Atomic-Level Modelling for Predicting Interface Strength in Resin Molded Structures*

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Abstract

In the framework of atomistic-level modeling, a new technique for predicting the interface strength of the resin-mold structure has been proposed. We show that our proposed interfacial fracture energy is effective in determining the adhesion strength of three kinds of interfaces between epoxy resin and metals (Cu, Fe and Al). We also discuss the multi-scale connection between nano-scale adhesion and macro-scale interface strength in terms of interface roughness. When the interface with roughness is subject to shear load under vertical residual stress in experiments, FEM analysis taking account of the effect of interface roughness shows that local debonding (mode-I) due to the tensile stress induces global delamination. Our proposed method for dealing with local mode-I debonding by use of molecular dynamics is found to be effective in simulating the interfacial fracture with the shear load.

Key words: Resin Molded Structure, Interfacial Fracture Energy, Atomic-Level Modelling, Interfacial Strength

1. Introduction

Resin materials are light in weight and have high mechanical strength, so they are widely used in electrically powered devices as insulating materials, such as insulating rods and insulating vessels. These materials are fabricated by molding resins in cylindrical metals and ceramics (1), (2). For the resin molded insulators to perform safely, adhesion between the resin and metal needs to be strong. By correctly evaluating the interface strength of the resin molded structures, we can improve the reliability of electrically powered devices.

In the resin molded structures, forces due to friction, pressure, and adhesion are applied to the interface between the metal and resin. Each of these forces strongly affects the characteristics of resin molded structures. Therefore, to correctly evaluate the interface strength of such a structure, we need to take account of all these forces.

In our previous paper, we reported an experimental investigation of the mechanical strength of metal-resin interfaces in resin molded structures (3). We evaluated the interface strength of resin molded products by using a finite-element model with the adhesion characteristics of the interface measured by experiments; we showed that the experimental method is effective in determining the interface strength. To experimentally measure the adhesion characteristics of interfaces, however, we have to fabricate resin molded structures with an insert material and resin material and measure the shear force between these...
materials every time we change the materials used in products. Thus, to improve the efficiency of material design, we need a technique to select an appropriate insert-metal material by predicting the adhesion strength of interfaces.

Therefore, to select an appropriate material efficiently, we present a technique to qualitatively predict interface adhesion strength by using molecular-dynamics calculations that take interfacial atomic interaction into account. Moreover, we applied the proposed technique to the interface strength between an epoxy resin and insert metals and showed that the trend of interfacial fracture energy agrees well with the adhesion-strength index measured in an experiment.

2. Interface Debonding Experiment inside Resin Molded Structure (3)

In our previous study, we investigated the metal-resin interaction by measuring the shear force at the metal-resin interfaces of a resin molded object that we fabricated. In this chapter, to compare the experimental results with molecular-dynamics calculations, we analyze the forces applied to the interface used in the previous study by taking account of the resin molding process.

2.1 Experimental methods

A metallic mold was used to fabricate the resin test piece for the interface debonding experiments on the resin molded structure. In the metallic mold, a metallic pillar was used as an insert material. After the metallic pillar was inserted, liquefied epoxy resin was poured into the metallic mold to a thickness of 10 mm, as shown in Fig. 1(a). Then, air was removed from the resin in vacuum. The epoxy resin was joined to the metallic pillar by a hardening reaction caused by an increase in temperature, and the resin was separated from the mold. This was how a test piece (Fig. 1(b)) was fabricated. The mold was kept in a furnace at the primary cure temperature (85°C) for 7 hours and then at the secondary hardening temperature (130°C) for 24 hours. After that, the mold, still in the furnace, was cooled to room temperature at 7°C/h. Figure 2 shows the resin temperature during the molding process. The maximum temperature change during the molding process was 110°C, and the highest temperature was 130°C. Because the glass-transition temperature of the epoxy resin used in this study is 140°C, the molding process was not significantly influenced by the viscous characteristics of the resin near the glass-transition temperature.

In the heat-hardened-type resin molded structure, residual stress $\sigma_{\text{res}}$ induced by volume change due to resin hardening and by the difference in thermal expansion between the resin and metal is applied to the metal-resin interface as pressure, as shown in Fig. 3(a). Figure 3(b) shows a laser-beam microscope image of the metal-resin interface. The interface has a periodic pattern induced by the wave-like surface profile of the metal. We measured shear force $f_x$ and displacement $x$ by applying compressive pressure to the interface to push the metal pillar out of the resin material. Oxygen-free high-conductivity copper (C1011), steel for general structures (SS400), and aluminum (A1050) were used as materials for the metal pillar. In addition, the surface roughness $Ra$ of the three materials was set at the same value.

![Resin Molded Structure](image)

(a) Pouring of resin (b) Test piece

Fig. 1: Process of molding resin
2.2 Shear-force measurements

Table 1 shows the values of the maximum shear force $f_{\text{max}}$ for each metal pillar. The maximum shear force is the critical shear force at which adhesive fracture occurs at the interface. We have not experimentally verified the starting point of the fracture. Because initial defects may exist inside the interface, the starting point may not only exist at an end of the interface but also on the inside\(^{(4)-(6)}\). In Table 1, $\sigma_{\text{pm}}A_0$ represents the pressure force due to the residual stress, where $A_0$ is the effective adhesion area. The pressure $\sigma_{\text{pm}}$ is calculated by using the difference between the thermal expansion coefficients of the materials and the temperature differences. Table 1 shows that the $\sigma_{\text{pm}}A_0$ of steel (Fe) is 25% larger than that of copper (Cu) because of the larger difference of the thermal expansion coefficient between Fe and resin than that of Cu and resin. Table 1 also shows that the maximum shear force $f_{\text{max}}$ of Fe is the same as that of Cu. By taking account of the effect of pressure force on the maximum shear force, we can conclude that Cu has stronger adhesion with the resin than Fe. By defining an adhesion-strength index ($\mu + B$) through use of the adhesion coefficient $B$ and the coefficient of friction $\mu$, we can express the maximum shear force as follows.

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Fe</th>
<th>Al</th>
</tr>
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<tbody>
<tr>
<td>$f_{\text{max}}$ (kN)</td>
<td>33</td>
<td>33</td>
<td>7</td>
</tr>
<tr>
<td>$\sigma_{\text{pm}}A_0$ (kN)</td>
<td>59</td>
<td>75</td>
<td>44</td>
</tr>
<tr>
<td>$f_{\text{max}}/\sigma_{\text{pm}}A_0$</td>
<td>0.55</td>
<td>0.44</td>
<td>0.15</td>
</tr>
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</table>
In this study, we experimentally verified that Eq. (1) is valid when sufficient pressure is applied to the metal-resin interface. The adhesion-strength index for each material is obtained by dividing $f_{\text{max}}$ of Eq. (1) by $\sigma_{\text{pm}A_0}$. This index represents the adhesion characteristic of each insert material with the resin, which does not contain the influence of the pressure force due to the residual stress, and it increases in the order Cu > Fe > Al. We consider that $\mu + B$ indicates the force needed to separate the metal/resin interface.

3. Evaluation of Adhesive Bond Strength by Molecular Dynamics Method

3.1 Evaluation of adhesion strength in debonding mode I

The adhesion strength of the interface in a resin molded structure is determined by using the molecular-dynamics method (7), (8). The schematic view of the interfacial fracture energy for mode I is shown in Fig. 4. The interfacial fracture energy is defined as the difference between the potential energy of the metal-resin connected state and that of the metal-resin separated state. We used a crystal-like resin whose molecule structure is shown in Fig. 5. We used 16 resin molecules (4 layers of molecules) on the metal model (thickness $\times$ length $\times$ width = 0.84 $\times$ 2.3 $\times$ 2.3 nm). We set the crystal texture of the metal so that the plane of the greatest atomic density, which is the (111) plane in face-centered-cubic (fcc) structures, was parallel to the metal-resin interface. The reason we assumed this texture is that the plane of the greatest atomic density is energetically stable and that it is most likely to appear on the surface of the metal. We used the molecular dynamics software Discover (Accelrys Inc.) and used a consistent valence force field (CVFF) (9) as interatomic potentials. The interface structure relaxed at 20°C is shown in Figs. 6, 7, and 8 for Cu, Fe, and Al, respectively. The viewpoint of these figures is normal to the interface; each single atomic layer of the metal and the resin at the interface is shown instead of all the atomic layers, as that would make these figures too complicated. To calculate the interfacial fracture energy, we obtained the resin-metal separated state by eliminating the interatomic potential between the resin and metal. The interfacial fracture energies that we obtained from the calculation were 0.573, 0.462, and 0.079 J/m$^2$ for Cu, Fe, and Al, respectively, and the adhesion strength with resin increased in the same order as the experimental results (Cu > Fe > Al) shown in Chapter 2.

Next, we discuss the dominant factor in the increase in the adhesion strength with the resin in terms of the lattice mismatch, which we have found to be the dominant factor in metal/metal interface strength (8). To discuss the lattice mismatch, we define the unit length of the resin lattice as the distance between the second-nearest-neighbor carbon atom pair (0.250 nm) in the six-membered ring in Figs. 6, 7, and 8. We also define the unit length of the metal lattice as the distance between the nearest-neighbor atom pair. By using these definitions to analyze Fig. 6, we found that the lattice mismatch between the unit length of the resin (0.250 nm) and that of copper (0.256 nm) is about 2%. This small lattice mismatch is considered to make the atomic configurations of the resin and copper fairly regular with almost the same lattice period.
Fig. 4 Method for calculating interfacial fracture energy

Fig. 5 Molecular structure of crystalline-like resin

Fig. 6 Resin/copper interface structure obtained from molecular dynamics

Fig. 7 Resin/iron interface structure obtained from molecular dynamics

Fig. 8 Resin/aluminum interface structure obtained from molecular dynamics
In contrast, Fig. 8 shows that the lattice mismatch between the unit length of resin (0.250 nm) and that of aluminum (0.286 nm) is about 14%, and this large lattice mismatch makes the atomic configurations of the resin and aluminum irregular. The lattice of iron in Fig. 7 is characterized by a triangle with two 0.248-nm sides and one 0.286-nm side. The lattice mismatch between 0.248 nm and 0.250 nm is 0.008%. However, the lattice mismatch between 0.286 nm and 0.250 nm is about 14%. The small lattice mismatch (0.008%) and the large one (14%) are considered to lead to intermediate interface strength between that for the structures in Figs. 6 and 8.

3.2 Evaluation of adhesion strength in debonding mode II

In this section, we use a mode-II model, which gives the shear displacement to the resin connected with the metal underlayer, as shown in Fig. 9. Figure 10 shows an example of the atomic configurations where all the resin molecules are given the 0.25-nm displacement. The interfacial strain energy during the shear deformation is calculated, and the shear-fracture energy can be obtained as the maximum strain energy. We used the same crystal-like resin as in the previous section, and the resin-molecule structure is shown in Fig. 5.

In calculations, we used only one resin molecule (Fig. 5) on the metal model (thickness × length × width = 0.63 × 2.3 × 2.3 nm). If we used a thicker resin layer with more resin molecules, the phenomenon would become too complicated because the shear deformation would occur not only at the interface but also inside the resin. This inside deformation would make the maximum shear-deformation energy larger than the energy needed to cause the interfacial shear fracture. By using only one resin molecule, we were able to avoid the inside deformation.

We set the crystal texture of the metal so that the plane of the greatest atomic density, which is the (111) plane in fcc structures, was parallel to the metal/resin interface. The reason we assumed this texture is that the plane of the greatest atomic density is energetically stable and that it is most likely to appear on the surface of the metal. If we dealt with all the directions, it would take a long time to calculate the statistical average over the directions. Accordingly, we dealt only with the [110] direction, in which the shear fracture energy is smaller than that in any other direction. We used the same interatomic potential (CVFF) as in mode I in the previous section.

The relationship between the interfacial strain energies of Cu, Fe, and Al and the resin displacement during the shear-deformation calculation is shown in Fig. 11. This figure shows that the interfacial strain energies take maximum values, and these values are considered to be the shear-fracture energies. The values are 0.651, 0.532, and 0.091 J/m² for Cu, Fe, and Al, respectively. Thus, the shear-fracture energy increases in the same order as the adhesion strength index (Cu > Fe > Al) obtained by the experiment shown in Chapter 2, the same as in mode I.
The experimental condition in which the shear stress was applied to the resin with the pressure force was more similar to that of the mode-II simulation than that of the mode-I simulations. However, only the shear slip deformation occurs, and the tensile deformation and adhesive fracture do not occur in the mode-II simulations because the tensile stress is not applied.

3.3 Debonding propagation mode

The reason that adhesive fracture does not occur in the mode-II simulations with the same condition as that of the experiment is the negligence of the interface roughness. Thus, to confirm the effect of the interface roughness we carried out a finite-element analysis by using the observed interface profile.

Figure 12 shows the surface roughness data $h(x)$ in a $300 \times 300 \, \mu m$ region obtained by observing the surface profile at 150-times expansion.

To investigate the effect of the interface profile on the debonding characteristics, we used the axial-symmetry finite-element model shown in Fig. 13(b) with the interface roughness data shown in Fig. 13(a). To analyze the phenomenon, we applied the interfacial pressure in the radial direction and applied the shear load in the axial direction.

The radial stress distribution at the interface and the stress distribution along the axial direction are shown in Figs. 13(c) and 13(d), respectively. We found that the tensile stress occurs at the end of a cut trace and the mountain-like parts, so debonding is considered to propagate under tensile stress. Published papers by Persson and others describe similar effects of interface roughness on debonding characteristics\(^{(11)-(13)}\).
In an actual interface, the mode-I type tensile deformation locally occurs due to the interface roughness, and mode-I debonding propagates due to this tensile deformation, even when no tensile load is applied. Therefore, the interfacial fracture energy obtained from the mode-I molecular-dynamics simulations is considered to be effective in determining the adhesion strength that can be compared with the experimental results.

4. **Comparison between interfacial fracture energy and adhesion strength index**

In Fig. 14, we compare the adhesion strength index measured in a micro-level experiment with the interfacial fracture energy obtained by mode-I atomic-level simulations. The left y-axis of Fig. 14 shows the experimental results, and the right one shows the simulation results. The adhesion strength trend of the simulation agrees well with that of the experiment. Cu has the strongest adhesion with the resin while Al has the weakest.

We consider that the adhesion strength index and interfacial fracture energy that deals with atomic debonding are effective in showing the adhesion strength because they agree well with each other. The atomic-level calculation is effective not only in clarifying a dominant factor, such as the lattice mismatch, but also in predicting the adhesion strength efficiently.
5. Summary

In this paper, a technique to select appropriate materials efficiently by qualitatively predicting the adhesion strength of interfaces from the interfacial fracture energy was presented. In this technique, the fracture energy, which agrees well with the adhesion strength index obtained from experiments, is calculated. We applied this technique to the interface between resin and three metals (Cu, Fe, and Al) and showed that this technique is effective in predicting the adhesion strength.

We investigated the debonding propagation mode by taking account of the interface roughness; we found that tensile stress, which causes local mode-I debonding, occurs due to the interface roughness even when macroscopic mode-II displacement is applied. Therefore, the interfacial fracture energy obtained from the mode-I molecular-dynamics simulations is considered to be effective for comparing the simulation results with the experimental results of macroscopic mode-II deformation.

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