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Strong Adhesion and High Wettability at Polyetheretherketone-Resin/Titanium-Dioxide Interface Obtained with Crystal-Orientation Control

Tomio Iwasaki, Yosuke Kawahito

***Abstract*—**The adhesion strength and wettability at the interfaces between a polyetheretherketone (PEEK) resin and titanium dioxide (TiO_2) have become more important because direct joining of PEEK resin and titanium (Ti), whose surface has usually the oxide (TiO_2), is needed not only in vehicles such as airplanes, automobiles, and space vehicles, but also in medical devices such as implants. To realize strong joint between the PEEK resin and TiO_2, the dependence of the adhesion strength and wettability on crystal orientations of rutile TiO_2 were investigated by using molecular simulations. Molecular dynamics simulations were conducted by combining quantum-mechanics equation of electrons with Newton's equation of motion of nuclear coordinates (atomic coordinates). By putting a PEEK-resin sphere on a rutile TiO_2 surface and by heating the system to 650 K, the contact angles at the interfaces were calculated to evaluate the wettability. After the system is cooled to 300 K from 650 K, to evaluate the adhesin strength, the adhesive fracture energy is calculated as the difference between the energy of the PEEK-TiO_2 attached state and that of the PEEK-TiO_2 detached state. The results of the contact angles showed that PEEK resin on the TiO_2(100) and that on the TiO_2(001) surface has low wettability with large contact angles. On the other hand, PEEK resin on the TiO_2(110) surface has high wettability with a small contact angle. The results of the adhesive fracture energies showed that the adhesion at the PEEK-resin/TiO_2(100) and PEEK-resin/TiO_2(001) interfaces are weak. On the other hand, the adhesion at the PEEK-resin/TiO_2(110) interface is strong. To clarify the reason that the higher wettability and stronger adhesion are obtained at the PEEK/TiO_2(110) interface than at the at the PEEK/TiO_2(100) and PEEK/TiO_2(001) interfaces, atomic configurations at the interfaces were visualized. The atomic configuration at the PEEK/TiO_2(110) interface showed that the lattice-matched coherent interface is realized, and the atomic density is high. On the other hand, the atomic configuration at the PEEK/TiO_2(001) interface showed the lattice-unmatched incoherent interface. The atomic configuration at the PEEK/TiO_2(100) interface showed that the atomic density is very low although the lattice-matched interface is realized. Therefore, the lattice matching and the high atomic density at the PEEK/TiO_2(001) interface are considered to be dominant factors in the high wettability and strong adhesion.

***Keywords*—**Adhesion, direct joining, PEEK, TiO_2, wettability.

I. Introduction

DIRECT joining of carbon fiber-reinforced plastics (CFRP) and light metals such as titanium (Ti), aluminum (Al), and magnesium (Mg) attracted the attention as the weight of vehicles such as airplanes, automobiles, and space vehicles is reduced to cut carbon dioxide (CO_2) emissions [1]-[3]. Although an epoxy resin is often used as the plastics for CFRP, it is difficult to recycle it because it requires special recycling processes [2]. So, a PEEK resin, which is thermoplastic resin with high mechanical strength and heat resistance, has attracted the attention as the plastics for CFRP because it is easier to be recycled than the epoxy resin, which is thermosetting resin [4], [5]. However, it is more difficult to obtain strong adhesion and high wettability at the PEEK-resin/other-material interface than at the epoxy-resin/other-material one. So, a method for improving the adhesion and wettability at PEEK-resin/other-material interface has been investigated by use of molecular simulation. Because titanium (Ti), which has thermal expansion ratio close to CFRP, is often used in airplanes, this paper describes the adhesion and wettability at the PEEK/TiO_2 interface, which is important in direct joining of PEEK and Ti, whose surface has usually the oxide (TiO_2). As far as PEEK and TiO_2 are concerned, the results of this study can be applied to various fields, as shown in the following examples. TiO_2 is often used as a filler in a PEEK resin to improve the mechanical strength and the ultraviolet resistance [6]. In addition, the PEEK/TiO_2 combination has been used in medical devices such as implants [7]. When the PEEK/TiO_2 combination is used in implants, PEEK is covered with TiO_2. Accordingly, the results of this study can be applied to various fields.

II. Method of Molecular Simulation

A. Basic Method

The quantum molecular dynamics simulations were conducted by combining quantum-mechanics equation of electrons with Newton's equation of motion of nuclear coordinates (atomic coordinates) [8]. The functional functions and basis functions for structure optimization of the system were performed by using B3LYP/6-31G* [9]. Based on the structure obtained with structure optimization, the functional functions and basis functions of the electric charge calculation were performed by using MP2/6-31G*. The molecular simulation results were visualized by using Materials Studio made by Dassault Systemes [10].

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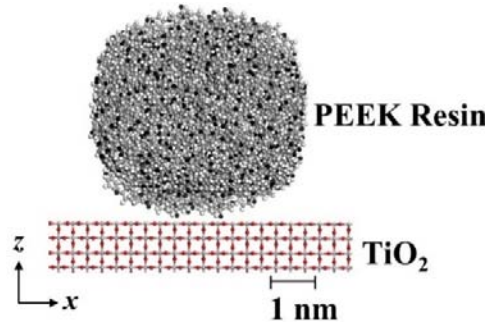

Fig. 1 Initial state of simulation for analyzing wettability at the PEEK/TiO_2(110) interface before relaxing simulation

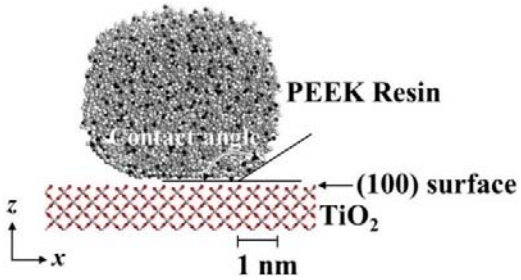

Fig. 2 PEEK/TiO_2(100) interface obtained at 650 K

B. Wettability Analysis Method

By putting a PEEK-resin sphere on a rutile TiO_2 surface (Fig. 1) and by heating the system to 650 K, the contact angles at the interfaces were calculated to evaluate the wettability. The smaller the contact angle, the higher the wettability is. By changing the crystal orientation of the rutile TiO_2 surface, the dependence of the wettability on the crystal orientation is investigated.

C. Adhesion Analysis Method

After the system is cooled to 300 K from 650 K, which is the temperature of contact angle calculation, to evaluate the adhesion strength, the adhesive fracture energy is calculated as the difference between the energy of the PEEK-TiO_2 attached state and that of the PEEK-TiO_2 detached state [11]. The larger the absolute value of the adhesive fracture energy is, the stronger the adhesion strength is. By changing the crystal orientation of the rutile TiO_2 surface, the dependence of the adhesion strength on the crystal orientation is investigated.

III. Results and Discussions

A. Results of Contact Angles and Wettability

By putting a PEEK-resin sphere on a rutile TiO_2 surface (Fig. 1) and by heating the system to 650 K, the interface structure shown in Fig. 2 is obtained in case of TiO_2(100). From this structure the averaged contact angle is obtained as 138.7 degrees. In case of TiO_2(001) the averaged contact angle is obtained as 124.2 degrees, as shown in Fig. 3. On the other hand, in case of TiO_2(110) the averaged contact angle is obtained as 74.2 degrees, as shown in Fig. 4. From these results, the wettability of PEEK/TiO_2(110) is much higher than that of PEEK/TiO_2(001) and PEEK/TiO_2(100) in the following order:

PEEK/TiO_2(110) > PEEK/TiO_2(001) > PEEK/TiO_2(100)

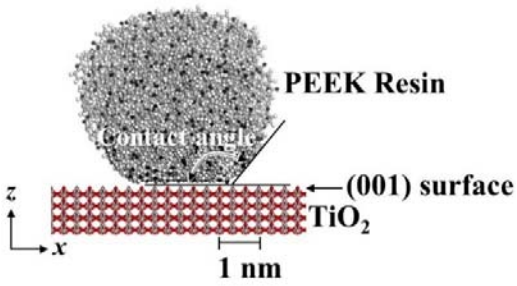

Fig. 3 PEEK/TiO_2(001) interface obtained at 650 K

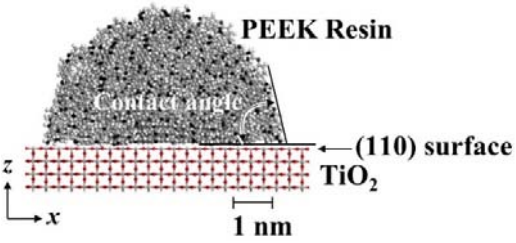

Fig. 4 PEEK/TiO_2(110) interface obtained at 650 K

B. Results of Adhesion Strength

After the system is cooled to 300 K from 650 K, which is the temperature of contact angle calculation, to evaluate the adhesin strength, the adhesive fracture energy that is calculated as the difference between the energy of the PEEK-TiO_2 attached state and that of the PEEK-TiO_2 detached state. The values of the adhesive fracture energies are expressed as the energy per unit contact area, and the unit is J/m^2. The result of the adhesive fracture energy corresponding to each crystal orientation is shown in Table I, where the contact angles are also shown. From this table, it was found that the adhesion strength of PEEK/TiO_2(110) is much stronger than that of PEEK/TiO_2(001) and PEEK/TiO_2(100) in the following order: PEEK/TiO_2(110) > PEEK/TiO_2(001) > PEEK/TiO_2(100). This is the same order as the wettability, as shown in the previous section. To clarify the electron density at the interfaces, the isosurfaces (100 electrons/nm^3) of the electron density at the PEEK/TiO_2(110), PEEK/TiO_2(001), and PEEK/TiO_2(100) interfaces are shown in Figs. 5, 6, and 7, respectively. From these figures, the stronger interface (PEEK/TiO_2(110)) has higher electron density than PEEK/TiO_2(001) and PEEK/TiO_2(100).

TABLE I
Contact Angle and Adhesive Fracture Energy at Interfaces

Interface	Contact Angle (degrees)	Adhesive Fracture Energy (J/m^2)
PEEK/TiO_2(100)	138.7	0.217
PEEK/TiO_2(001)	124.2	0.264
PEEK/TiO_2(110)	74.2	0.691

In the next section, to clarify the reason that the PEEK/TiO_2(110) interface has the highest wettability and the strongest adhesion, the atomic configurations of the interfaces are visualized, and the lattice matching between the PEEK resin and TiO_2 is investigated.

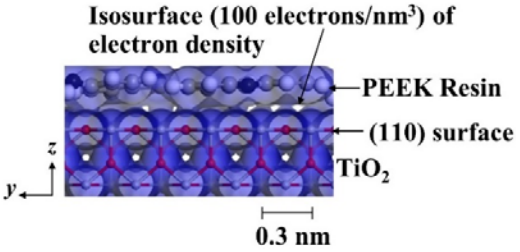

Fig. 5 Isosurface (100 electrons/nm^3) of the electron density at the PEEK/TiO_2(110) interface

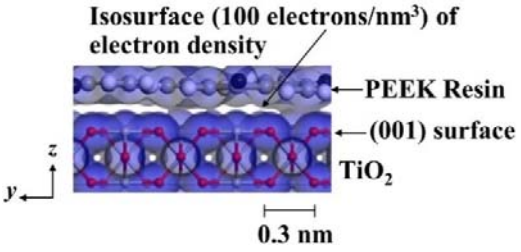

Fig. 6 Isosurface (100 electrons/nm^3) of the electron density at the PEEK/TiO_2(001) interface

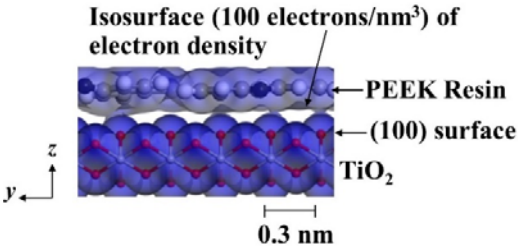

Fig. 7 Isosurface (100 electrons/nm^3) of the electron density at the PEEK/TiO_2(100) interface

C. Lattice Matching and Atomic Density of TiO_2 Surface

The atomic configurations at the PEEK/TiO_2(110), PEEK/TiO_2(001), and PEEK/TiO_2(100) interfaces are shown in Figs. 8, 9, and 10, respectively. At the bottom views of the interfaces in these figures, small spheres are atoms of the PEEK resin, and large spheres are atoms of TiO_2. In Fig. 8, many benzene rings of the PEEK resin are located on the hexagon patterns of TiO_2(110) lattice, and the lattice matching is found to be particularly good. Furthermore, the atomic density of TiO_2(110) is remarkably high (20.8 atoms/nm^2). On the other hand, Fig. 9 shows that many benzene rings of the PEEK resin are located irregularly on the lattice of the TiO_2(001) surface and that the lattice matching is worse than that at the PEEK/TiO_2(110) interface (Fig. 8), although the atomic density of TiO_2(001) is fairly high (15.5 atoms/nm^2).

Fig. 10 shows that many benzene rings of the PEEK resin are located on the oxygen atoms of the TiO_2(100) surface, and the lattice matching is found to be fairly good. However, the atomic density of TiO_2(100) is extremely low (7.36 atoms/nm^2), and this low density is the reason that the wettability and adhesion of PEEK/TiO_2(100) is lower than those of PEEK/TiO_2(110).

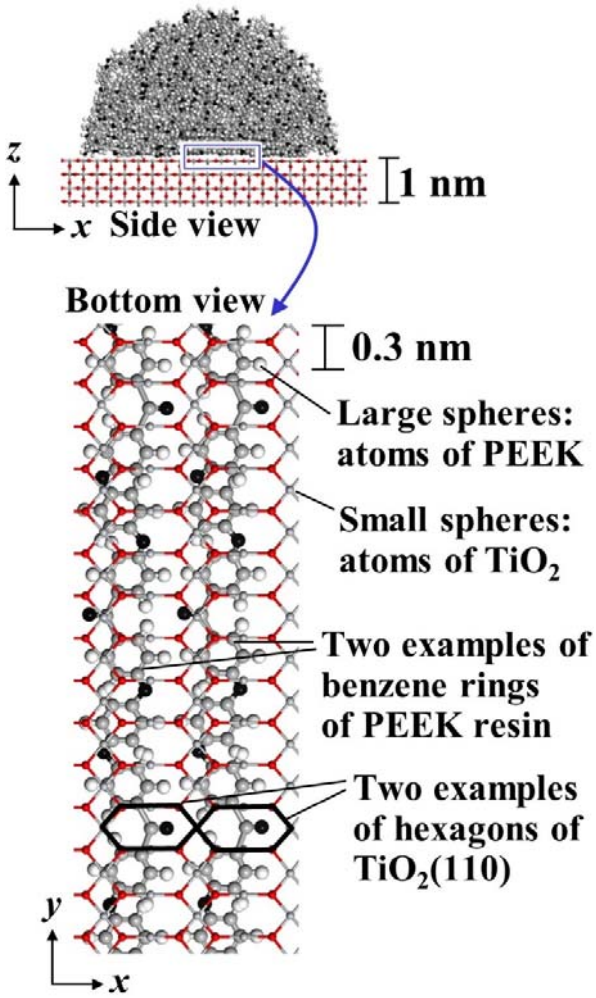

Fig. 8 Lattice-matched coherent interface between PEEK resin and TiO_2(110) plane, where the atomic density is remarkably high

From these results, both of the lattice matching and atomic density are considered to be dominant factors in the wettability and adhesion strength at the PEEK/TiO_2 interface.

IV. Conclusions

In order to obtain strong joint between the PEEK resin and a kind of light metal, Ti, whose surface has TiO_2, the adhesion strength and wettability at PEEK/TiO_2 were investigated by using molecular simulations. Especially, the dependence of those interface properties on crystal orientations of rutile TiO_2 were studied. In the molecular simulations, atomic coordinates and electron states at the interfaces were obtained by solving a combination of quantum-mechanics equation of electrons and Newton's equation of motion of nuclear coordinates, which equal atomic coordinates. By using a PEEK-resin sphere on the rutile TiO_2 surface as an initial model and by heating the model to 650 K, the contact angles at the interfaces were obtained. The wettability was evaluated from the contact angle. After the system is cooled to 300 K from 650 K, the adhesive fracture energy was calculated to evaluate the adhesion strength.

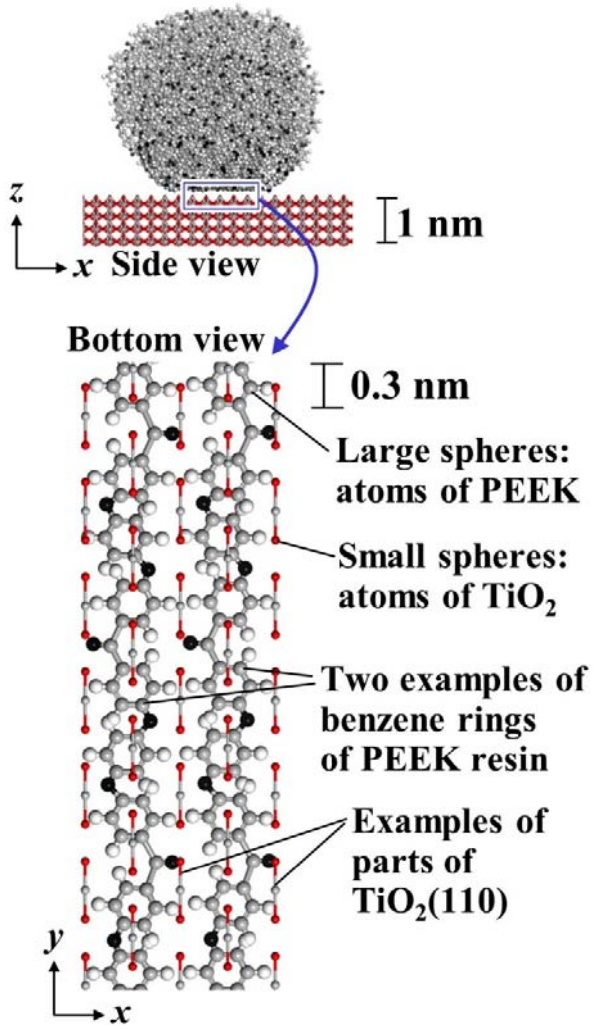

Fig. 9 Lattice-mismatched incoherent interface between PEEK resin and TiO_2(001) plane, where the atomic density is fairly high

From the obtained contact angles, it was found that the wettability of the PEEK/TiO_2(100) and PEEK/TiO_2(001) interfaces is extremely low. On the other hand, the wettability of the PEEK/TiO_2(110) interface is fairly high. From the adhesive fracture energies, it was found that the adhesion at the PEEK/TiO_2(100) and PEEK/TiO_2(001) interfaces is extremely weak. On the other hand, the adhesion at the PEEK/TiO_2(110) interface is fairly strong.

To clarify the reason for the dependence of the wettability and adhesion strength on the crystal orientation of TiO_2, the atomic configurations at the interfaces were visualized. From the atomic configuration at the PEEK/TiO_2(110) interface, it was found that the lattice-matched coherent interface is formed, and that the atomic density is remarkably high. On the other hand, from the atomic configuration at the PEEK/TiO_2(001) interface, it was found that the lattice-unmatched incoherent interface is formed although the atomic density is fairly high. Furthermore, from the atomic configuration at the PEEK/ TiO_2(100) interface, it was found that the atomic density is extremely low although the lattice-matched coherent interface is formed. Accordingly, the small lattice mismatch and the high atomic density at the PEEK/TiO_2(001) interface are dominant factors in the high wettability and strong adhesion strength.

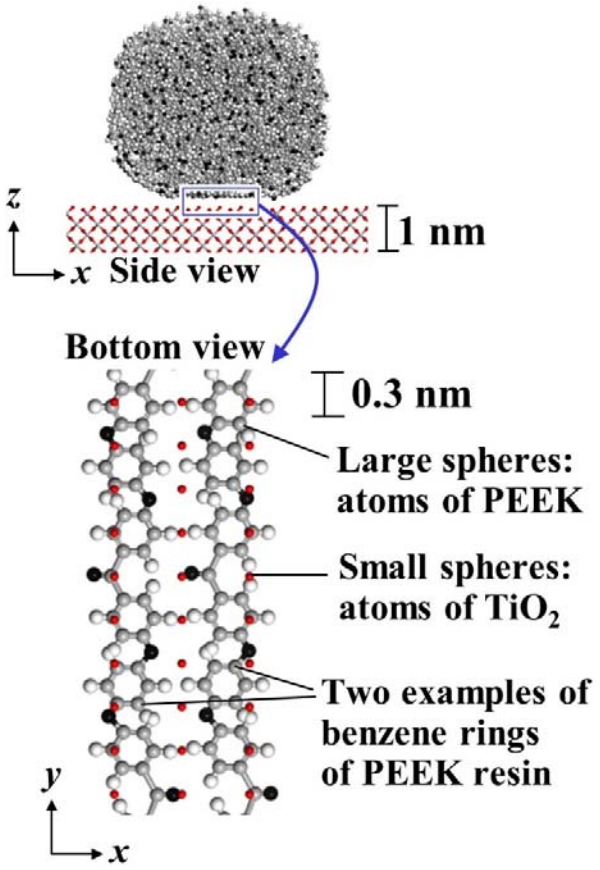

Fig. 10 Lattice-matched coherent between PEEK resin and TiO_2(100) plane, where the atomic density is very low

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