[Review Paper]

Behavior and Mechanisms of Degradation of Thermosetting Plastics in Liquid Environments

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Behavior and mechanisms of degradation of thermosetting plastics used as FRP-matrix and GFRP in liquid environments are reviewed based on our experimental findings.   The forms of chemical degradation were classified into three types, 'surface reaction type,' 'corrosion layer forming type' and 'penetration type.'   The mechanism of each type is dependent on the chemical structures of the resin, the reactivity between resins and liquids, and the diffusivity of liquid in the resins.

The corrosion rate was defined as change of corrosion thickness with immersion time in the 'surface reaction' and 'corrosion layer forming type' corrosion.   By applying the concept of corrosion rate, the residual thickness of the non-corroded region after corrosion could be predicted.   For 'surface reaction' and 'corrosion layer forming type' corrosion, a life-prediction method was proposed using the master curve focused on retention of flexural strength after corrosion.   For 'penetration type corrosion,' the weight change was important to predict the initiation of decrease in mechanical strength.

Introduction

Plastics, elastomers and composites are widely used as construction materials and also as coating or lining materials in corrosive environments.   For example, PVC (polyvinyl chloride), corrosion resistant FRP (fiber reinforced plastics) and rubber linings are generally used for HCl storage tanks[1].   Therefore, these materials are quite important for various industries.   However, severe degradation is sometimes observed even in these polymeric materials because of the combined effects of material and environmental liquid.   In fact, several accidents causing injury or death have occurred recently involving HCl storage tanks.   Therefore, the study of the corrosion behavior and mechanisms, and development of general methods to predict the life of polymeric materials are essential.   Here our investigations of corrosion of plastics and FRPs in liquid environments are described.

1.   Degradation Phenomena

Plastics in contact with liquid environments undergo two types of degradation, physical and chemical degradation.

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1. 1.   Physical Degradation

Liquid molecules penetrate into the plastics in contact with liquid environments.   The liquid molecules penetrate and diffuse between the molecular chains of the polymer, causing the material to swell with associated reduction in the physical and mechanical properties of the material.

If the polarities of the plastics and liquid are different, liquid absorption eventually reaches an equilibrium after some exposure, whereas if the polarities are similar, the solvation phenomenon occurs, as the polymer molecules are surrounded by liquid molecules, resulting in physical dissolution of the polymeric molecular chains after breaking of the inter-molecular bonding of the chains[2].   If the penetrated liquid is discharged before salvation occurs, the physical and mechanical properties may recover to the initial level.

The affinity between liquid and plastic can be evaluated by the solubility parameter given in Eq. (1)[3,4].

$$\delta = \left(\frac{\Delta E}{M/D} \right)^{1/2} = \left(\frac{\Delta E \cdot D}{M} \right)^{1/2} \tag{1}$$

where, δ is the solubility parameter, ΔE is the energy of vaporization (J/mol), and M/D is the molecular volume, D the density and M the molecular weight.   Solubility parameters are obtained for the plastics (δ_P) and solvents (δ_S).   Maximum affinity will be attained at $\delta_P =$
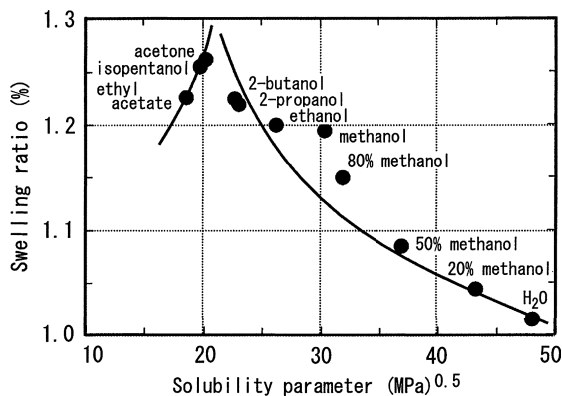
Fig. 1 Relationship between Swelling Ratio and Solubility Parameter for ortho-UP Immersed into Several Organic Solutions at 50°C

Fig. 2 IR Spectra of MTHPA-EP before and after Immersion into NaOH Solution of 40 wt%, 80°C, 360 h

δ_S. **Figure 1** shows that the volume change of orthophthalic type unsaturated polyester resin (ortho-UP) by immersion into various organic solvents at 50°C reaches the maximum when the solubility parameter of the solvent δ_S is equal to that of the resin δ_p (= 9-11)[5].

1. 2. Chemical Degradation

Polymers with special functional groups and/or bonds, tend to degrade by chemical reaction under some environmental conditions, especially in contact with liquids. This chemical degradation results from breakage, addition, crosslinking, etc. in the molecular chain, which is called corrosion. Oxidation, hydrolysis, transesterification, and salt formation are all examples of such chemical reactions.

Oxidizing agents such as O_2, O_3, H_2O_2 and $NaClO_4$ attack the unsaturated bonds in resin structures, and causes severe oxidative corrosion. Plastics exposed to the atmosphere are degraded gradually by the action of O_2 and sunlight. This type of corrosive reaction is called auto-oxidation[6].

Hydrolytic reaction is the most typical pathway of chemical degradation in corrosive liquids. Plastics including ester bonds in the main and/or crosslinking chains, such as unsaturated polyester (UP) and epoxy resin (EP), suffer chemical attack by acid and alkali, followed by scission of the polymer chains.

The ester group reacts with acid to form carboxylate by the following reaction.

$$R-C\diagdown^{O}_{OR'} + H_2O \rightleftharpoons R-C\diagdown^{O}_{OH} + HOR' \quad (2)$$
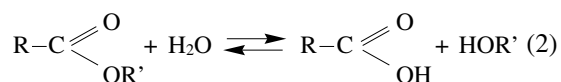
The carboxylate group reacts with alkali and the following reaction proceeds irreversibly[7].

$$R-C\diagdown^{O}_{OH} \xrightarrow{NaOH} R-C\diagdown^{O}_{ONa} \quad (3)$$
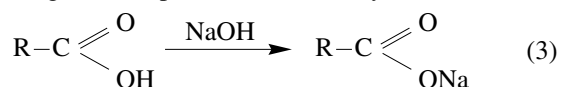
The mechanism of hydrolytic corrosion based on Eqs. (2) or (3) can be followed by IR (infrared) spectroscopy before and after degradation of plastics. **Figure 2**
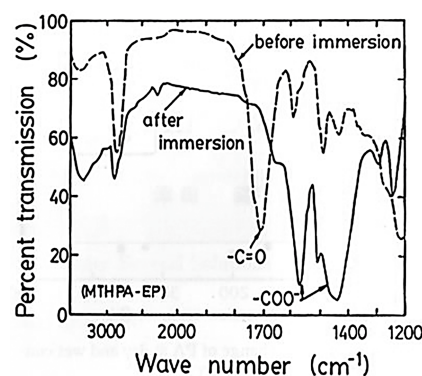
shows the change in the IR spectrum of epoxy resin (EP) immersed in NaOH solution. The ester peak near to 1720 cm⁻¹ becomes smaller and the carboxylate anion peaks at near 1570 cm⁻¹ and 1440 cm⁻¹ appear and enlarge, showing that the corrosion occurs by Eq. (3).

Plastics with ester bonds in a chemical structure will cause corrosion by a transesterification reaction in alcohol environments. The reaction is as follows.

$$\sim ROC \qquad COR\sim \qquad R'OC \qquad COR' \qquad (4)$$
$$+ R'OH \longrightarrow \qquad + HOR\sim$$
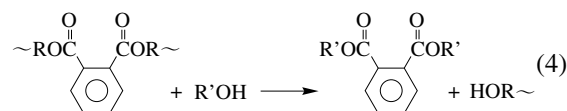
After immersion into alcohol, the test specimens were removed, wiped off using filter paper, and left for 1 h at room temperature. Then, their weight was measured and defined as the wet weight. The specimens were dried completely in a drying oven, and the weight was measured and recorded as the dry weight. The weight change was calculated as the ratio of the weight gain or loss to the weight before immersion. The wet-weight change is the sum of the weight gain by permeation of liquid into the plastic and weight loss by dissolution of the plastic. The mechanical strength was also measured under wet and dry conditions. **Figure 3** shows the weight change and retention of flexural strength under conditions after immersion of ortho-UP in ethanol[5]. The wet weight increased and flexural strength decreased due to the penetration of ethanol into the resin. On the other hand, the dry weight showed no gain in the early period of immersion, but decreased gradually with time. The dry strength showed the same tendency as the dry weight with time. The dry strength rapidly recovered to the original level, and then decreased with increasing time. The behavior in the early period was categorized as physical degradation and the behavior after longer term immersion as chemical degradation through the reaction of Eq. (4).
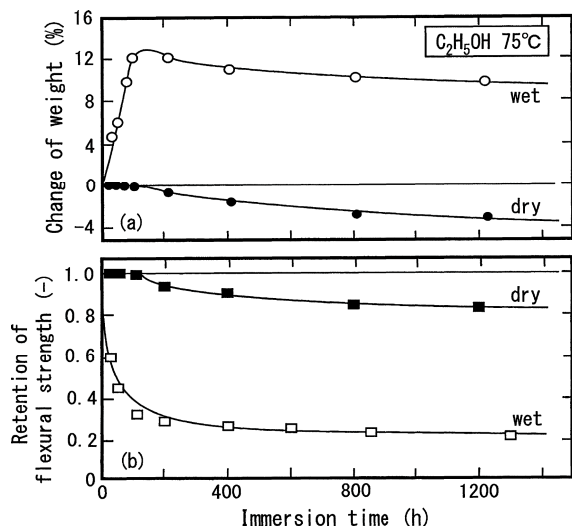
Fig. 3　Change of Weight (a) and Flexural Strength (b) under Wet and Dry Conditions for ortho-UP Immersed into Ethanol at 75°C

2. Corrosion Behavior and Mechanism of Plastics in Liquid Environments

The corrosion behavior and mechanism of plastics are discussed mainly with reference to typical matrix resins for GFRP (glass fiber reinforced plastics).

2. 1. Corrosion Behavior

Isophthalic type UP (iso-UP) and bisphenol-A type epoxy (EP) resins were used as specimens. Iso-UP was closslinked with styrene, EP was cured with phthalic anhydride (methyl-tetrahydrophthalic anhydride: MTHPA) or menthane diamine (*p*-menthane-1,8 diamine, MDA). The chemical structures of the closslinked resins are shown in **Fig. 4**[2),8)].

2. 1. 1 MTHPA-EP in NaOH Solution

The epoxy resins cured with MTHPA (MTHPA-EP) were immersed into NaOH solution of 0-40 wt% at 50-80°C. The resin was dissolved into solution resulting in viscous corroded product on the surface which could be wiped off easily with paper. **Figure 5** shows the typical results of weight change as a function of immersion time. At first, weight increased by penetration of liquid into the resin, then decreased by dissolution of the resin, and finally increased again by absorption of liquid into the viscous corroded products. The thickness of the resin was measured after wiping off the corroded products, and the corrosion thickness (*x*) was calculated by following equation.

$$x = (h_0 - h)/2 \tag{5}$$

where h_0 is the thickness of the original specimen and h is that of the immersed specimen. The thickness increased with increasing immersion time, and also increased with increasing concentration and temperature as observed in **Fig. 6**. A linear relationship between corrosion thickness and immersion time (*t*) was ob-
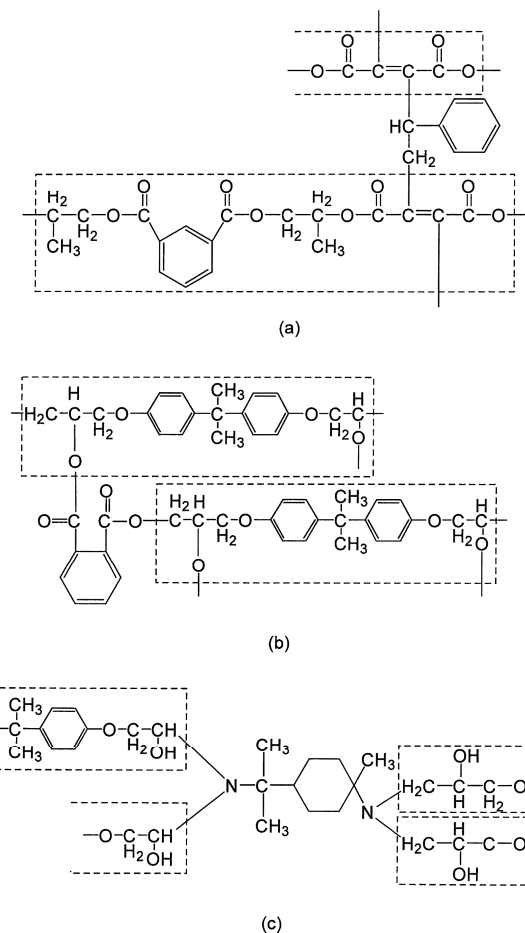
(a) iso-UP, (b) MTHPA-EP, (c) MDA-EP.

Fig. 4　Chemical Structures of Cured Resins

tained as;

$$x = k_1 t \tag{6}$$

where k_1 is a constant[8)].

With the decrease in the specimen thickness, the apparent flexural strength decreased as shown in **Fig. 7**. The retention of flexural strength was defined as the ratio of fractured load of immersed specimen to that before immersion.

2. 1. 2. Iso-UP in NaOH Solution

The isophthalic type UP resins were immersed into NaOH solution at almost the same conditions of concentration and temperature as the MTHPA-EP experiments. The weight change showed the same behavior with immersion time as in **Fig. 5**. The change in flexural strength is shown in **Fig. 8**[9)].

The cross section of the immersed specimen was observed under an optical microscope as shown in **Fig. 9**. A layer of color change could be clearly observed on the surface of the specimen. This layer was thicker on the specimen immersed in KOH solution, as shown in **Fig. 9 (b)**. The chemical structure of the color change layer was analyzed by infrared method and similar
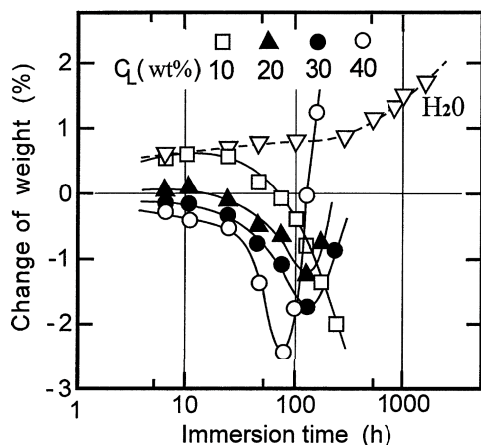
Fig. 5 Change of Weight for MTHPA-EP Immersed into NaOH Solutions of Several Concentrations at 80°C
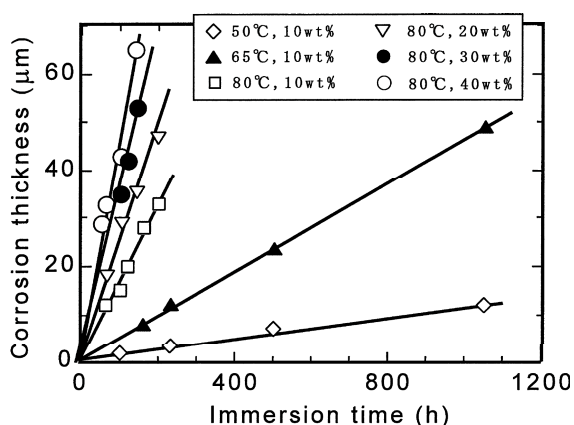

Fig. 7 Change of Flexural Strength with Immersion Time for MTHPA-EP in NaOH Solutions at Several Conditions of Concentration and Temperature

Fig. 6 Change of Corrosion Thickness with Immersion Time for MTHPA-EP in NaOH Solutions at Several Conditions of Concentration and Temperature

Fig. 8 Change of Flexural Strength with Immersion Time for iso-UP in 10 wt% NaOH Solutions at Several Temperatures

results were obtained to those shown in **Fig. 2**. The corrosion was based on the hydrolytic reaction in Eq. (3). The thickness of the unchanged central region of the specimen was measured with the optical microscope, and substituted for h in Eq. (5), giving the corrosion thickness (x). **Figure 10** shows the relationship between corrosion thickness and immersion time at several temperatures. The corrosion thickness (x) was proportional to the square root of immersion time as;

$$x = k_2\sqrt{t} \quad \text{or} \quad x^2 = k_3 t \quad (7)$$

where k_2 and k_3 are both constants.

The thickness of the color change layer observed by microscopy agreed with that of the corroded layer observed by infrared spectroscopy as shown for the 80°C result in **Fig. 10**. This means that the color change layer shown in **Fig. 9** was also the corroded layer. Penetrated liquid was observed only in the corroded layer (color change layer) with EDS (Energy Dispersive X-ray Spectrometer) analysis.
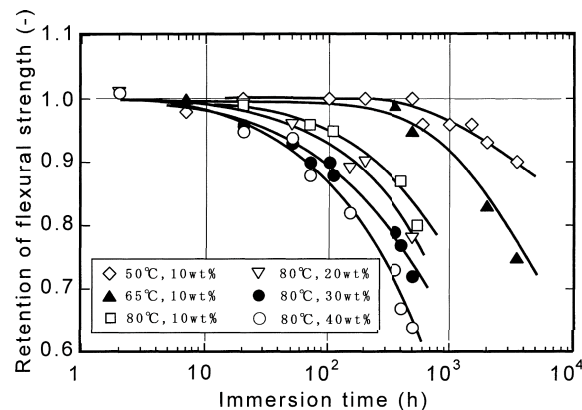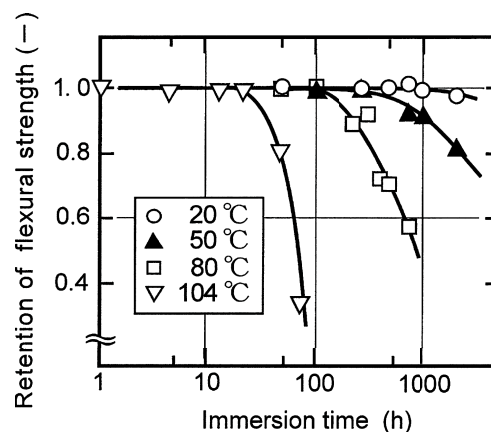
If the same plastic was immersed into KOH solution, a highly swollen corroded layer was observed (**Fig. 9 (b)**) and the corrosion thickness was proportional to immersion time as shown in **Fig. 11**, according to the following relationship[8].

$$x = k_4 t \quad (8)$$

where k_4 is a constant.

2. 1. 3. MDA-EP in H_2SO_4 Solution

Figure 12 shows the change in weight and flexural strength of epoxy resin cured with menthane diamine (MDA-EP) immersed into H_2SO_4 solution. After the weight change (solid symbols) reached an equilibrium state, the flexural strength (open symbols) began to decrease. Extremely high weight change was observed in comparison with **Fig. 5**.

2. 2. Corrosion Forms

The plastic/environmental liquid systems show three different forms, called the 'surface reaction type,' 'corrosion layer forming type,' and 'penetration type' respectively.
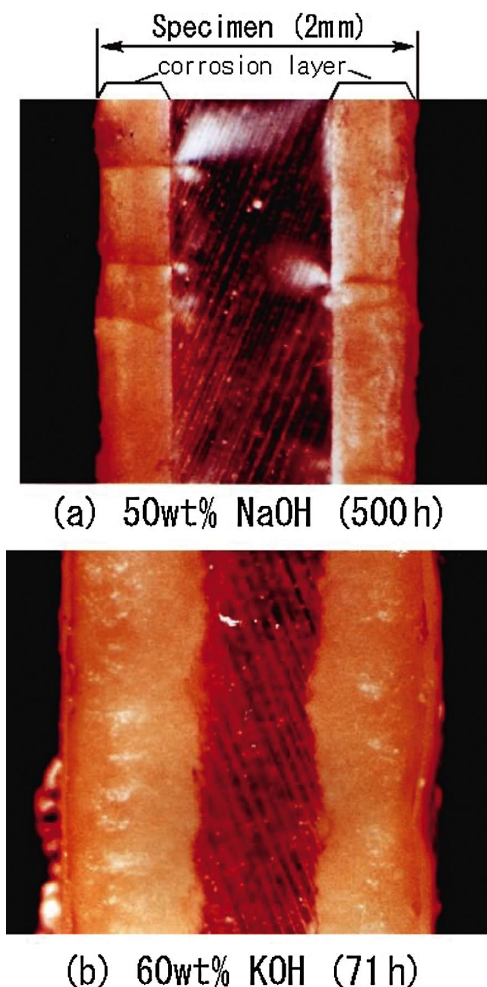
(a) 50wt% NaOH (500h)

(b) 60wt% KOH (71h)

Fig. 9 Cross Section of iso-UP Specimens Immersed into (a) 50 wt% NaOH Solution, 500 h, and (b) 60 wt% KOH Solution, 71 h, at 80°C
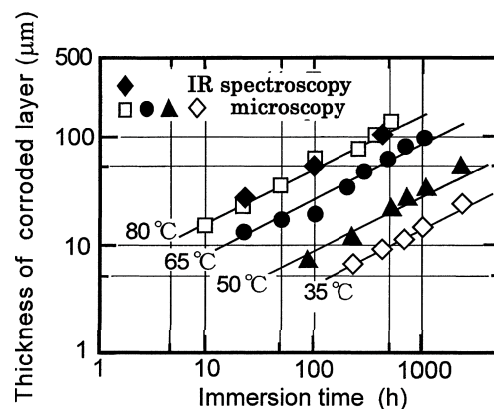

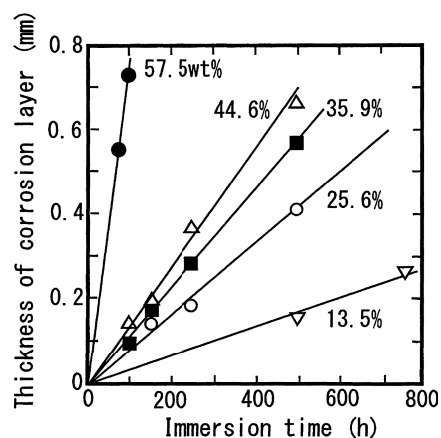Fig. 10 Change of Corrosion Layer Thickness with Immersion Time for iso-UP in 10 wt% NaOH Solutions at Several Temperatures

Fig. 11 Change of Corrosion Layer Thickness with Immersion Time for iso-UP in KOH Solutions at Several Concentrations at 80°C

2. 2. 1. Surface Reaction Type

This form was observed when the corrosion product could be dissolved into the liquid from the surface of the plastic, and the corrosion developed uniformly over the entire surface. This type of corrosion occurs when low molecular weight compounds are produced by the corrosion reaction from both the main chain and the cross-linking chain. In MTHPA-EP, the main chain of EP is crosslinked by ester bonds with hardener (MTHPA) as shown in **Fig. 4**. The scission of the molecular chain was caused by the hydrolysis reaction (Eq. (3)) with NaOH solution at the cross-linking part, and both parts of the main chain and hardener dissolved in the liquid because of their low molecular weights. The same type of corrosion was observed for alicyclic epoxy resin in NaOH, and amine cured epoxy resin in nitric acid[10]~[12].

2. 2. 2. Corrosion Layer Forming Type

This type of corrosion was recognized when part of the corrosion products was dissolved and the residual part was left as the corrosion layer as shown in **Fig. 9**. In the iso-UP/NaOH system, corrosion progressed through the hydrolysis reaction at the ester bond in the main chain, whereas the cross-linking part with styrene retained the initial chemical structure because of the stable C–C bonds. This part has high molecular weight (long chain), so did not dissolve but formed the corrosion layer. The same type of corrosion was observed for orthophthalic type UP in NaOH, and novolak type vinylester resin in alkaline solution, etc.[8]

2. 2. 3. Penetration Type

The corrosion behavior was characterized by a two-step process of diffusion and reaction. In the case of MDA-EP immersed into H_2SO_4, the penetrated H_2SO_4 reacted with the amine to form amine salts. In this period, the acid ion coordinated with the amine group and no scission of the polymer chain occurred. A large amount of acid penetrated, so the clear liquid-penetrated region could be observed.

2. 3. Corrosion Mechanisms

These three types of corrosion are determined by the relative penetration rates of liquid by diffusion into the resin (D) and the rates of consumption of diffused liquid by chemical reaction (K).

If $D \ll K$, the reactant liquid which reaches virgin resin by diffusion is consumed immediately by chemical reaction, and then the 'surface reaction type' or 'corrosion layer forming type' occur. The difference between these forms is caused by the solubility of the corrosion product in the liquid. If the product has high solubility, the 'surface reaction type' is observed, and if low solubility, the 'corrosion layer forming type' is seen.

The most common factor which determines the solubility is the molecular weight of the corrosion product. Therefore, the number of repeated units (n) in the main chain becomes the factor that determines whether the 'surface reaction type' or 'corrosion layer forming type' is observed. In epoxy resin cured with phthalic anhydride shown in **Fig. 13**, if $n = 0$ the 'surface reaction type' was observe, whereas if $n \geqq 1$ the 'corrosion layer forming type' was observed[8]. Because of the severe entanglement of the long polymer chain ($n \geqq 1$), the corrosion products were difficult to dissolve.

If $D \gg K$, reactant liquid penetrates into the resin with large diffusion rate and the corrosion reaction proceeds slowly. After all reactive sites in the resin are occupied by liquid, the scission reaction occurs at all reactive sites. This behavior is the 'penetration type.'

If D and K are similar, degradation proceeds gradually with liquid penetration. This behavior was observed in the PA (polyamide)/H_2SO_4 system[13),14)].

The mechanisms of the three forms of corrosion are summarized in **Table 1**. Compared to the corrosion
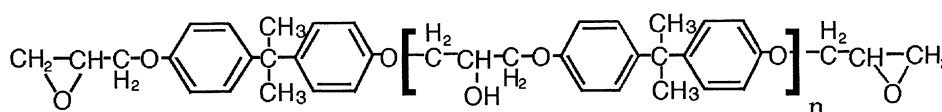
of metals, the 'surface reaction type' corresponds to uniform corrosion of metal, and the 'corrosion layer forming type' to formation of a rough oxide film under high temperature oxidation[15]. The 'penetration type' is characteristic of plastics.

3. Rate Equations and Life Prediction

3. 1. Equations of Corrosion Rate

Generally the corrosion rate defined by an increasing rate of corrosion thickness can be expressed by;

$$\frac{dx}{dt} = k \cdot x^{\alpha} \cdot C_L{}^{\beta} \tag{9}$$

where x is the thickness of the corroded part, t is the immersion time, k is the rate constant, C_L is the concentration of the liquid, and α and β are constants.

The rate constant k can be represented by Arrhenius' equation;

$$k = k_0 \exp(-E/RT) \tag{10}$$

where k_0 is the frequency factor, E is the activation energy, R is the gas constant and T is the temperature.

If C_L and T are constant, Eq. (9) can be simplified as

$$\frac{dx}{dt} = A_1 x^{\alpha} \tag{11}$$

where A_1 is constant.

In the case of the 'surface reaction type,' the corrosion rate is independent of x, that is $\alpha = 0$ in Eq. (11), so Eq. (6) can be derived. In the case of the 'corrosion layer forming type,' if the corrosion layer shows resistance to penetration of the liquid through the layer which increases with the thickness of the layer, $\alpha = -1$ and Eq. (7) can be obtained. If the layer has no resistance to penetration of the liquid, $\alpha = 0$ and Eq. (8) can be obtained. This behavior was recognized for iso-UP immersed in KOH solution. The corrosion layer was highly swollen as shown in **Fig. 9(b)**, so liquid could penetrate easily with no resistance.

The effects of concentration and temperature of the liquid are shown in **Figs. 14** and **15**[9], and the following relation was obtained.

(a) MTHPA-EP in NaOH solution

$$x = A_1 \exp(-9444/T) \cdot C_L{}^{0.56} \cdot t \tag{12}$$

(b) iso-UP in 10 wt% NaOH solution

$$x = A_2 \exp(-6420/T) \cdot t^{1/2} \tag{13}$$

(c) iso-UP in KOH solution at 80°C

$$x = A_3 \cdot C_L \cdot t \tag{14}$$

Using these equations, the thickness of the corrosion layer after immersion at arbitrary concentrations and temperatures can be predicted.
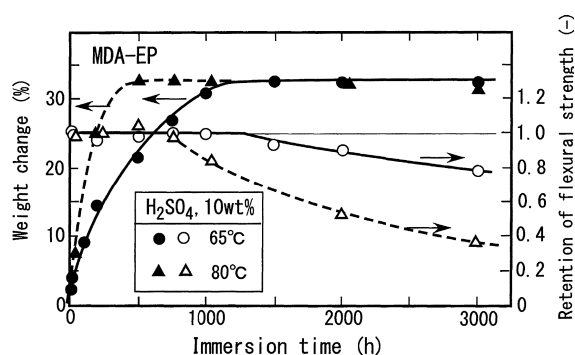
Fig. 12 Change of Weight and Flexural Strength of MDA-EP Immersed into 10 wt% H_2SO_4 Solutions

Fig. 13 Chemical Structure of Bisphenol-A Type Epoxy Monomer

Table 1 Mechanisms of the Three Forms of Corrosion

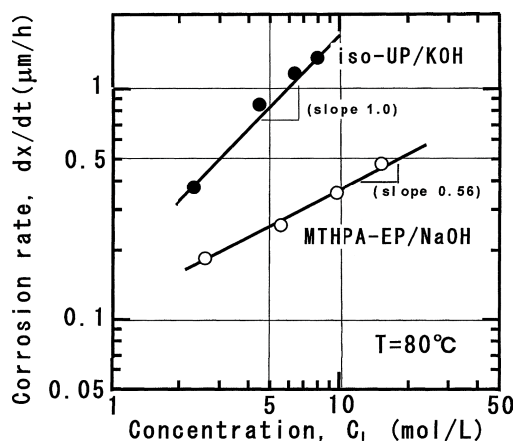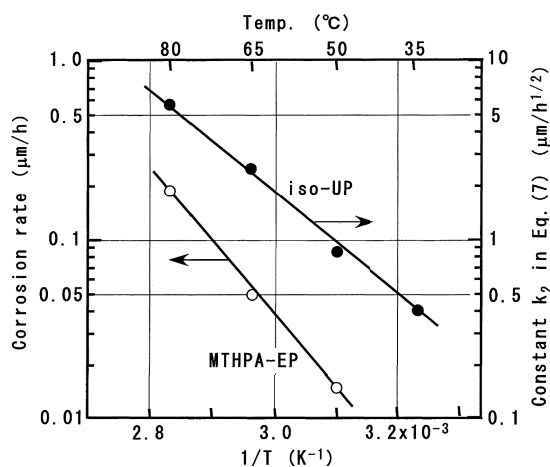| Form of corrosion	Reaction rate (K) and diffusion rate (D)	Solubility of corrosion product	Corrosion rate equation
Surface reaction type	$D \ll K$	high	$x \propto t$
Corrosion layer forming type	$D \ll K$	low	$x \propto t^{1/2}$ or $x \propto t$
Penetration type	$D \gg K$	low	

Fig. 14 Effect of Concentration on Corrosion Rate of iso-UP in KOH Solution, and MTHPA-EP in NaOH Solution at 80℃

Fig. 15 Effect of Temperature on Corrosion Rate of MTHPA-EP, and Constant k_2 in Eq. (7) for iso-UP at 10 wt% NaOH Solution

3. 2.　Life Prediction
3. 2. 1.　Surface Reaction Type and Corrosion Layer Forming Type

In the case of the 'surface reaction type,' as the thickness of the specimen decreased with increasing immersion time, the strength of the specimen after immersion decreased.　In the case of the 'corrosion layer forming type,' as the corrosion layer had no strength, the strength of the specimen after immersion also decreased.　In both cases, residual strength was dependent on the thickness of the residual specimen or non-corroded
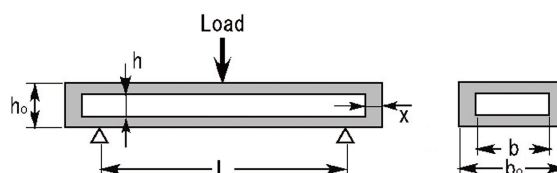

Fig. 16 Specimen for Flexural Test and Corroded Part

region beneath the corrosion layer.

The flexural strength before immersion (σ_0) is expressed as

$$\sigma_0 = \frac{3P_0 L}{2b_0 h_0{}^2} \qquad (15)$$

where b_0, h_0 and L are the width, thickness of the original specimen, and span in the three-point flexural test, and P_0 is the breaking load.　The thickness of the non-degraded part (h) in the specimen decreased with immersion, according to

$$h = h_0 - 2x \qquad (16)$$

from Eq. (5).　The width of specimen (b) also decreased as shown in **Fig. 16**.

$$b = b_0 - 2x \qquad (17)$$

Therefore, the specimen after immersion was fractured at a lower load of P' compared to the original load (P_0), and the flexural strength σ' is given as follows.

$$\sigma' = \frac{3P'L}{2(b_0 - 2x)(h_0 - 2x)^2}$$

Where σ' is the strength of the non-degraded part, and is equal to the initial value of σ_0.　The decrease in strength was evaluated by retention of flexural strength (RFS) which was defined by the ratio of P' to P_0.　By equating Eq. (15) to Eq. (18), RFS can be expressed as

$$\text{RFS} = \frac{P'}{P_0} = \frac{(b_0 - 2x)(h_0 - 2x)^2}{b_0 \cdot h_0{}^2} \qquad (19)$$

This equation shows that the retention of flexural strength varies only with x.　Therefore, a master curve can be obtained by plotting RFS with the right terms of Eqs. (12)-(14) as shown in **Figs. 17** and **18**[9),16)].　By using these master curves, the retention of strength after long-term immersion at any concentration and temperature can be predicted.

3. 2. 2　Penetration type

In the case of the 'penetration type,' the lowering of strength started after weight uptake was saturated as shown in **Fig. 12**.　Therefore, the concept of corrosion
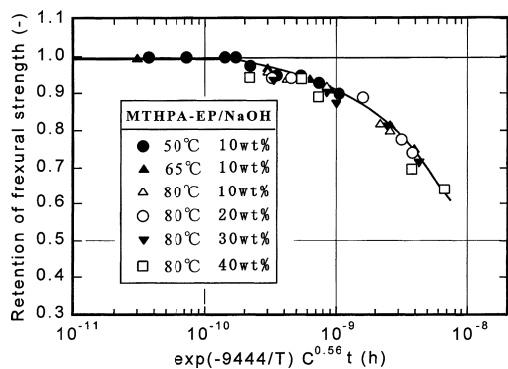
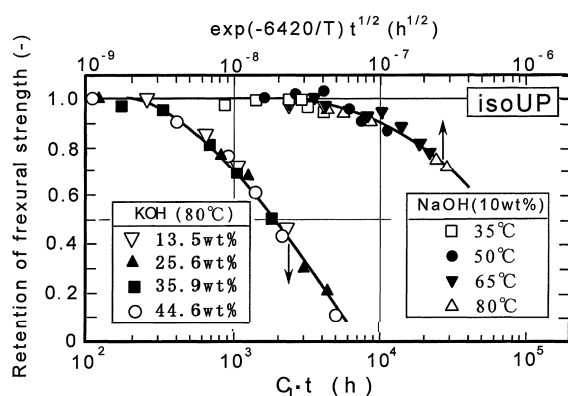Fig. 17 Master Curve of Strength Change of MTHPA-EP Immersed in NaOH Solutions

Fig. 18 Master Curves of Strength Change of iso-UP Immersed in NaOH and KOH Solutions
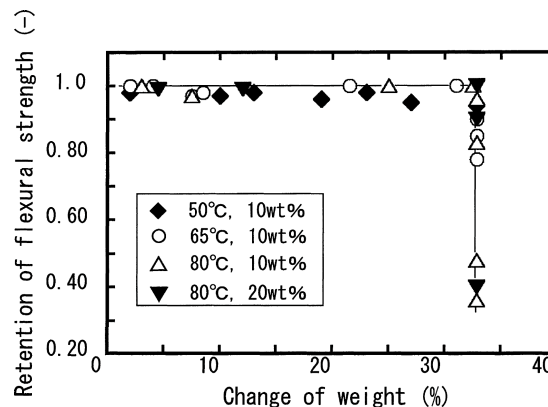

Fig. 19 Relationship between Retention of Flexural Strength and Change of Weight for MDA-EP Immersed into H_2SO_4 Solutions

layer was formed.

In the surface reaction and corrosion layer forming types, corrosion thickness directly affected the residual strength of materials after corrosion. Based on the concept of corrosion rate, master curves were obtained incorporating temperature, concentration, immersion time, and flexural strength after corrosion. Using the master curves, the life of resins under arbitrary conditions of temperature and concentration could be predicted.

rate is not applicable but the weight change is more important. **Figure 19** shows the relationship between weight change and strength in the MDA-EP/H_2SO_4 system. After 33 wt% gain of H_2SO_4 solution, the flexural strength decreased abruptly. Therefore, continuous check of weight change is useful to predict the life.

Conclusions

The corrosion behavior and mechanisms of plastics in liquids were investigated experimentally. Chemical degradation (called corrosion) occurred as three forms, the 'surface reaction type,' the 'corrosion layer forming type,' and the 'penetration type.' Each form was determined by the relationship between the penetration rate of liquid by diffusion and the chemical reaction rate. If the chemical reaction rate was higher than the penetration rate, the 'surface reaction type' or the 'corrosion layer forming type' occurred, but if the penetration rate was considerably higher than the chemical reaction rate, then the 'penetration type' occurred. If the corrosion product was soluble with low molecular weight, the surface reaction was predominant, and if the corrosion product had high molecular weight, the corrosion

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要　　旨

液体環境における熱硬化性プラスチックの劣化とその機構

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　FRP のマトリックスとして使われている熱硬化性樹脂および FRP の液体環境における劣化挙動，機構について著者らの実験結果に基づき概説した。化学的劣化すなわち腐食について詳細な検討を行った結果，腐食形態は「表面反応型」，「腐食層形成型」および「全面浸入型」の三つに分類でき，各形態の腐食機構は樹脂の化学構造，樹脂と液の反応性，樹脂中への液の拡散浸入速度に依存することを示した。

　「表面反応型」および「腐食層形成型」に対して，腐食深さの経時変化を腐食速度と定義することにより，腐食後の非腐食部厚さの経時変化を数式化できた。これに基づき，曲げ強度保持率に対するマスターカーブを用いる寿命予測法を提案した。
　また，全面侵入型については，強度低下の開始を予測する因子として重量変化が重要であることを示した。

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