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Destruction of metal–resin adhesion due to water penetrating through the resin

H. OHNO, K. ENDO, Y. ARAKI
Department of Dental Materials Science, School of Dentistry, Higashi-Nippon-Gakuen University, Ishikari-Tobetsu, Hokkaido, Japan
S. ASAKURA*
Division of Materials Science and Chemical Engineering, Faculty of Engineering, Yokohama National University, Yokohama, Kanagawa, Japan

Polymethyl methacrylate (PMMA) film bonded by 4-META dental adhesive resin to mild steel was used as a specimen to study the mechanism of water permeation into the adhesive interface. Degradation of the adhesion interface after immersion in water was investigated by measurement of peeling area after imposing thermal stress using liquid nitrogen. The amount of water penetrated at the interface was calculated from the solution to Fick's second equation. The degradation at the interface is discussed with respect to the water content. Water enters the interface by diffusion through the resin rather than by passage along the interface. The interface is broken by water when the water content at the interface reaches 48% of the equilibrium water concentration of PMMA. Observation through the PMMA film shows no change in the mild steel surface at 48% equilibrium water concentration; at 95% water content many small white spots appear on the surface. The surface colour gradually changes to black due to the formation of corrosion products.

1. Introduction

Recently, marked developments have been made in the study of dental adhesive resin. The development of PMMA adhesive resin (4-META resin) [1] containing the adhesive monomer, 4-methacryloxyethyl trimellitate anhydride (4-META), and compounds [2] containing acidic phosphate groups which have excellent adhesive properties to both tooth substances and dental alloys, has given rise to technical innovation in dentistry. However, a major problem awaiting solution also in industrial applications is to attain good durability of bonding joints exposed to water. Generally, joints of dental adhesive resin bonded to dental alloys weaken in wet environments though adhesion is strong in dry environments. One example is the separation or peeling at the bonded interface of metallic dentures bonded with acrylic resin, which occurs after long-term use in the oral environment. Metal bridges bonded to teeth also fall off after extended use. There have been, however, no reports to clarify the degradation mechanism of the adhesion interface between dental adhesive resin and alloys.

Both the permeation path of water to the adhesion interface and the water content which degrades the interface were determined in the present study.

2. Materials and methods

2.1. Permeation path of water to the adhesion interface

Two specimen types were examined to determine whether the predominant path of water permeation to the interface is (1) diffusion through the resin, or (2) transported along the metal/resin interface.

The first type (Type A) has no exposed bond joints; the resin is a 0.2 mm PMMA film bonded with 4-META resin on an 18 mm × 18 mm metallographically polished mild steel plate with sealed bond joints, as shown in Fig. 1a. The second type (Type B) has exposed bond joints as shown in Fig. 1b, and was bonded with three different PMMA films, 0.1, 0.2 and 0.3 mm in thickness. Immediately after bonding with 4-META resin, a 20 kg load was applied for 5 min to the two types of specimen to maintain the 4-META resin thickness of 0.05 mm. The specimens were stored in a dry chamber at 37 °C for 24 h for adequate curing before immersion in distilled water at 37 °C. Changes in the mild steel surface were observed through the resin film after different periods of immersion.

2.2. Degradation of adhesion interface by immersion in water

To investigate the degradation of the adhesion interface, a 0.2 mm thick PMMA film was bonded with 0.05 mm thick 4-META resin on the 18 mm × 18 mm metallographically polished mild steel plate described above. The specimens were stored in a dry chamber at 37 °C for 24 h before immersion in 37 °C distilled water. After immersion, the specimens were subjected to 20 thermal cycles from liquid nitrogen (− 195.8 °C) to 40 °C water, each for 1 min. The resin film peels

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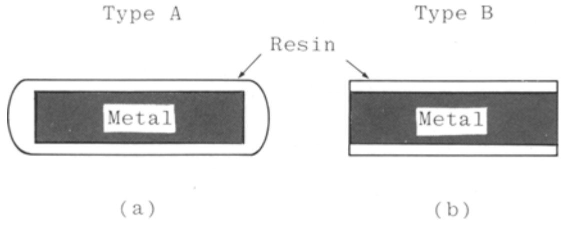

Figure 1 Specimen models for observation of the intrusion path of water to the adhesion interface of the metal/resin; Type A has no joint exposed to water, Type B has exposed joints.

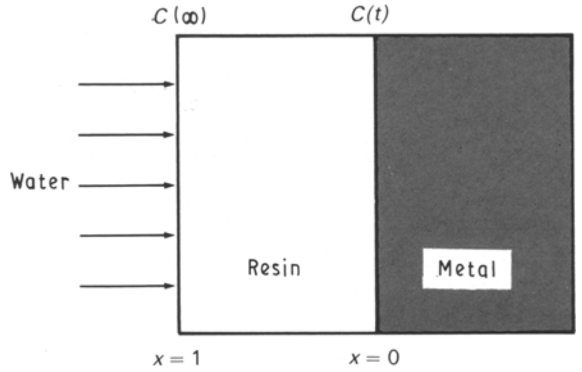

Figure 2 Diffusion model to calculate water content at the adhesion interface.

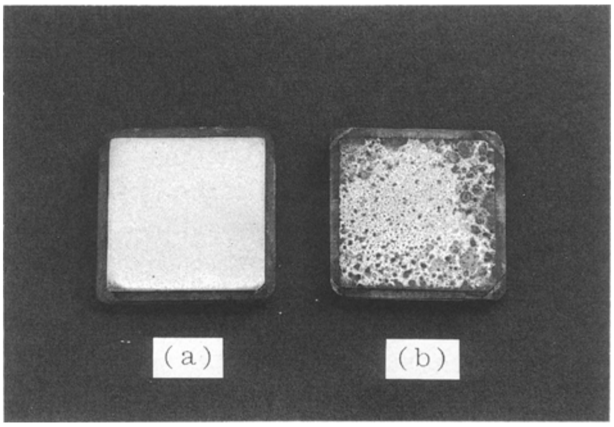

Figure 3 Type A specimen (Fig. 1) (a) before and (b) after immersion in water at 37 °C for 5 days

from the mild steel surface by thermal stress when there is degradation at the adhesion interface, and the peeled areas were measured for each immersion time.

2.3. Analysis of water content at the adhesion interface

Water content at the adhesion interface was calculated from the solution to Fick's second equation [3]. The water content at the interface of the metal and a bonded resin film of thickness l, as shown in Fig. 2, is given by Equation 1, assuming that there is no flux of water at the interface with the metal

$$\frac{C(t)}{C(\infty)} = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1} \times \exp[-D(2n+1)^2\pi^2 t/4l^2] \qquad (1)$$

where $C(t)$ is the concentration at the interface ($x = 0$) and $C(\infty)$ is the concentration at equilibrium, D is the diffusion coefficient, and t is time. Because the diffusion coefficient of water molecules through PMMA depends on temperature and water content, the minimum ($C = C_\infty$), $D_{\min}$, and the maximum ($C = 0$) $D_{\max}$, values, of D at 37 °C were estimated from these values at 25 °C reported in the literature [4] using the equations,

$$D(T)_{C=0} = a_{C=0}\exp(-b/T) \qquad (2)$$

$$D(C)_T = D(O)_T\exp(-kC) \qquad (3)$$

where $a_{C=0}$, b, and k are constant. The constant b was determined to be 4.621×10^3 K from the slope of the linear portion of $\ln D$ versus $1/T$ plot in the temperature range 25–70 °C reported by Kawasaki and Sekita [5], assuming that b was independent of water content. The constants a and k, which were assumed to be independent of temperature, were determined to be 7.343×10^{-2} cm^2 s^{-1} and 3.416×10^1 based on the data reported in the literature [4]. $D_{\min}$ ($C = C_\infty$) and $D_{\max}$ ($C = 0$) values thus obtained were 1.414×10^{-8} and 2.484×10^{-8} cm^2 s^{-1}, respectively.

3. Results

3.1. Permeation path of water to the adhesion interface

Fig. 3 shows the surface states of the mild steel of Type A specimens shown in Fig. 1a. Fig. 3a and b were obtained from the specimens kept in a dry environment and in water for 5 days, as observed through the resin film. There is no change on the surface of the specimen in (a), and many black spots on the surface of the specimen in (b) after immersion. After immersion for several hours, white spots appeared on the surface, then changed to brown and finally became black after 5 days.

Fig. 4 shows surface states of Type B specimens with three different film thicknesses, (a) 0.15, (b) 0.25, and (c) 0.35 mm, after immersion for 5 days. The change in the surface appearance is more remarkable with thinner films. Both resin films of 0.15 and 0.25 mm separate completely from the metal surface, while the 0.35 mm film was only partially separated.

The results in Figs 3 and 4 indicate that diffusion of water molecules to the resin/metal interface is primarily through the resin layer and not by transport along the resin/metal interface.

3.2. Degradation of the adhesion interface by immersion in water

Fig. 5 shows repeated measurements of the relationship between the peeled area (%) of resin films and immersion time (min), measured after the thermal cycles. The peeled area covers only a few per cent after short immersion times, below 100 min. After longer immersion times, over 200 min, the separation induced by thermal stress covers the whole metal surface, and there is a critical immersion time for interface

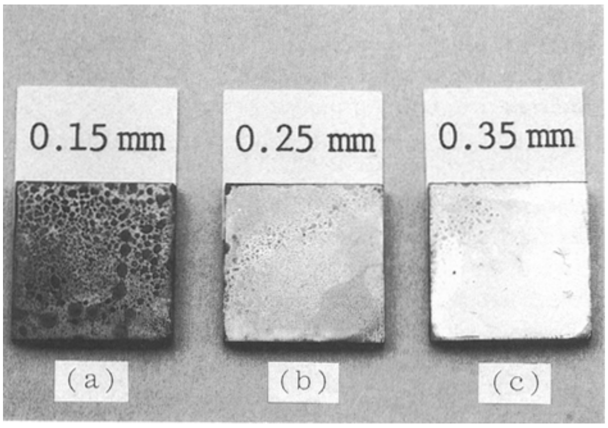

Figure 4 Type B specimen (Fig. 1) with different resin thicknesses, (a) 0.15, (b) 0.25, and (c) 0.35 mm, after immersion in water at 37 °C for 5 days.

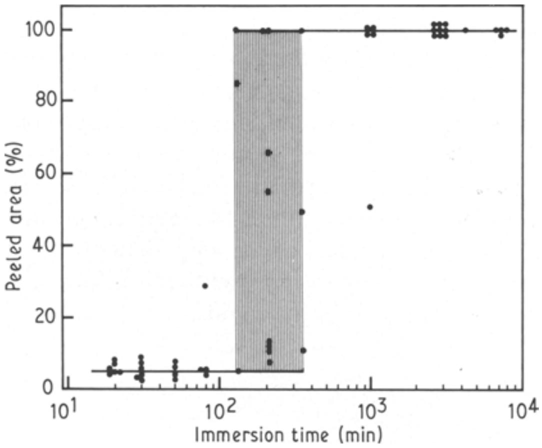

Figure 5 Peeled area of resin film and immersion time in water after thermal cycling.

failure near 200 min. This indicates that failure occurs at the interface when the water content here reaches a critical value.

3.3. Analysis of water content at the adhesion interface

Fig. 6 shows the relationship between film thickness and water content, $C(t)/C(\infty)$, at the interface, obtained from Equation 1. At 0.1 day immersion, the ranges of results calculated using $D_{\min}(C = C_\infty)$ or $D_{\max}(C = 0)$, are represented by the shaded area. The relations between the film thickness and the water content with respect to the equilibrium water concentration of PMMA represented at other times were all obtained using the average D value at 37 °C. The water content leading to interface failure is calculated to be approximately 48% of the equilibrium water concentration of PMMA because the experimental data in Fig. 5 were obtained from a resin film of 0.25 mm and interface failure appears at an immersion time near 200 min.

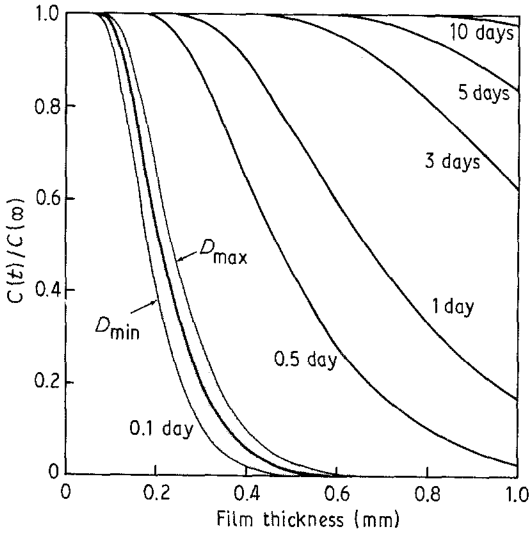

Figure 6 Relationship between film thickness and water content at the adhesion interface with immersion period.

Further experiments were performed to determine the immersion period necessary for white spots to appear on the steel surface. Three PMMA films of 1.0, 1.5, or 2.0 mm, were bonded on mild steel with 4-META resin in the manner described previously, and the surface states were observed after immersion in water. On the 1.0 mm thick resin specimens, white spots appeared after 10 days, with the 1.5 mm thick resin after 20 days, and with the 2.0 mm resin after 31 days. Water content at the interface, which produces the white spots on the steel surface, was calculated to be 95% of the equilibrium concentration from the immersion period and resin thickness.

Fig. 7 shows the relationship between immersion period in water and film thickness with the water content at the adhesion interface at 48% (interface failure), 95% (white spots), and 100% equilibrium water concentration.

4. Discussion

Durability in wet surroundings is also a property of prime importance in adhesively bonded metal structures in the bio-materials field. Many investigations [6–15] of industrial applications have studied degradation due to moisture permeation into bonded joints. However, no such studies have been reported in the bio-materials field. Dental adhesive resin (4-META resin) which is a comonomer with MMA, containing 5 mass % 4-META (shown in Fig. 8) having both hydrophilic and hydrophobic groups, bonds strongly with tooth structures [16] and dental alloys [17]. However, weakening of the joints by immersion in water has been observed in some dental alloys.

Brewis *et al.* [11] have reported that water molecules enter joints by diffusion through the adhesive rather than by passage along the interface in the bonding of aluminium/epoxy resin. This has also been shown for bonding of aluminium alloy/polysulphone with scanning TEM (STEM) and X-ray photo electron spectroscopy (XPS) by Ko and Wightman [15], and also with adhesion of dental adhesive resin/mild steel by the experiments in the present study.

The kinetics of the fracture mechanism are governed by the rate of diffusion of water through the adhesive to the interface [13, 18].

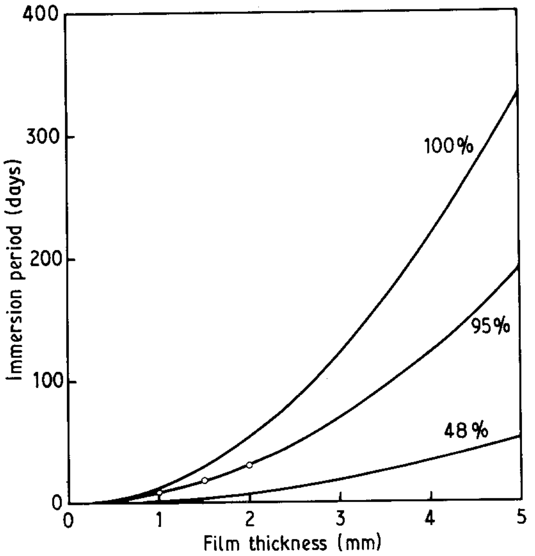

Figure 7 Relationship between the immersion period in water and the film thickness for the water content at the adhesion interface to reach 48% (interface failure occurs), 95% (white spots appear), and 100% equilibrium water concentration. The notation indicates experimental points at which white spots were observed.

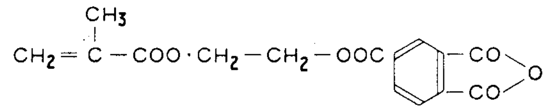

Figure 8 Chemical structure of dental adhesive monomer 4-META (4-methacryloxyethyl trimellitate anhydride).

Water molecules diffuse through the PMMA and 4-META resin because the diameter of water molecules is less than 0.28 nm, smaller than the interchain distance in the resin, and because the polarity of the carbonyl group in PMMA attracts water molecules. As a result, PMMA has an equilibrium water concentration of approximately 2 mass %.

The diffusion rate of water molecules through polymer materials may be treated as Fickian [18, 19] or non-Fickian [14]. In the present study, the diffusion rate was calculated as Fickian. Interface failure occurs by thermal stress when the water content at the interface reaches 48% of the equilibrium water concentration.

Masuhara [20] has proposed an adhesion mechanism for metal and 4-META resin where side chains of 4-META bond with hydroxyl groups on the metal surface by forming hydrogen bonds. It is considered that water molecules which permeate to the interface break the hydrogen bonds with the 4-META side chain, resulting in degradation of the interface, and failure when 48% water content is reached.

Brewis *et al.* [13] have reported a linear relation between the joint strength of aluminium alloy/epoxide-polyamide and the water content of the joints. The water content here is the average concentration of water in the adhesive and not the water content at the interface itself. The relationship between the degradation of the adhesive interface and the water content at the interface of the mild steel/4-META adhesive resin is not linear but discontinuous as shown in Fig. 5. The presence of water at the interface leads to changes in the appearance of the fracture: for dry joints fracture occurs near the epoxy resin/metal interface, while water-soaked joints show fracture at the interface between the adhesive and the iron oxide [9]. In the present study, interface separation appeared after immersion times longer than 200 min, indicating a change in the surface state of the mild steel. The changes in the metal surface at the adhesion interface after exposure to water have been reported for cases where corrosion of the iron oxide leads to considerable increases in the oxide thickness [9]. With aluminium, moisture permeation at the interface causes the surface oxide layer to convert to a hydroxide with accompanying changes in morphology and bond strength [12, 21].

In the present study there were no changes in the surface state up to the time when 48% water content was reached, at 95% water content the surface of the mild steel changed to white spots, then to brown ones, and finally the spots became black. It is therefore concluded that destruction at the interface occurs by breakdown of hydrogen bonds with 48% of the equilibrium water concentration, and that it is followed by corrosion forming iron hydroxide.

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