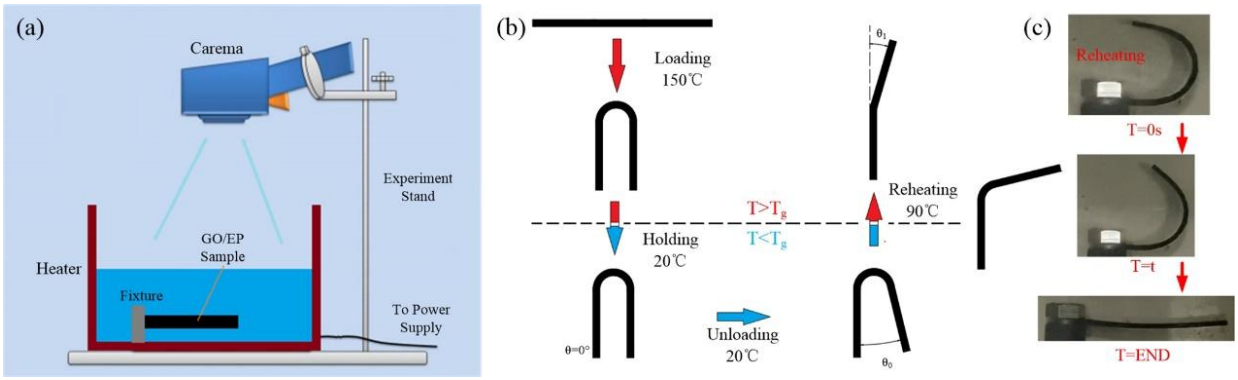


Figure 2. Schematic of (a) experimental device, (b) thermal cycle, and (c) recovery process.

The shape fixity ratio refers to the shape retention of the shape memory material at room temperature after it is heated and deformed. The shape fixity ratio R_F is calculated by Equation (1) [39].

$$R_F = \frac{180° - \theta_0}{180°} \tag{1}$$

The shape recovery ratio represents the deformation recovery of the shape memory GO/EP composites after deformed and cooled. The shape recovery ratio R_V can be expressed as Equation (2).

$$R_V = \frac{180° - \theta_1 - \theta_0}{180° - \theta_0} \quad (2)$$

3. Molecular dynamics analysis

3.1 Simulation parameters

In the molecular dynamic simulation, the E-51 polymer chain is synthesized from bisphenol A and epichlorohydrin (see Figure 3(a) and (b)). As shown in Figure 3(c), the model unit cell contains 200 polymer chains and 60 DDM molecules, which is represented as N-link. The connection ratio is 25% and the outermost carbon atoms of GO are partially oxidized to hydroxyl groups by passivating hydrogen (as shown in Figure 3(d)). Van der Waals force exists between the GO sheet and the EP, and there is a chemical bond between the GO functional group and the EP molecule. As shown in Figure 3(e), the bonding ratio is 100 %. The initial density is 1.5 g/cm^3. The model size is 49.79×49.79×49.79 Å. Before the simulation, the model uses the Forceite module to minimize the energy under the NPT condition, and the force field is set as CAMPASS II to minimize the potential energy of the unit cell.

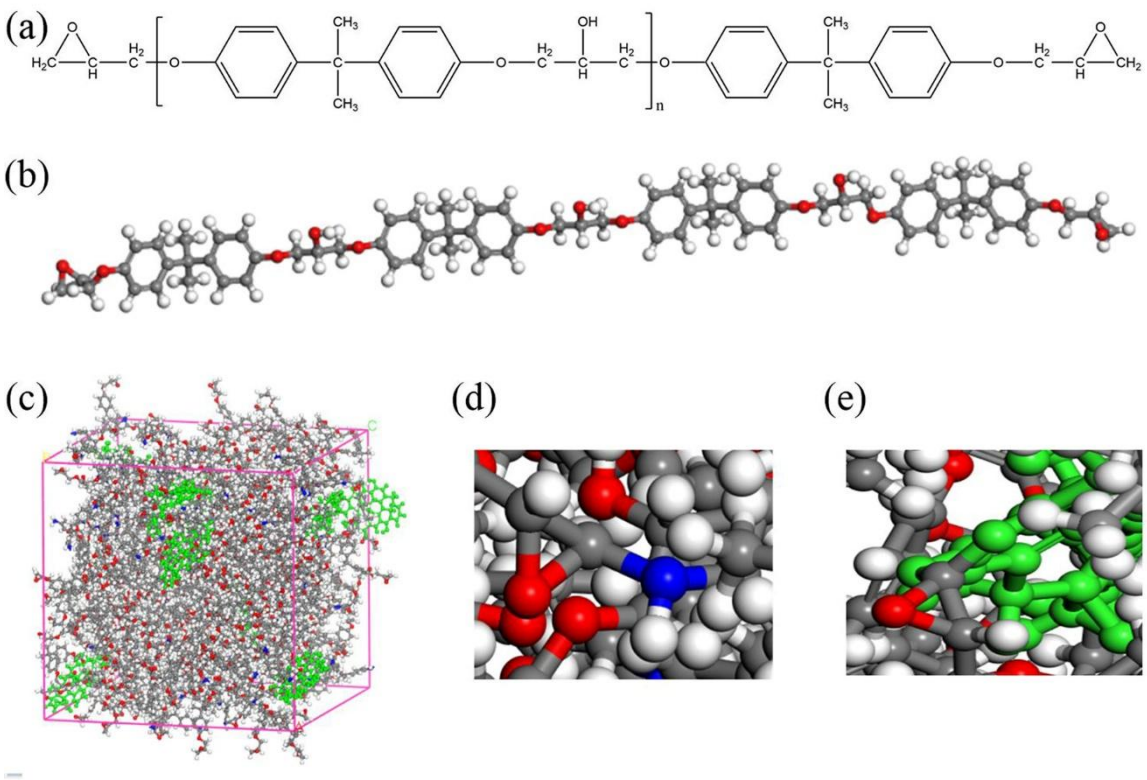


Figure 3. Schematic diagram of (a) E-51 molecular formula, (b) E-51 molecular model, (c) shape memory GO/EP model, (d) cross-linking between EP and DDM, and (e) EP and GO bonding.

3.2 Validation of molecular dynamics model

The T_g was calculated by molecular dynamics and the correctness of molecular dynamics simulation was verified by comparing the experimental data with the simulation results [38]. In molecular dynamics simulation, the relaxed structure of the shape memory EP unit cell was heated to 500 K under NPT conditions, and balanced for 50 ps under the pressure of 0.1 MPa. Then the heated structure was cooled to 300 K at a cooling ratio of 2 K/ps under NPT conditions. The thermal expansion formula is as follows [39].

$$3\alpha \cong \frac{1}{V_0}\frac{\partial V}{\partial T} = \rho_0 \frac{\partial V}{\partial T} \tag{3}$$

Where V_0 and ρ_0 denote the volume and density of the unit cell, α

215 denote the linear thermal expansion coefficient.

216 According to Equation (3), the specific volume change of shape
217 memory GO/EP composites can be represented by a regression line. As
218 shown in Figure 4, it can be seen that the specific volume-temperature
219 curve has an obvious discontinuity. This discontinuity is due to the fact
220 that the shape memory GO/EP composites are a glassy solid before
221 reaching the glass transition temperature. After heating, the molecular
222 fluidity is small, so the volume changes slowly and the specific volume
223 changes quickly. While, when the temperature is higher than the glass
224 transition temperature of shape memory GO/EP composites, the material
225 presents rubber colloidal state and the fluidity increases greatly, so the
226 volume changes rapidly and the specific volume changes slowly.
227 Therefore, the intersection of the two regression lines is the glass
228 transition temperature. The glass transition temperature of the SMP
229 material shown in Figure 4 is 331 K and the error of the DSC experiment
230 result is 3.33 %, which is within the allowable range of error, indicating
231 that the molecular dynamics simulation results of the model are credible.

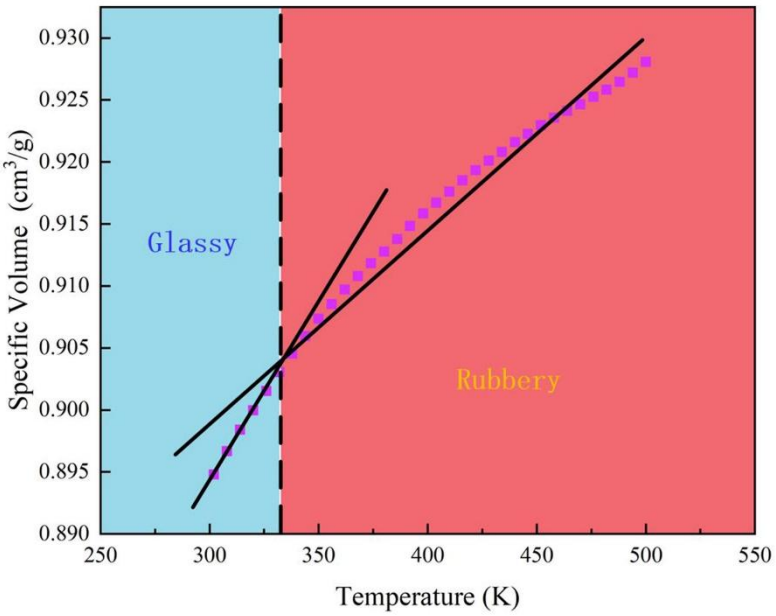


Figure 4. Specific volume-temperature diagram.

3.3 Shape recovery ratio

As shown in Figure 5, GO was embedded in the shape memory EP in a random distribution form in the unit cell. Thermal mechanical cycle simulation of unit cell was performed. The first step was to apply a stress of 1 GPa to the unit cell under the NPT conditions. The force field was set as CAMPASS II, and the Souza-Martins condition. The temperature was set as 423 K, and the duration is 5000 fs. During the process, the unit cell was stretched. The second part is to maintain the stress. The cell is cooled at 290 K for 5000 fs under NVT condition, and the cell length remains unchanged during the process. The third step is to remove the external force of NPT process, the temperature is 290 K for 5000 fs. In this process, the cell length will return to a small section. The last step is the reheat process. The temperature was set as 423 K for 30000 fs under

the NPT condition. During this process, the cell length will slowly recover.

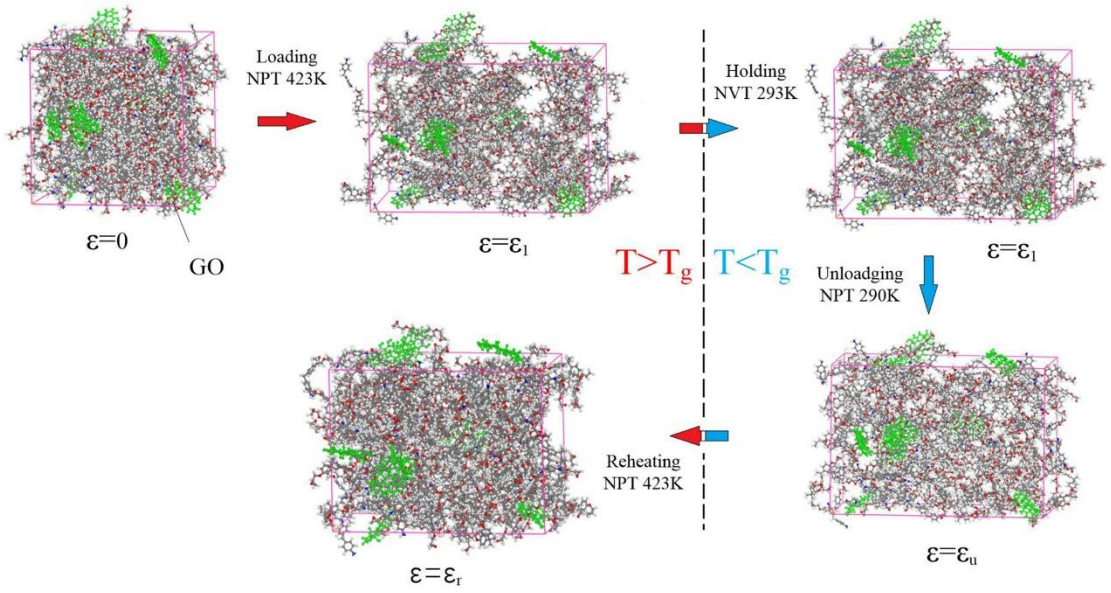


Figure 5. Thermo-mechanical simulation process.

4. Results and discussion

4.1 Characterization

4.1.1 SEM analysis

The SEM results were as shown in Figure 6. The yellow circle shows the GO layer. It can be seen that GO is evenly distributed in the EP matrix and there are no defects such as pores inside the sample, which indicating that the sample is well prepared. The use of ethanol can uniformly disperse GO in the EP matrix as much as possible, and the dispersibility of GO has a direct effect on the shape memory performance of the shape memory GO/EP composites.

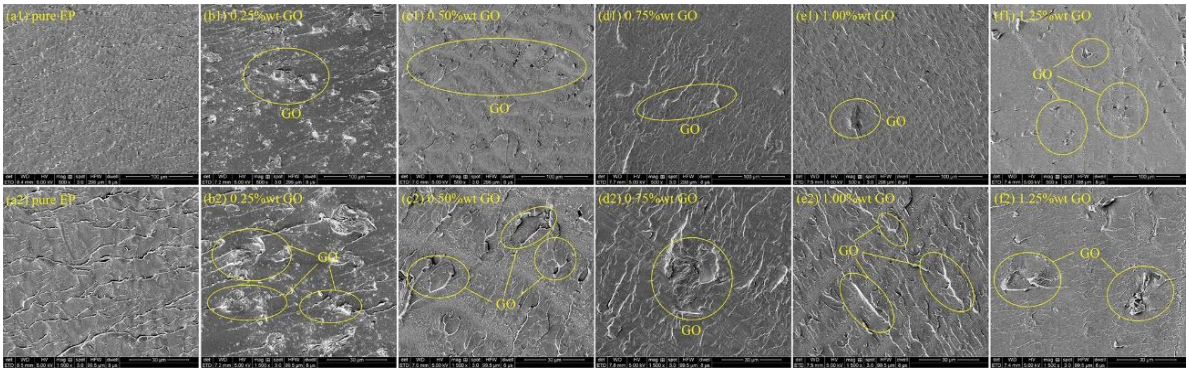


Figure 6. SEM micrographs of the liquid nitrogen cryogenic fractured surfaces of the specimens. (a1) and (a2) pure shape memory EP; (b1) and (b2) 0.25 wt% GO; (c1) and (c2) 0.50 wt% GO; (d1) and (d2) 0.75 wt% GO; (e1) and (e2) 1.00 wt% GO; (f1) and (f2) 1.25 wt% GO.

4.1.2 Glass transition temperature analysis

Figure 7 shows the DSC curves of shape memory GO/EP composites with different GO contents. The determination of the glass transition temperature is based on the deviation of the baseline on the DSC curve. According to the standard committee of ICTA, the intersection of the tangent line of the front edge of the curve and the front baseline is the glass transition temperature. Thus the results of glass transition temperature are shown in Table 2.

Table 2. Glass transition temperature values

GO contents（wt%）	Tg (℃)
0	60.00
0.25	43.20
0.50	45.60
0.75	47.10
1.00	48.20
1.25	49.05

For pure shape memory EP, the glass transition temperature is 60 ℃.

The glass transition temperature of the shape memory materials with GO is lower than 60 ℃, and the glass transition temperature increases with the increase of GO content. The glass transition temperature of the shape memory GO/EP composites with 1.25 wt% is 10.95 ℃ lower than that of pure shape memory EP. However, compared that of shape memory GO/EP composites with 0.25 wt% GO doping, the glass transition temperature with 1.25 wt% was increased by 5.85 ℃. The DSC results show that GO can reduce the glass transition temperature.

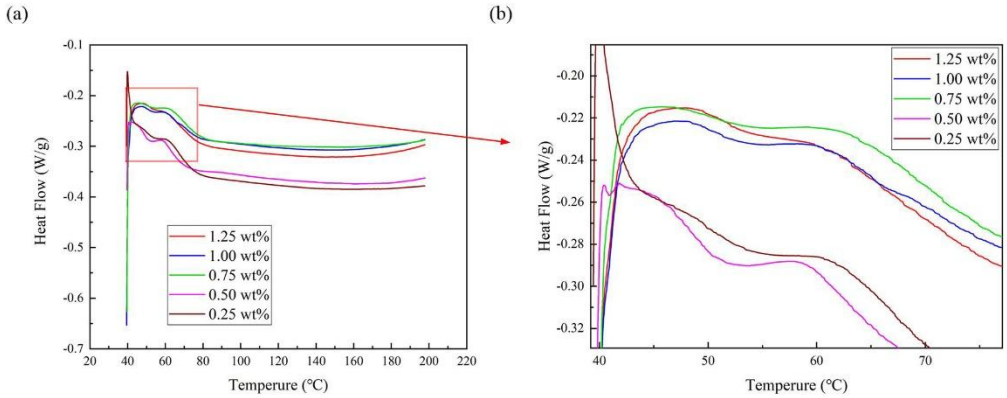


Figure 7. The DSC curves with different GO contents.

4.3 Shape fixity ratio and shape recovery ratio analysis

It can be seen from Figure 8(a) that with the increase of GO content, the shape fixity ratio of shape memory GO/EP composites decreased. The shape fixity ratio of the shape memory material with GO content of 1.25 wt% is 91.60%, which is 8.40% lower than that of the pure shape memory EP. With the increase of GO content, the shape recovery ratio of shape memory GO/EP composites shows an upward trend. The shape recovery ratio of the shape memory composites with GO content of 1.25

wt% is 99.40%, while the shape recovery ratio of the pure shape memory EP is only 85.50%. Figure 8(b) shows the angle change of the shape memory material with time. It can be seen from the figure that the shape memory material with GO content of 1.25 wt% has recovered 79.60% (reaching 133.00 °) in the first 30 s, while the shape recovery of the pure shape recovery EP did not return to 131.00 °until 160 s.

From Figure 8(b), it can be seen that with the increase of GO content, the shape recovery speed of shape memory GO/EP composites increases first and then decreases. The fast recovery interval of shape memory GO/EP composites is ahead of time, and slow recovery area in the early stage is shortened rapidly. When the GO content is 1.25 wt%, the rapid recovery starts from the initial recovery time, which is 30 s earlier than the pure shape memory EP.

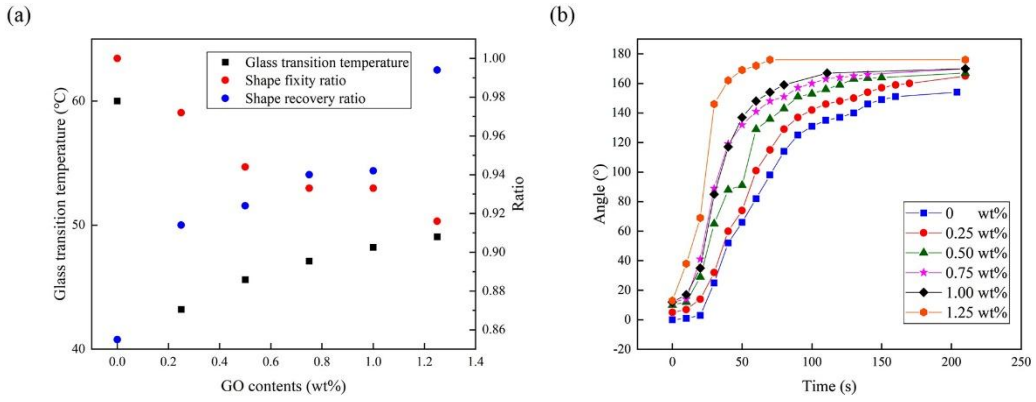


Figure 8. (a) Glass transition temperature/shape fixity ratio/shape recovery ratio with GO contents, and (b) Angle graph with time.

As shown in Figure 9, as the GO content increases, the angle of the shape memory GO/EP composites at the end of the rapid recovery also increases, and the angle of the shape memory GO/EP composites with the

GO content of 1.25wt% at the end of the rapid recovery is 162.00 °. Moreover, the recovery completion time of shape memory GO/EP composites also decreases rapidly with the increase of GO contents. When the GO content is 1.25 wt%, it only takes 70 s to complete the entire recovery process, while pure shape memory EP requires 204 s. It shows that the addition of GO can promote the recovery of the shape memory GO/EP composites, which shorting the total recovery time and accelerating the recovery speed.

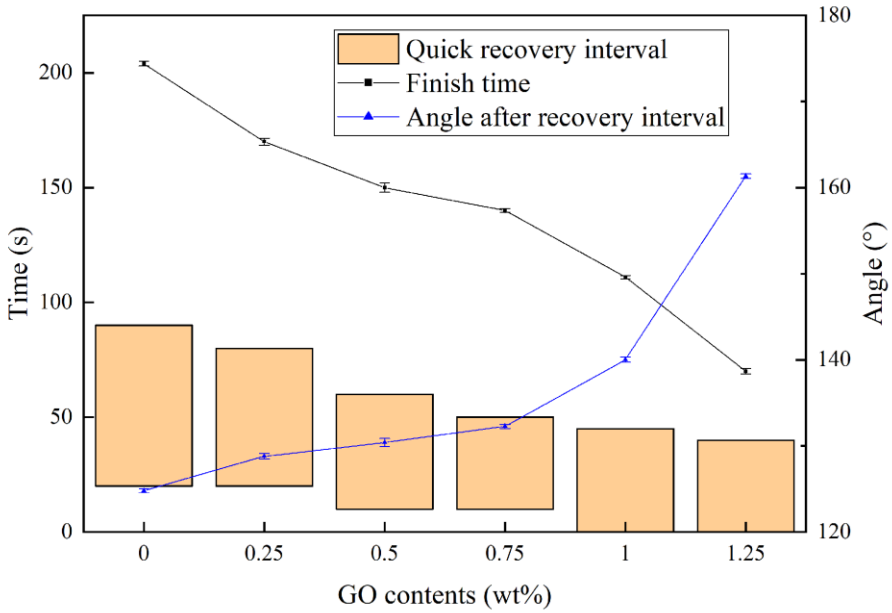


Figure 9. Quick reply interval and reply time.

4.4 Molecular dynamics analysis

4.4.1 Shape recovery ratio analysis

The shape recovery ratio refers to the ratio of the difference between the strain after stretching (ε_r) and the strain after recovery is completed (ε_1). Thus, the shape recovery ratio shown in Figure 5 can be expressed

by Equation (4) [39]:

$$\varepsilon_R = \frac{\varepsilon_1 - \varepsilon_r}{\varepsilon_1} \quad (4)$$

Converting the unit cell strain ε into the length *L*, the shape recovery ratio can be written as Equation (5) by the length after stretching (L_r) and the length after recovery is completed (L_1):

$$L_R = \frac{L_1 - L_r}{L_1} \quad (5)$$

As shown in Figure 10(a), during the stretching process, since the GO sheets cannot be stretched and deformed. Under the action of the intermolecular force between the GO and EP around the GO, the molecular distance of EP around GO will not be enlarged. The red circle in Figure 10(b) shows the EP molecules with recovery deformation around GO, and the blue circle shows the EP molecules without recovery deformation. It can be seen that the EP around the GO recovers faster, which is due to the intermolecular force generatiod between the GO sheet and the surrounding EP. The intermolecular force will promote the contraction of the molecular chain of the EP. This also explains the reason why the shape retention ratio decreases after GO doping.

In addition, the thermal conductivity of the GO sheet is much higher than that of the shape memory EP. When the temperature of the epoxy resin near the GO sheet inside the composite is higher than other positions, this also promotes the shrinkage of the epoxy resin molecular

chain near the GO sheet. This also explains why the shape retention ratio of the material decreases after GO is introduced into the shape memory EP.

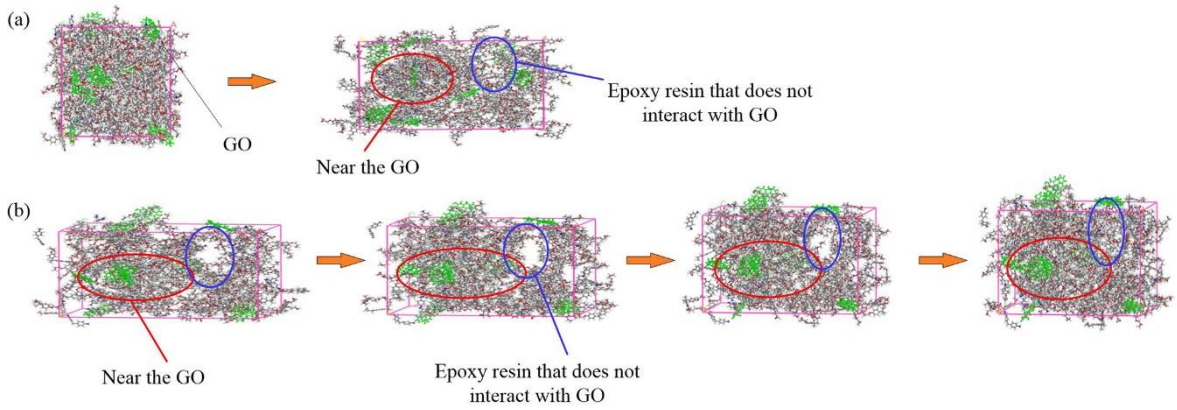


Figure 10. (a) The stretching process and (b) recovery process of the unit cell.

According to the calculation of Equation (5), the recovery data were drawn in Figure 11(a). During the stretching process of the unit cell, the GO sheet will not be stretched and deformed under the action of intermolecular force between the GO and the EP around the GO. The molecular distance of EP around GO will not be excessively enlarged. Therefore, the strain of GO-EP is smaller than that of pure shape memory EP under the same stress. In the recovery process of unit cell, it can be seen that the unit cell with GO takes less time to reach the same strain than the unit cell of pure shape memory EP, and the rapid recovery interval is achieved earlier than that of pure shape memory EP, which is in accordance with the experimental results shown in Fig. 11(b).

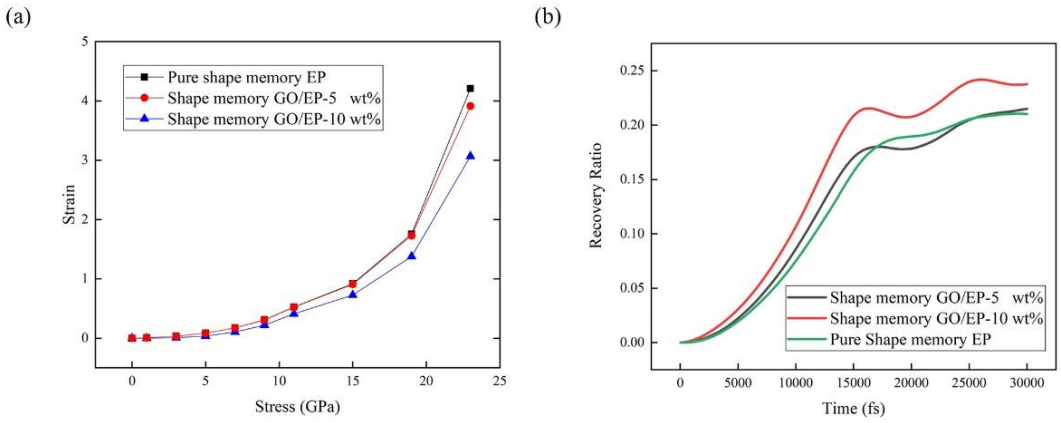


Figure 11. (a) Stress-strain graph during stretching, and (b) strain versus time graph during recovery.

4.4.2 Influence of GO agglomeration

The uneven distribution or agglomeration of GO in shape memory EP will directly affect the shape memory characteristics. Compared with the uniformly dispersed unit cell (Figure 12(a)) and the agglomerated unit cell (Figure 12(b)), it can be seen that when GO is uniformly dispersed, the oxygen-containing functional groups at the edge and inside of GO lamellae are fully combined with EP molecules. As shown in the red circle in Figure 12(a), when GO agglomerations, the distance between GO lamellae is significantly reduced, and the functional groups that GO interact with EP molecules only exist at the edge of GO sheets. The oxygen-containing functional groups in GO and part of the edge are blocked, resulting in less EP molecules combined with GO than that of GO is uniformly dispersed with the same mass fraction. Thus, the shape recovery performance of the shape memory GO/EP composites is reduced.

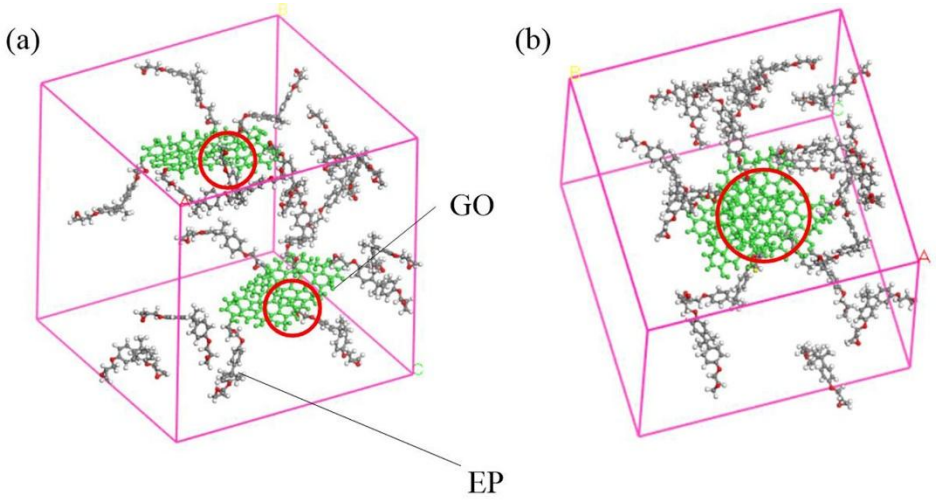


Figure 12. Unit cell of (a) GO uniform dispersion, and (b) GO agglomeration.

It can be seen from Figure 13 that for shape memory GO/EP composites with 10 wt% GO content, the shape recovery effect of GO agglomeration is 14.38% lower than that of the GO uniformly dispersed material. Moreover, compared with pure shape memory EP, the shape recovery ratio is 3.30% lower and the recovery speed in the early stage is slower than that of GO uniformly dispersed composites. With the increase of GO mass fraction, the distribution of GO in the cell becomes denser and the GO lamellar spacing is smaller, which is similar to agglomeration and affects the shape recovery performance. For the material with GO content of 15 wt%, the shape recovery ratio is further reduced to 20.34%, which is 3.25% lower than that of the pure EP, and the initial recovery ratio is also lower than that of the pure EP.

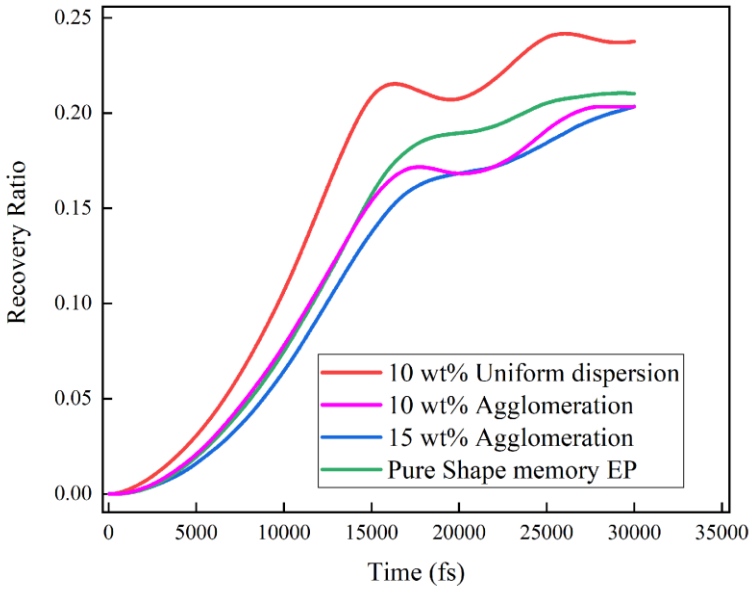


Fig. 13. The effect of GO agglomeration on shape recovery property.

4.4.3 The influence of the direction of the GO sheets

As shown in Figure 14(a), a unit cell with one GO sheet was analyzed, and the shape recovery molecular dynamics simulation was performed in the X and Y directions. The simulation results show that the shape recovery effect of the unit cell along the X direction is better (see Figure 14(b)). The simulation results show that the shape recovery ratio is 33.67% at 30000 fs, which is 28.5% higher than that of pure shape memory EP. In the Y direction, the recovery ratio is 27.61%, which is 3.57% lower than that of pure shape memory EP. In addition, the shape recovery curves along X direction and Y direction coincide completely at the initial stage of shape recovery, which indicating that different directions do not affect the shape recovery speed of materials in the initial shape recovery stage.

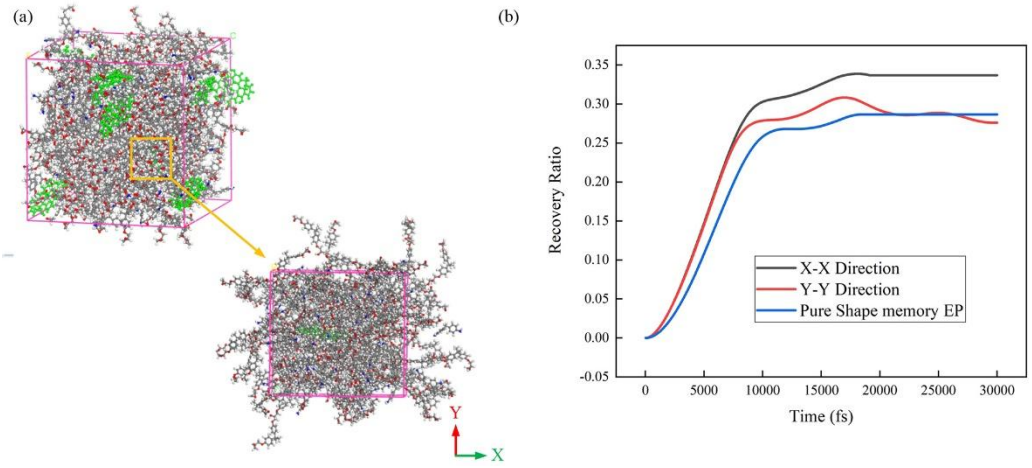


Figure14. Schematic of (a) shape recovery, and (b) recovery effect in different directions.

5. Conclusions

In this paper, the shape recovery properties of shape memory GO/EP composites were studied by preparing shape memory GO/EP composites and establishing molecular dynamics simulation model. The results show that the glass transition temperature of shape memory GO/EP composites increases with the increase of GO content, and the shape memory properties of shape memory GO/EP composites are improved. The main conclusions are as follows:

(1) With the increasing of GO content, the shape retention ratio of shape memory GO/EP composites decreases, while the shape recovery ratio rises. The fast recovery interval is advanced, and the slow recovery interval of initial recovery is shortened rapidly. The fast recovery interval of shape memory GO/EP composites with 1.25 wt% GO is 30 s earlier than that of pure shape memory EP.

(2) Through molecular dynamics simulation, it is found that the aggregation of GO in the shape memory GO/EP composites reduces the

recovery performance. The shape recovery effect of shape memory GO/EP composites with 10 wt% GO content is 14.38% lower than that of uniform dispersion and 3.2% lower than that of pure shape memory EP.

(3) The simulation results indicate that the tensile recovery ratio perpendicular to the GO direction is 21.73% higher than that along the GO direction, while recovery in different directions does not affect the recovery ratio of the material in the initial shape recovery stage.

Author contribution statement

Long Chen: Conceptualization, Data curation, Writing-review & editing, Methodology. **Yeqin Shen**: Formal analysis, Methodology, Writing-original draft. **Zhanqiang Liu**: Formal analysis, Methodology. **Qinghua Song**: Data curation, Writing-review & editing. **Chaozong Liu**: Conceptualization, Supervision.

Acknowledgements

This work is supported by the Natural Foundation of Shandong Province (Grant No. ZR2019BEE068), and Natural Science Foundation of Guangdong Province (Grant No. 2020A1515111208). The authors thank the referees of this paper for their valuable and very helpful comments.

References

[1] Kong, D. Y.; Li, J; Guo, A. R.; Xiao X. L. High temperature electromagnetic shielding shape memory polymer composite. Chem. Eng. J. 2021, 408, 127365.

[2] Niels, V. H.; Filip E., D. P. Fast healing of polyurethane thermosets using reversible triazolinedione chemistry and shape-memory. Macromolecules 2018, 51, 3405-3414.

[3] Meurer, J.; Agudo, J. A. R.; Zechel, S.; Hager, M. D.; Schubert, U. S. Quantification of triple-shape memory behavior of polymers utilizing tension and torsion. Compos. Pt. A-Appl. Sci. Manuf. 2021, 222, 2000462.

[4] Xiao, Y.; Zhou, S.; Wang, L.; Gong, T. Electro-active shape memory properties of poly(e-caprolactone)/functionalized multiwalled carbon nanotube nanocomposite, ACS Appl. Mater. Interfaces 2010, 2, 3506-3514.

[5] Uranbey, L.; Unal, H. I.; Calis G, Gumus OY, Katmer S, Karatas C. One-pot preparation of electroactive shape memory polyurethane/carbon black blend. J. Mater. Eng. Perform. 2021, 30, 1665-1673.

[6] Du, L.; Xu, Z. Y.; Fan, C. J.; Xiang, G.; Yang, K. K.; Wang, Y. Z. A fascinating metallo-supramolecular polymer network with thermal/magnetic/light-responsive shape-memory effects anchored

by Fe3O4 nanoparticles. Macromolecules 2018, 51, 705-715.

[7] Yu, X. J.; Zhou, S. B.; Zheng, X. T.; Guo, T.; Xiao, Y.; Song, B. T. A biodegradable shape-memory nanocomposite with excellent magnetism sensitivity. Nanotechnology 2009, 20, 235702.

[8] Li, Y.; Chen, H. M.; Liu, D.; Wang, W. X.; Liu, Y.; Zhou, S. B. PH-responsive shape memory poly(ethylene glycol)–poly(e-caprolactone)-based polyurethane/cellulose nanocrystals nanocomposite. ACS Appl. Mater. Interfaces. 2015, 7, 12988-12999.

[9] Defize, T.; Thomassin, J. M.; Ottevaere, H.; Malherbe, C. ; Eppe, G.; Jellali, R.; Alexandre, M.; Jerome, C.; Riva, R. Photo-cross-linkable coumarin-based poly(epsilon-caprolactone) for light-controlled design and reconfiguration of shape-memory polymer networks. Macromolecules 2019, 52, 444-456.

[10] Wang, T. J.; Zhao, J.; Weng, C. X.; Wang, T.; Liu, Y. Y.; Han, Z. P.; Zhang, Z. A bidirectionally reversible light-responsive actuator based on shape memory polyurethane bilayer. Compos. Pt. A-Appl. Sci. Manuf. 202, 144, 106322.

[11] Leverant, C. J.; Zhang, Y. F.; Cordoba, M. A.; Leo, S. Y.; Charpota, N.; Taylor, C.; Jiang, P. Macroporous superhydrophobic coatings with switchable wettability enabled by smart shape memory

polymers. Adv. Mater. Interfaces. 2021, 8, 2002111.

[12] Chan, B. Y. Q.; Low, Z. W. K.; Heng, S. J. W.; Chan, S. Y.; Owh, C.; Loh, X. J. Recent advances in shape memory soft materials for biomedical applications. ACS Appl. Mater. Interfaces. 2016, 8, 10070-10087.

[13] Ren, L. Q.; Li, B. Q.; Song, Z. Y.; Liu, Q. P.; Ren, L.; Zhou, X. L. Bioinspired fiber-regulated composite with tunable permanent shape and shape memory properties via 3d magnetic printing. Compos. B Eng. 2019, 164, 458-466.

[14] Alghamdi, S. S.; John, S.; Choudhury, N. R.; Dutta, N. K. Additive manufacturing of polymer materials: progress, promise and challenges. Ploymers 2021, 13, 753.

[15] Hu, J. L.; Zhu, Y.; Huang, H. H.; Lu, J. Recent advances in shape memory polymers: structure, mechanism, functionality modeling and applications. Prog. Polym. Sci. 2012, 37, 1720-1763.

[16] Jian, W.; Wang, X. D.; Lu, H. B.; Lau, D. Molecular dynamics simulations of thermodynamics and shape memory effect in CNT-epoxy nanocomposites. Compos. Sci. Technol. 2021, 211, 108849.

[17] Srivastava, S.; Biswas, A.; Senapati, S.; Ray, B.; Rana, D.; Aswal, V. K.; Maiti, P. Novel shape memory behaviour in IPDI based polyurethanes: influence of nanoparticle. Polymer 2017, 110,

514 95-104.
515 [18] Yu, Z. W.; Wang, Z. Q.; Li, H.; Teng, J. X.; Xu, L. D. Shape memory
516 epoxy polymer (SMEP) composite mechanical properties enhanced
517 by introducing graphene oxide (GO) into the matrix. Materials 2019,
518 12, 1107.
519 [19] Dhand, V.; Mittal, G.; Rhee, K. Y.; Park, S. J.; Hui, D. A short review
520 on basalt fiber reinforced polymer composites. Compos. Part B 2015,
521 73, 166-180.
522 [20] Sliozberg, Y. R.; Kroger, M.; Henry, T. C.; Datta, S.; Lawrence, B.
523 D.; Hall, A. J. A chattopadhyay computational design of shape
524 memory polymer nanocomposites. Polymer 2015, 127, 123476.
525 [21] Idumah, C. I.; Odera, S. R. Recent advancement in self-healing
526 graphene polymer nanocomposites, shape memory, and coating
527 materials. Polym -Plast. Technol. Mater. 2020, 59, 1167-1190.
528 [22] Meng, Q. H.; Hu, J. L.; Zhu, Y. Shape-memory
529 polyurethane/multiwalled carbon nanotube fibers. J. Appl. Polym.
530 Sci. 2007, 106, 837-848.
531 [23] Deka, H.; Karak, N.; Kalita, R. D.; Buragohain, A. K. Biocompatible
532 hyperbranched polyurethane/multi-walled carbon nanotube
533 composites as shape memory materials. Carbon 2010, 48,
534 2013-2022.
535 [24] Gopinath, S.; Adarsh, N. N.; Nair, P. R.; Mathew, S. Shape-memory

polymer nanocomposites of poly(epsilon-caprolactone) with the polystyrene-block-polybutadiene-block-polystyrene-tri-block copolymer encapsulated with metal oxides. ACS Omega 2021, 6, 6261-6273.

[25] Jana, R. N.; Yoo, H. J.; Cho, J. W. Synthesis and properties of shape memory polyurethane nanocomposites reinforced with poly(e-caprolactone)-grafted carbon nanotubes. Fibers Polym. 2008, 9, 247-254.

[26] Ashori, A.; Fallah, A.; Ghiyasi, M.; Rabiee, M. Reinforcing effects of functionalized graphene oxide on glass fiber/epoxy composites. Polym. Compos. 2018, 39, E2324-2333.

[27] Wang, C. C.; Zhao, Y. Y.; Ge, H. Y.; Qian, R. S. Enhanced mechanical and thermal properties of short carbon fiber reinforced polypropylene composites by graphene oxide. Polym. Compos. 2018, 39, 405-413.

[28] Lee, C. G.; Wei, X. D.; Kysar, J. W.; Hone, J. Measurement of the elastic properties and intrinsic strength of monolayer graphene. Sci. 2008, 321, 385-388.

[29] Yang, Q. R.; Zhang, Z. L.; Gong, X. F.; Yao, E. R.; Liu, T.; Zhang, Y.; Zhou, H. S. Thermal conductivity of graphene-polymer composites: implications for thermal management. Heat Mass Transfer 2020, 56, 1931-1945.

[30] Koziol, M.; Jesionek, M.; Szperlich, P. Addition of a small amount of multiwalled carbon nanotubes and flaked graphene to epoxy resin. J. Reinf. Plast. Compos. 2017, 36, 640-654.

[31] Ligati, S.; Lavi, A. O.; Keyes, J.; Ziskind, G.; Regev, O. Enhancing thermal conductivity in graphene-loaded paint: Effects of phase change, rheology and filler size. Int. J. Therm. Sci. 2020, 153, 106381.

[32] Kim, J. T.; Kim, B. K.; Kim, E. K.; Park, H. C.; Jeong, H. M. Synthesis and shape memory performance of polyurethane/graphene nanocomposites. React. Funct. Polym. 2014, 74, 16-21.

[33] Luo, X.; Wu, Y. P.; Guo, M. L.; Yang, X.; Xie, L. Y.; Lai, J. J.; Li, Z. Y.; Zhou, H. W. Multi-functional polyurethane composites with self-healing and shape memory properties enhanced by graphene oxide. J. Appl. Polym. Sci. 2021, 138, 50827.

[34] Xu, L.; Cui, L.; Li, Z.; Lu, H. H.; Qi, X. M.; Wang, W. J.; Jin, X. X.; Dong, Y. B.; Fu, Y. Q.; Jiang, W. B.; Ni, Q. Q. Thermodynamic coupling behavior and energy harvesting of vapor grown carbon fiber/graphene oxide/epoxy shape memory composites. Compos. Sci. Technol. 2021, 203, 108583.

[35] Ghosh, T.; Karak, N. Interpenetrating polymer network/functionalized-reduced graphene oxide nanocomposite: As an advanced functional material. J. Appl. Polym. Sci. 2021, 138,

50499.

[36] Wick, C. D.; Peters, A. J.; Li, G. Q. Quantifying the contributions of energy storage in a thermoset shape memory polymer with high stress recovery: A molecular dynamics study. Polymer 2021, 213, 123319.

[37] Yang, H.; Zheng, X. R.; Sun, Y. G.; Yu, K; He, M. C.; Guo, Y. F. A molecular dynamics study on the surface welding and shape memory behaviors of Diels-Alder network. Comput. Mater. Sci. 2017, 139, 48-55.

[38] Zhang, X. J.; Yang, Q. S.; Leng, J. S. How graphene oxide affects shape memory properties and strength of poly(L-lactide-co-e-caprolactone). J. Intell. Mater. Syst. Struct. 2020, 31, 2152-6214.

[39] Amini, M.; Hasheminejad, H.; Montazeri, A. Experimentally guided MD simulation to enhance the shape memory behavior of polymer-based nanocomposites: Towards elaborating the underlying mechanism. Compos. Pt. A-Appl. Sci. Manuf. 2020, 138, 106055.

Cover letter

Long Chen
School of Mechanical Engineering, Shandong University
Room 1210, The Innovation Building, No. 250061 Jingshi Road, Lixia District, Jinan, China

18/08/2021

Dear Chief-Editor,

We wish to submit an original research article entitled "**Investigation of the effects of graphene oxide on thermodynamic performance of shape memory GO/EP composites**" for consideration by **Journal of Materials Science & Technology.**

We confirm that this work is original and has not been published elsewhere, nor is it currently under consideration for publication elsewhere.

In this paper, we prepared shape memory GO/EP composite and the shape recovery properties of shape memory GO/EP composites were studied by preparing shape memory GO/EP composites and establishing molecular dynamics simulation model. This is significant because the heat transfer and shape memory performance of the anti-/deicing structure plays a significant role, which directly influencing the anti-/deicing efficiency and flight safety.

We believe that this manuscript is appropriate for publication by **Journal of Materials Science & Technology** because it matches the scope of this journal, which focus on thermodynamics of composite materials.

We have no conflicts of interest to disclose.

Please address all correspondence concerning this manuscript to me at 812612937@qq.com

Thank you for your consideration of this manuscript. We look forward to hearing from you.

Sincerely,

Long Chen

Declaration of interests

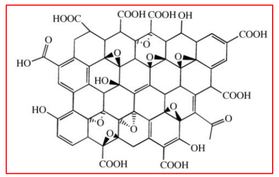
☑ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

HIGHLIGHTS:

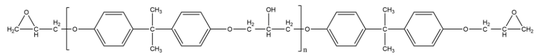
- A shape memory GO/EP composite was prepared by introducing GO sheets into shape memory EP and the molecular dynamics model was established.
- The anti-icing time of the shape memory GO/EP composites was shortened by 18.84s, and the anti-icing efficiency was increased by 49.90%.
- The deicing time of samples with shape memory function decreased from 136 s to 45 s, and the deicing efficiency increased by 66.91%.
- The GO doping content has a direct effect on the anti-/deicing performance of the shape memory GO/EP composites.

Graphical Abstract

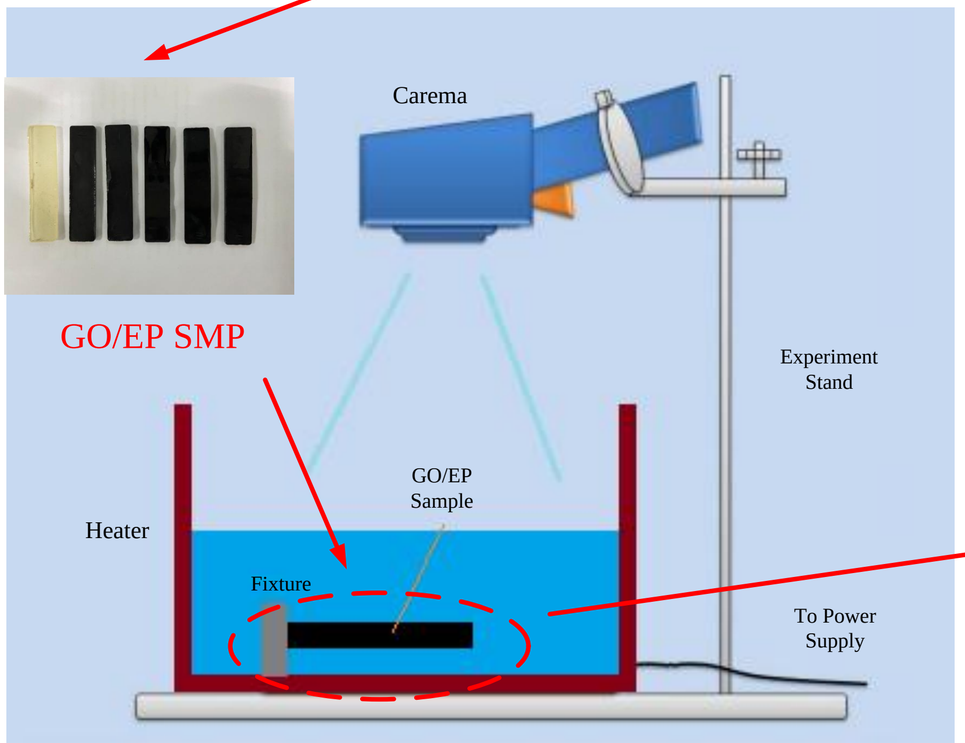


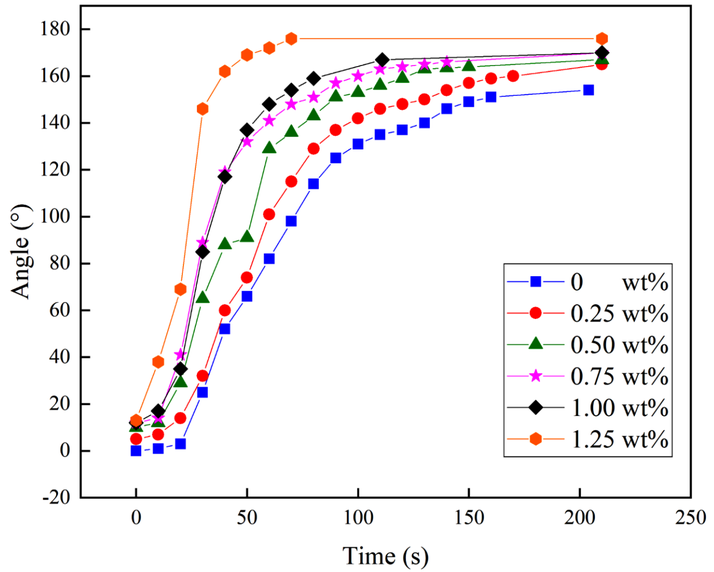
Graphene oxide

+



Epoxy resin E51





T=0s

T=t

T=END