Interfacial Properties of Graphene Oxide/Epoxy Resin Coatings in Corrosive Environments

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Abstract: Graphene oxide/epoxy composite coatings have attracted much attention from researchers due to their excellent anti-corrosion properties. Graphene oxide as a two-dimensional nano-filler can enhance the overall properties of epoxy resin coatings. In the paper, models of graphene oxide/epoxy composite coatings with different permeation degrees are constructed respectively. The interfacial interaction between GO and epoxy resin and the adsorption properties of epoxy coating with metal are analyzed from an atomic perspective by molecular dynamics simulations. The results indicate that the interfacial adsorption effect of the epoxy coating on the protected metal is stronger than the interfacial bonding of GO on the epoxy resin matrix. Simulations of models with different degrees of permeation suggest that the permeation of the NaCl solution occupies the interfacial space and reduces the adhesion between the two interfaces.

1. Introduction

Graphene oxide/epoxy composite (GO/EP) coatings have excellent anti-corrosive properties [1], but seawater permeation is inevitable. The permeation of seawater can lead to severe degradation of the performance of the polymer composite coating [2]. Previously, the anticorrosion property of the epoxy coating has been investigated in experiments [3,4]. Researchers have also analyzed the diffusion properties of water in polymers through molecular dynamics (MD) simulations to investigate the bonding state of water and epoxy resin (EP) and their effects on the properties of the composites [5]. However, these simulation efforts have paid little attention to the interaction with GO-EP under the influence of water and the adsorption of the epoxy coating to the metal interface.

Especially in the interface of GO-EP, water permeation affects the bond strength between them [6]. The experimental characterization of the interactions amongst water, GO, and EP is a challenging task. MD simulations have received attention in recent years as a complement to experiments to accomplish atomic characterization problems. The dynamic process of the corrosive medium in the coating and its diffusion behavior can be obtained by MD simulation [7,8].

Epoxy coating and metal substrate interface adsorption performance is also a significant indicator of the coating corrosion resistance property. The diffusion of NaCl solution between the epoxy coating and the metal interface will lead to further aggravation of corrosion and, eventually, the exfoliation of the epoxy coating. The adsorption properties of polymer coatings also play an essential role in corrosion resistance [9]. Graphene oxide can improve the anticorrosion properties of EP coatings and enhance the adsorption of the coatings to metals. However, there is still a certain gap in the understanding of the interface adsorption property between the epoxy coating and metal substrate in a corrosive environment. Inspired by these problems, MD simulation is carried out in this paper to provide new insights into the interfacial and adsorption properties of NaCl solutions on GO/EP coatings.

2. Molecular dynamics modeling and simulation methods

To investigate the influence of NaCl solution on the GO-EP interaction and the adsorption of epoxy coating with the metal interface, a GO/EP coating permeation model is developed, and MD simulations are performed using LAMMPS. The simulation considers only the permeation of the solution. No electrochemical reactions occur. The permeation medium is a 3.5% mass fraction NaCl solution, mostly water molecules.

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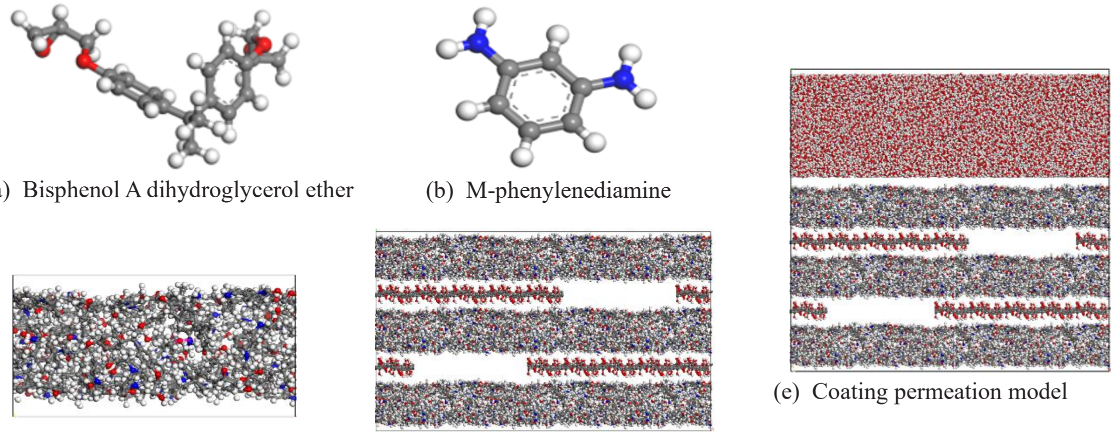


(a) Bisphenol A dihydroglycerol ether (b) M-phenylenediamine (c) EP monomer (d) GO/EP composite coating model (e) Coating permeation model

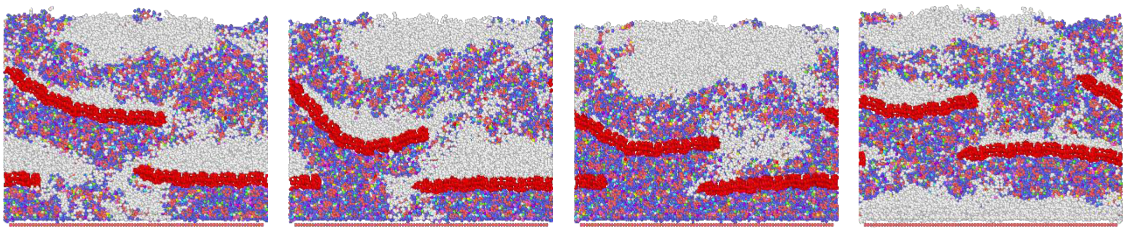
Figure 1. Coating model

As indicated in Figure 1, the GO/EP coating uses a laminated structure in the z-direction due to the large size of the coating model. Three EP layers and two lapped GO pieces are laminated together to form the coating, where the single EP layer is made of EP unit cell supercell. As is indicated in Figure 1(c), the EP monomer is modeled by bisphenol A diglycidyl ether (DGEBA) and m-phenylenediamine (MPD) curing agent at a molar ratio of 1:1. The initial density of the model is set to 1.0 g/cm^3, the model size is 36×38×60 Å, and the crosslinking degree is controlled to 90%. The cross-linked model is 3×3 arrayed in x and y directions to obtain the requested monolayer EP layer, and the model size is 110×115×20 Å. The GO/EP coating permeation model is a NaCl solution with a thickness of 36.8 Å over GO/EP coating. The simulations are performed with periodic boundary conditions, and the GO/EP coating is relaxed for 100 ps each under the canonical ensemble, isothermal-isobaric ensemble, and canonical ensemble (NVT, NPT, NVT). The EP molecular chains can fully wrap the nanomaterials and finally reach the equilibrium state. After the relaxation of the GO/EP coating, it is compounded with the NaCl solution. The permeation simulation is performed after the relaxation of the NVT ensemble for 200 ps.

3. Results

3.1 Analysis of permeation results

As shown in Figure 2, the NaCl has permeated to the bottom of the coating at 2000 ps, and the GO has been deformed and displaced. With increased permeation time, GO deformation recovers partly after more downward diffusion of NaCl solution at 3000 ps, which has a strong impact on the study of the interaction of GO with EP and the adsorption between coating and metal interface. Permeation is a continuous process, and GO deformation could not recover before, thus losing its barrier effect.



1000 ps 2000 ps 3000 ps 5000 ps

Figure 2. GO/EP composite coating permeation simulation results

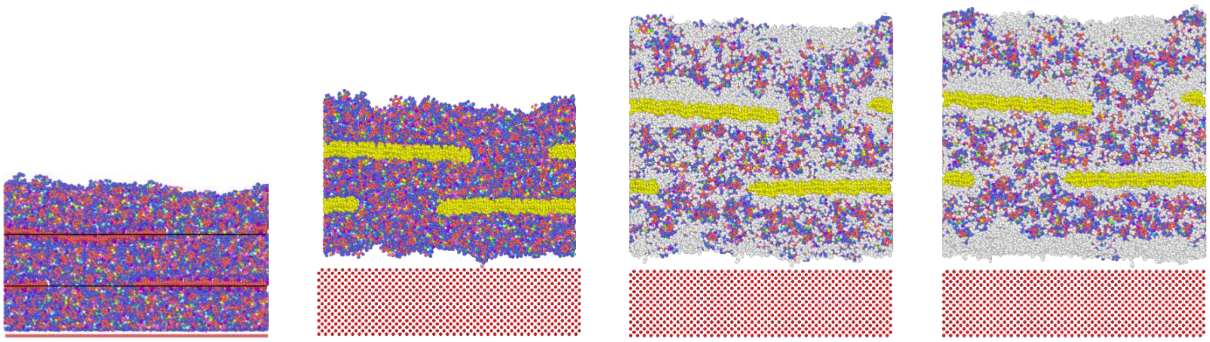
3.2 Overlap modeling analysis

The results show that the NaCl solution of this thickness could not achieve a continuous permeation process. The GO/EP coating contains less NaCl solution in the surface layer at the late stage of penetration, and most of the atoms reach the lower layer, which has a great impact on the testing of interfacial properties. Multiple attempts using different thicknesses of NaCl solution and different permeation rates also yield the same results, so the following solution is selected.

Based on the above findings, the overlapping modeling approach is used to directly model GO/EP coatings with different degrees of permeability. Two models of GO/EP coating and NaCl solution are overlapped, and then the model is set to reach a reasonable configuration by energy minimization and relaxation. The NaCl solution is added to the free volume of GO/EP coating.

The GO/EP composite coating model shown in Figure 3(a) is divided into three parts from top to bottom according to the black line, which is defined as the first part, the second part, and the third part. According to the results in Figure 2, the NaCl solution amount is 55.78% of the total solution in the first part at 1000 ps, 38.80% in the second part at 2000 ps, and 30.68% in the third part at 5000 ps. The NaCl solution is compounded with EP according to the above three ratios. The post-permeation model with gradient distribution is built directly after energy minimization and relaxation.

The NaCl solution is compounded with the GO/EP coating according to the above three ratios and GO/EP-Fe-2 in Figure 3(c) is established. GO/EP-Fe-1 is an impermeable model and GO/EP-Fe-3 has a 3.9 Å thick NaCl solution added at the coating-metal interface of GO/EP-Fe-2. GO/EP-Fe-3 represents the further accumulation of permeable media at the interface. An iron substrate is placed underneath the coating, and relaxing the coating and the substrate will fully interact. In the figure, the red atom is the metal substrate, the yellow atom is GO, the white atom is the NaCl solution, and the other atoms are epoxy resin.

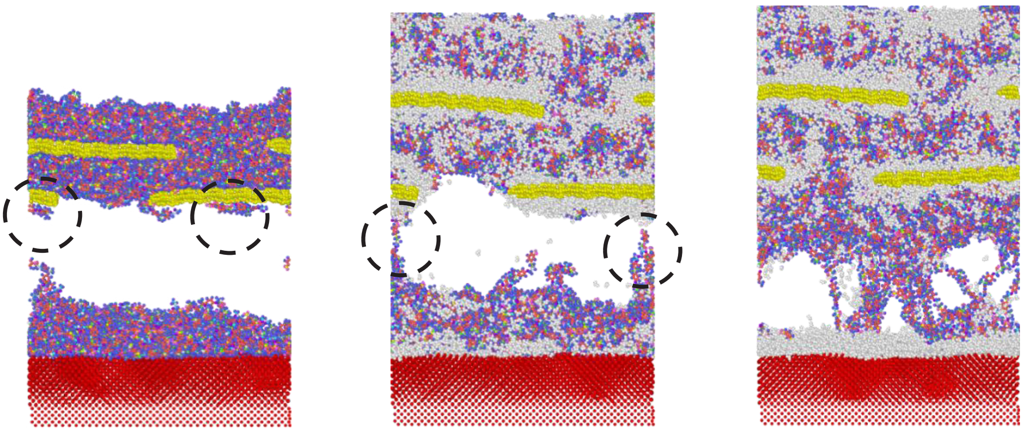


(a) GO/EP coating (b) GO/EP-Fe-1 (c) GO/EP-Fe-2 (d) GO/EP-Fe-3

Figure 3. Overlap modeling schematic

The stretching simulation of the coating is performed under the NVT system ensemble by fixing the top and bottom part of the atoms and applying a velocity of 0.001 Å/fs to the top fixed atoms and for 100 ps. As shown in Figure 4, the results show that GO/EP-Fe-1 is pulled apart at the interface between GO and epoxy resin, but some molecular chains are adsorbed on the undersurface of GO.

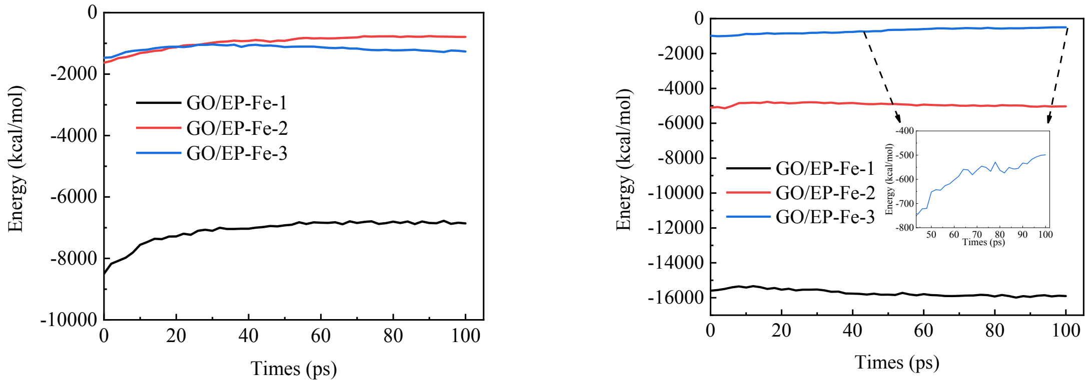
The interaction potential energy in Figure 5 also shows that the coating-metal interaction potential energy is higher than that between GO and the epoxy, so it is not pulled away from the coating-metal interface. The NaCl solution in GO/EP-Fe-2 occupies the surface of GO and reduces the interaction of GO and epoxy. However, most of the NaCl solution is water molecules. The water molecules, GO, and epoxy will form hydrogen bonds to weaken the damage caused by the NaCl solution [10]. Thus, there is still the adsorption of molecular chains at the interface. GO/EP-Fe-3 is pulled away from the coating-metal interface, and the accumulation with NaCl solution lowers the adsorption capacity of the coating.



GO/EP-Fe-1 GO/EP-Fe-2 GO/EP-Fe-3

Figure 4. Graph of coating stretching results

The interaction potential energy can be used to characterize the changes in the interfacial properties during the simulation. The low interaction energy means the strong interfacial bonding of the coating. The potential energy of GO/EP-Fe-1 in Figure 5(a) is lower than that of the other models during initiation and stretching. The results indicate that the GO/EP coating has better interfacial properties when not penetrated. The permeation of the NaCl solution destroys the GO-epoxy interface, resulting in higher potential energy values for GO/EP-Fe-2 and GO/EP-Fe-3.



(a) GO and epoxy resin (b) GO/EP coating and iron substrate

Figure 5. Interaction potential energy

The potential energy of GO/EP-Fe-1 in Figure 5(b) is lower than that of the other models during the onset and stretching. The results indicate that the GO/EP coating has better interfacial properties with the iron substrate when not penetrated. The permeation of NaCl solution leads to the destruction of the interface and the decrease of the adsorption capacity of the coating. Thus, the interaction potential energy of GO/EP-Fe-2 and GO/EP-Fe-3 also becomes larger with the deepening of the permeation. The interface between the coating and the iron substrate is pulled apart in GO/EP-Fe-3, corresponding to the gradual increase of the interaction potential energy in the enlarged figure.

4. Conclusions

In this paper, the interfacial interaction between GO and EP and the interfacial adsorption of epoxy coating with the metal are investigated by MD simulation. The results indicate that the interfacial adsorption of the epoxy coating to the metal is stronger than the interfacial bonding of GO to the epoxy matrix, which also indicates the excellent adsorption properties of the epoxy resin. Simulation results for different degrees of permeation of NaCl solution indicate that the permeation of NaCl solution occupies the interfacial space and weakens the bond between the two interfaces.

Interfacial properties play an essential role in the performance of fiber-reinforced polymers, and the fiber-polymer interface undertakes the important task of stress transfer. Epoxy coating and metal substrate interface adsorption performance is also an important guarantee that the coating of anti-corrosion properties gives full play. The results of this effort enhanced our comprehension of the properties of two interfaces of epoxy coatings in corrosive environments. In addition, the adhesion of the epoxy coating-metal is not a purely physical connection, and hydrogen bonds may be formed at the interface, which requires further analysis and research.

Acknowledgments

This work was funded by the National Natural Science Foundation of China (Project No. 11902010,11932002), which is gratefully acknowledged.

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