Surface interaction energy simulation of ceramic materials with epoxy resin[*]

Li Fei-Zhou[1), 2), **)], Lu Zheng-Lin[1)], Yang Zhi-Huai[1), 2)], Qi Kai[3)]

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Abstract: A new method to calculate the surface interaction energy of ceramic particles and epoxy resin network was investigated using the Material Studio software solution. Detailed simulations were performed with molecular dynamics (MD) method, using Amorphous Cell module, creating relatively simple surface models of polymer (epoxy resin) and ceramics (Al_2O_3, SiO_2 and SiC). The surface models obtained were used to calculate properties and the surface interaction energy of the materials studied. The computed results are in good agreement with the experimental data, confirming the ability to employ the described simulation method in theoretical evaluation of interaction between various filler or reinforcing materials and the polymer matrix.

Keywords: epoxy resin, simulation, interaction energy, ceramic material.

Symulacja energii oddziaływań powierzchni materiałów ceramicznych z żywicą epoksydową

Streszczenie: Testowano nową metodę obliczania energii oddziaływań powierzchni cząstek ceramicznych z żywicą epoksydową. Obliczenia wykonywano korzystając z oprogramowania Material Studio. Szczegółowe symulacje prowadzono metodą dynamiki molekularnej (MD) za pomocą modułu Amorphous Cell, tworząc modele powierzchni polimeru (żywicy epoksydowej) i materiału ceramicznego (Al_2O_3, SiO_2 lub SiC). Otrzymane modele posłużyły do obliczeń właściwości oraz energii oddziaływań powierzchni badanych materiałów. Uzyskano dobrą zgodność wyników symulacji z danymi doświadczalnymi, co potwierdziło możliwość zastosowania opisanej metody symulacji do teoretycznej oceny oddziaływania różnych napełniaczy ceramicznych z matrycą polimerową.

Słowa kluczowe: żywica epoksydowa, symulacja, energia oddziaływań, materiał ceramiczny.

In recent years, particle reinforced polymeric composites have drawn considerable attentions from materials scientists and engineers due to their superior physical, chemical, and mechanical properties [1].

Epoxy resins are commonly used in variety of applications due to their excellent properties such as thermal stability, adhesiveness, corrosion resistance, mechanical response [2—4], low density and electrical resistance. Despite their excellent bonding power and mechanical properties that lead to the wide application of epoxy resins, their poor thermal resistance and brittleness have constrained their usage in the more demanding fields. To improve the frictional wear and anti-corrosion surface properties of epoxy resin composites, different techniques have been studied. With the rapid development of manufacturing techniques, attention has been paid to epoxy resin composites that contain particle fillers. Commonly used methods are to manufacture thermally conductive composites by adding high-thermal conductivity fillers, and to manufacture wear-resistant coating and corrosion-resistant composites by adding inorganic particle fillers, such as Al_2O_3, SiO_2, SiC, Si_3N_4, *etc*. Fillers play an important role in the production of polymeric materials that can be used to improve the friction and wear resistance, chemical resistance, and physical, rheological, thermal, optical, and electrical properties of epoxy resin composites. Many researchers have investigated the thermal conductivity enhancement of composite materials including oxides (Al_2O_3, SiO_2, ZnO) [5—8], carbide (SiC) [9], and nitrides (AlN, BN, Si_3N_4) [10, 11]. In addition to the filler's physical and chemical properties, its morphology and size also have an effect on the performance of its composites. However, particle size and filler-matrix adhesion strength have serious impact on the dynamic crack initiation and the surface of molecular interaction

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[1)] Xi'an University of Technology, School of Material Science and Engineering, Xi'an 710048, China.

[2)] Baoji University of Arts and Sciences, Department of Mechanical, Baoji 721007, China.

[3)] Jiangsu University of Science and Technology, School of Material Science and Engineering, Jiangsu 212003, China.

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[**)] Author for correspondence; e-mail: lfz1010@sohu.com

in composites. Strengthening mechanisms such as crack deflection, crack-tip blunting, crack front twisting have been identified as a few possible reasons behind the differences seen in macroscopic fracture parameters.

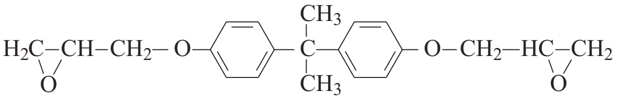
The correlation between interface stress, potential energy and interface fracture is a hot topic at present. However, existing studies mainly pay attention to the ability of composites only, and rarely consider the surface interaction energy of ceramics and polymer.

The aim of this study was application of molecular dynamics (MD) simulation method to simulate the interface fracture. Based on the simulation, the correlations between the interface stress, potential energy and the interface fracture were predicted, providing a basis for selecting the suitable reinforcing or filler particles. Material Studio is a software solution commonly used in the simulation of the surface interaction of organic and inorganic ceramic materials [12]. It was used to study the surface interaction energy of ceramic particles and epoxy resin network and predict the interface bonding effect. A detailed five-step procedure for the simulation is presented in the next section. Based on the results, some conclusions were drawn and presented in this paper.

MOLECULAR MODELING AND SIMULATION PROCEDURE

For the molecular modelling and simulation, a commercially available molecular dynamics (MD) simulation software package Material Studio 6.0 with the Compass force field simulation for inter- and intra-atomic interaction was used. Copolymer of epoxy resin based on diglycidyl ether bisphenol A (DGEBA), with the molecular structure given by formula (I), was chosen as a representative example because it is a common industrial component [13]. The reinforcing materials were Al_2O_3, SiO_2, and SiC. The simulation procedure consists of five steps.

Step 1 was a surface construction. Two two-dimensional (2D) active models were constructed for the crystal structures of Al_2O_3, SiO_2 and SiC on an atom-to-atom basis, and the crystal face [0 1 2] was cut. Relevant parameters were set in the CLEAVE SURFACE menu, and the respective lattice parameters of Al_2O_3, SiO_2 and SiC were obtained. According to the constructed model, the space group of Al_2O_3 is R-3C (D3D-6) with lattice parameters $a = b = 0.4759$ nm and $c = 1.2991$ nm, the space group of SiO_2 is P3221 (D3-6) with lattice parameters $a = b = 0.491$ nm and $c = 0.5402$ nm, and the space group of SiC is P63MC (C6V-4) with lattice parameters $a = b = 0.3078$ nm and $c = 1.0046$ nm.



(I)

In step 2 the surface was optimized. For this purpose molecular mechanics investigation was applied to keep the energy minimized. Linkages with different atoms are required for the Compass force field to be correctly calculated for the system, and the linkages would be removed after the force fields had been distributed, even the surface was ionic. After the initial microstructure was generated, the minimization of the potential energy of the model system was carried out, where a well-validated Compass force field [14] was used to obtain reasonable three-dimensional model. Followed by 5000 steps of energy minimization (MM) were 5000 steps of MD simulation to relax the central unit cell system. On this basis, the SuperCell of Al_2O_3, SiO_2 and SiC was created and the configuration parameters were $u = 3$ and $v = 3$. Then, the periodicity was converted from 2D to 3D as shown in Fig. 1.

Step 3 was a polymer building. First, DGEBA was using the build modules. Amorphous Cell module must be used in order to get reasonable polymer molecules. Lattice parameters of the DGEBA were the same as those described in step 1.

In step 4 DGEBA molecules were added to the surface. After the energy minimization of the surface and the obtaining of reasonable DGEBA molecules, the Layer module was utilized to add the DGEBA molecules to the surface. The layers included polymer, ceramics and vacuum, as it was shown in Fig. 2. The subsequent simulation was based on those layer structures.

The last was step 5. In this step, Disco Dynamics and Forcite MechProps were chosen for construction due to

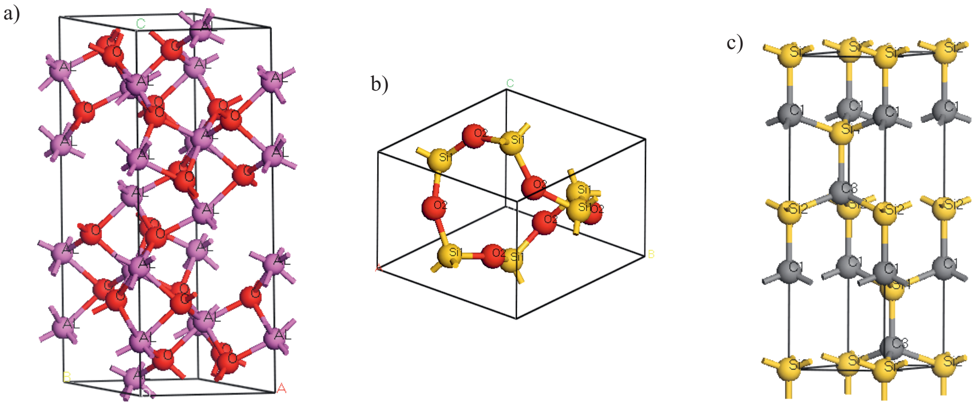


Fig. 1. Ceramic crystal structures of: a) Al_2O_3, b) SiO_2, c) SiC

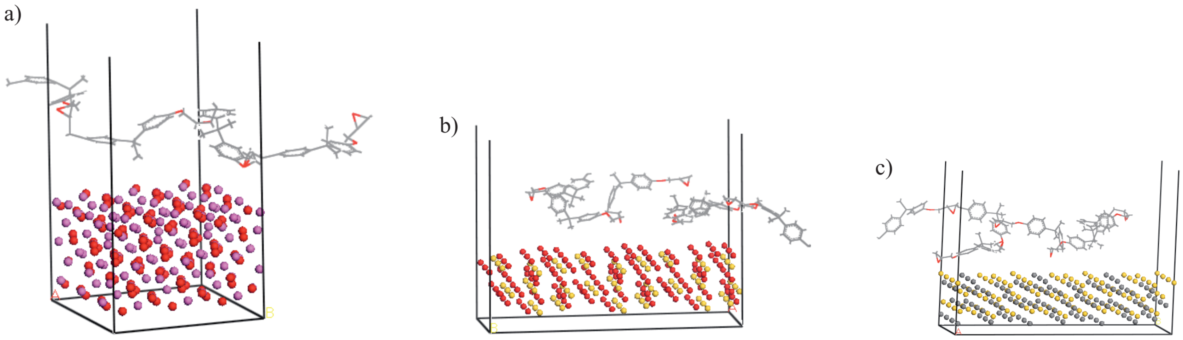


Fig. 2. Surface models of: a) Al_2O_3/DGEBA, b) SiO_2/DGEBA, c) SiC/DGEBA

their simplicity, while Compass was used to calculate the surface properties of the layer material. As for the non-bonding terms, van der Waals interaction energy and Coulombic interaction energy were included for both force fields, but no hydrogen bonding energy terms were explicitly included in the Compass.

RESULTS AND DISCUSSION

For the MD simulations, the input data set including constant number of molecules or atoms, volume and temperature (NVT) was used. The time step (*fs*) was set between 10 and 15 s throughout the whole simulation, and the temperature was kept at 297 K. Unless otherwise mentioned, all other parameters for the calculations were set up to default. To validate the resulting layer model, several cycles of 500 steps of molecular dynamics and 10 000 steps of energy minimization were performed with the model to reach equilibrium.

A mathematical description of this system is known as a force field, which was used to calculate the relative potential energy of the molecule (relative to other conformations of the same molecule). The interaction energy among molecules ($E_{interaction}$) was calculated according to the following equation:

$$E_{interaction} = E_{total} - (E_{surface} + E_{polymer}) \tag{1}$$

where: E_{total} — the total energy of the surface and the polymer, $E_{surface}$ — the energy of the surface after removing the polymer, $E_{polymer}$ — the energy of the polymer after removing the surface.

As it can be seen in Fig. 3, the total energy of both the surface and the polymer decreased immediately after the molecular dynamics simulation started. The Al_2O_3/DGEBA, SiC/DGEBA and SiO_2/DGEBA interface models reached the balance at 200 *fs*, 150 *fs* and 50 *fs*, respectively, as well as the lowest energy of interaction. Therefore, the selected parameters were correct. After a relatively stable stage has been reached, $E_{interaction}$ was calculated for each interface model. The results are presented in Table 1. The values of $E_{interaction}$ for the Al_2O_3/DGEBA, SiO_2/DGEBA and SiC/DGEBA were -118.66, -18.15 and 400.99 kcal/mol, respectively. The results showed that Al_2O_3/DGEBA had the strongest binding ability, followed by SiO_2/DGEBA, and SiC/DGEBA had the weakest. In other words, Al_2O_3/DGEBA is the optimal one for epoxy resin composites that contain particle fillers. Min Zhi Rong [15] studied the specific wear rate of the Al_2O_3-*g*-PAAM/epoxy resin and SiC-*g*-PAAM/epoxy resin, and found that the wear rate of the Al_2O_3-*g*-PAAM was significantly less than that of the SiC-*g*-PAAM/epoxy resin. It is generally known that silicon carbide has high hardness and is more stable than alumina, thus it should have lower wear rate, yet the result is just the opposite. This may be attributed to the fact, that $E_{interaction}$ of silicon carbide is higher than that of alumina, thus the force between its molecules is repulsion, which causes the molecules not binding well, leading to the poor abrasion resistance of the composites. According to the theory of surface free energy, Fowkes [16] proposed that the surface free energy of a solid is the sum of the energy of its individual components associated with specific interactions, as shown below:

$$\gamma_S = \gamma_s^d + \gamma_s^p + \gamma_s^h + \gamma_s^i + \gamma_s^{ab} + \gamma_s^o \tag{2}$$

where: $\gamma_s^d, \gamma_s^p, \gamma_s^h, \gamma_s^i, \gamma_s^{ab}$ — the energy of the dispersion, polar, hydrogen bonding, induction, and acid-base components, respectively, γ_s^o — the energy of all remaining interactions.

Table 1. Interaction energy components calculated for three reinforcing materials

Energy components	Al_2O_3	SiO_2	SiC
E_{total}, kcal/mol	-197 717.94	54 614.00	48 485.26
$E_{surface}$, kcal/mol	-198 165.28	855.93	41 144.25
$E_{polymer}$, kcal/mol	566.01	53 776.20	6940.01
$E_{interaction}$	-118.66	-18.15	400.99

In the case of surface-treated (or untreated) SiC, SiO_2 and Al_2O_3 particles, it can be regarded that some partial interactions originating from hydroxyl (-OH) groups absorbed on the SiC, SiO_2 and Al_2O_3 particles' surfaces and the pre-cured epoxy resin can contribute to an increased polar component of the surface free energy in eq. (2), which in turn leads to an enhanced wettability between the epoxy resin and the surface-treated SiC, SiO_2 and Al_2O_3 particles, as determined by FT-IR and XPS.

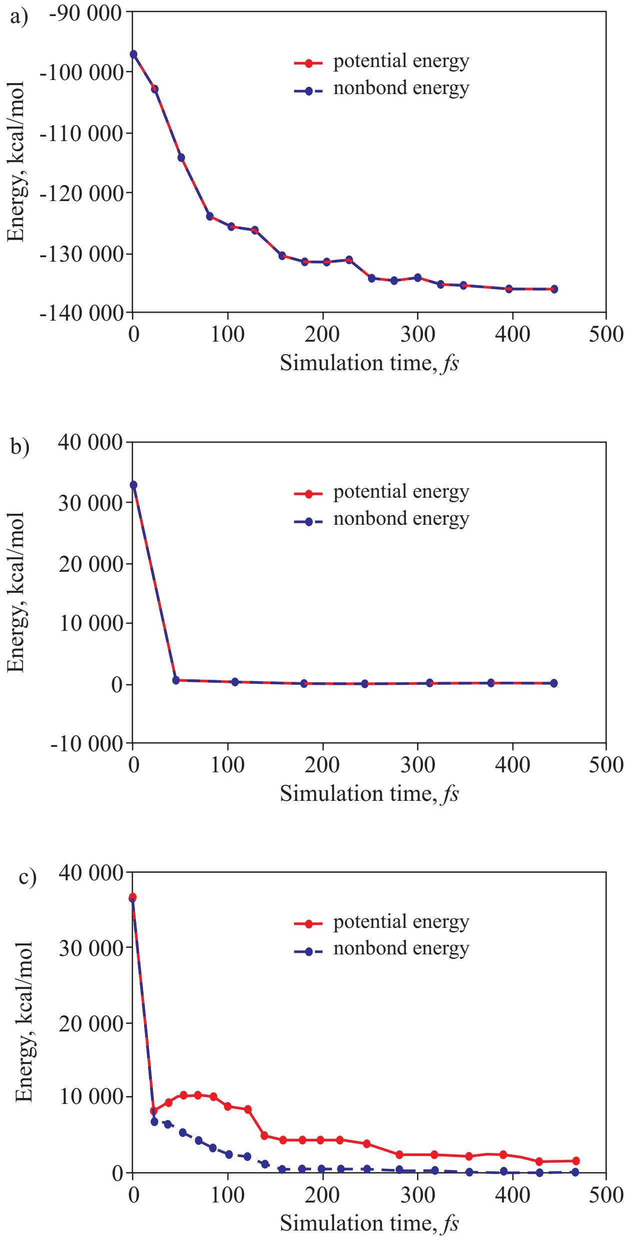


Fig. 3. Potential and non-bond interaction energy of: a) Al_2O_3/DGEBA, b) SiO_2/DGEBA, c) SiC/DGEBA

With other parameters being equal, the increase in γ_s^o resulted in a rise in γ_s^d. Since it was calculated that the interaction energy was γ_s^o, it can be concluded that Al_2O_3/DGEBA had the greatest surface free energy, followed by SiO_2/DGEBA, and SiC/DGEBA had the smallest.

Therefore, the computed results are in good agreement with the experimental data. It was concluded that the interaction energy is very important for the selection of proper filler materials or reinforcing materials and the preparation of epoxy resin composites, as well as the further increase of the interface bonding strength.

CONCLUSIONS

In this study, a new method for studying the surface interaction energy of ceramic particles and epoxy resin network was developed and applied to epoxy resin system based on DGEBA with Al_2O_3, SiO_2 and SiC. Detailed MD simulations using Amorphous Cell module were conducted with a relatively simple surface model of polymer and ceramics of a typical epoxy-ceramic system based on DGEBA and Al_2O_3, SiO_2 and SiC. The surface model was successfully generated and studied, and surface interaction energy was calculated to validate the theoretical reasons to select the proper filler materials.

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