CORROSION BEHAVIOR AND MECHANISM OF GLASS COMPOSITES IN ACIDIC SOLUTIONS

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SUMMARY: Glass composites (GFRP) is being used for chemical plants in place of steel. Some GFRP show serious degradation by corrosion in liquid environments. The object of this study is to clarify corrosion behavior and mechanism of GFRP in acidic solutions. Test materials used were isophthalic type unsaturated polyester resin with E glass fiber chopped strand mat. The corrosive environments were mainly 30 wt.% nitric acid solution. Corrosion behavior was evaluated by flexural strength, roughness, infrared spectrum analysis and corrosion depth. As the results of flexural strength for resin and GFRP, corrosion behavior was classified into four steps which corresponded to physical degradation by swelling, the formation of pits, oxidation corrosion and hydrolytic corrosion mechanisms. The resin with various additives of initiator, plasticizer and catalyst was investigated. When initiator and especially plasticizer contents were increased, pits, blisters and corrosion depth were increased. GFRP corrosion was classified into four regions of physical degradation, hydrolytic corrosion of the resin and corrosion of the resin - glass fiber interface. Moreover, the formation of pits was recognized as initial degradation and also after pitting corrosion, blister formation gave an abrupt increase of corrosion depth and a decrease of strength of the GFRP.

KEYWORDS: GFRP, corrosion, hydrolysis, blister, pitting, isophthalic type unsaturated polyester resin, initiator, corroded layer-forming type

1. INTRODUCTION

Glass composites (GFRP) of isophthalic type unsaturated polyester resin and glass mat which has superior moldability at normal temperature and atmospheric pressure are being used in place of steel for chemical plants because of there excellent combination of strength, corrosion resistance and economy. However, the problem of chemical degradation (corrosion) might be caused under the condition of severe service environments. Therefore, it is necessary to establish the method of corrosion resistant design and also the life prediction of the material.

A series of study on the corrosion behaviors of resin and GFRP have been made mainly in alkaline solutions [1-5], it was found that the forms of the resin corrosion were classified into three types, namely, surface reaction type, corroded-layer-forming type and penetration type [4].
In this study the corrosion behavior and mechanism of GFRP in acidic solutions was studied, and also the mechanism of pit and blister formation was discussed.

2. EXPERIMENTAL

2.1 Materials and Specimen

Test material used was isophthalic type unsaturated polyester resin with E glass fiber chopped strand mat, and additive content of methyl ethyl ketone peroxide (initiator), cobalt naphthenate (catalyst) and dimethyl phthalate (plasticizer) was varied as shown in Table 1.
Test specimens were cut from molded plates of 2 mm thickness cured at room temperature to 25 mm width and 60 mm length. Moreover, after cure was made at 100°C for 2h.

2.2 Test Method

Immersion tests were made in acidic solution at 80°C, and corrosion behavior in 30wt.% nitric acid solution was evaluated by flexural strength, microscopic observation, maximum roughness, infrared spectrum analysis (IR) and corrosion depth.

Table 1: Additive contents for resin.

<table>
<tr><th></th><th>Initiator [phr]</th><th>Plasticizer [phr]</th><th>Catalyst [phr]</th></tr>
<tr><td>resin (standard)</td><td>0.54</td><td>0.65</td><td rowspan="5">0.55</td></tr>
<tr><td>0.05 initiator</td><td>0.05</td><td>0.07</td></tr>
<tr><td>1.07 initiator</td><td>1.07</td><td>1.31</td></tr>
<tr><td>3.25 plasticizer</td><td rowspan="4">0.54</td><td>3.25</td></tr>
<tr><td>6.55 plasticizer</td><td>6.55</td></tr>
<tr><td>0.28 catalyst</td><td rowspan="2">0.65</td><td>0.28</td></tr>
<tr><td>1.65 catalyst</td><td>1.65</td></tr>
</table>

3. CORROSION BEHAVIOR OF RESIN AND GFRP IN ACIDIC SOLUTIONS

Tests were made for various acidic solutions, however, this paper reported the result of corrosion behavior in 30 wt.% nitric acid solution.
As the result of flexural test for resin and GFRP, the corrosion behavior proceeded by four steps as shown in Figure 1. Figure 2 shows the change of specimen surface at each step. The generation of pits could be observed and the number of pit was measured. The number of pit of specimen surface increased with immersion time as shown in Figure 1. Figure 3 shows the maximum roughness of specimen surface increased with immersion time similar to the behavior of number of pit, therefore the flexural strength was decreased remarkably with the abrupt increase of maximum roughness which represented the pit depth.
Each step of resin corresponded to physical degradation by swelling (step **I**), oxidation corrosion (step **II**), formation of pits (step **III**) and hydrolytic corrosion (step **IV**) respectively.

The degradation mechanism for each step was examined with IR and microscopic observation, and it was found that when the number of pits was degraded increased, the strength of the resin decreased abruptly. GFRP, on the other hand, with physical degradation (step **l**), oxidation corrosion (step **ll**) and hydrolytic corrosion for matrix resin (step **lll**) and also the interfacial corrosion between resin and glass fiber (step **lV**).

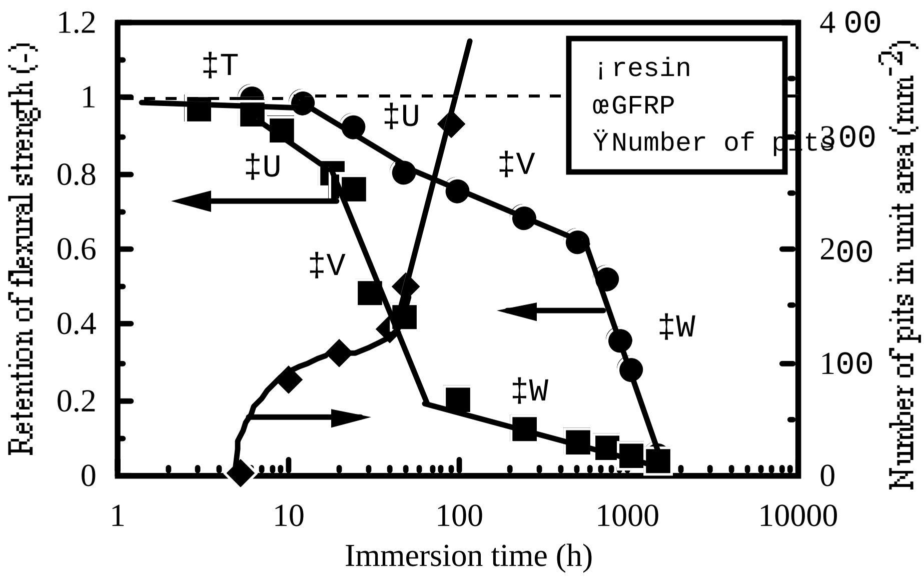

Figure 1: Variation of retention of flexural strength and number of pits in 30wt.% HNO_3 of resin and GFRP.

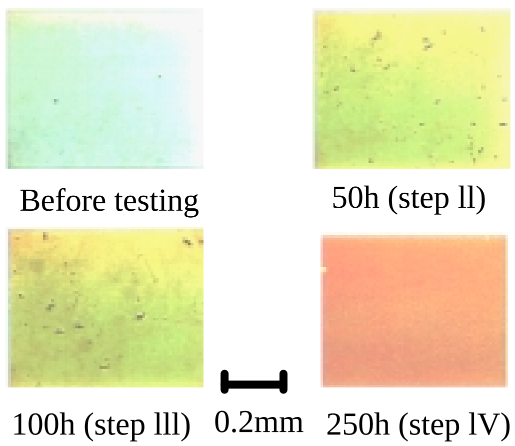

Figure 2: Appearance of resin surfaces after immersion at step **l** to **lV**.

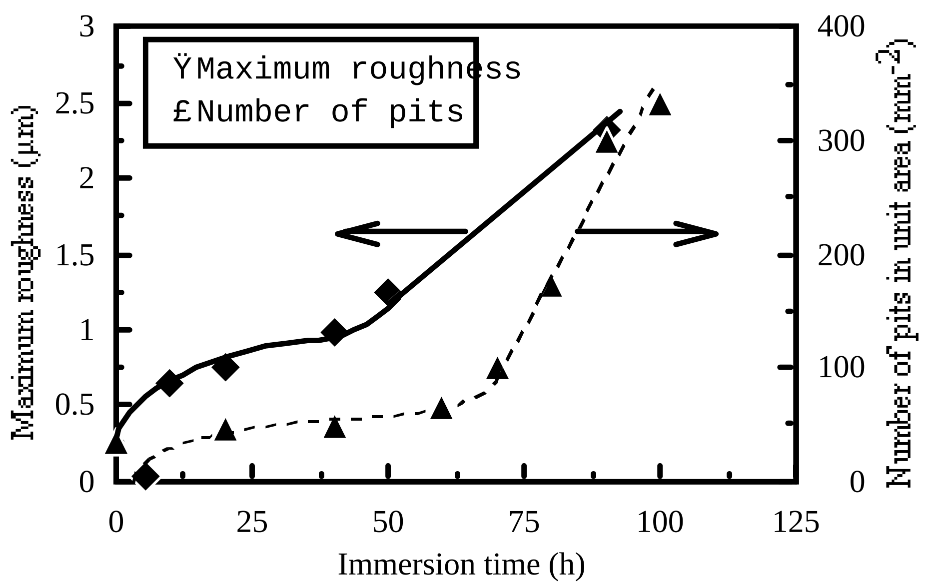

Figure 3: Variation of maximum roughness of specimen surface and number of pits in 30wt.% HNO_3.

By IR analysis and microscopic observation, the form of corrosion for the resin and GFRP was recognized to 'corroded layer-forming type'[4]. Corrosion depth was calculated by following equation (1) from microscopic observation of specimen cross section.

$$X = (\boldsymbol{t_0} - \boldsymbol{t})/2 \qquad (1)$$

where, $\boldsymbol{X}$ is corrosion depth $\boldsymbol{t_0}$, is the thickness of specimen before immersion, and $\boldsymbol{t}$ is that of non-corroded part after immersion.

Initially, corrosion depth increased linearly with root immersion time, but changed with three stages as shown in Figure 4. The change of specimen appearance was shown in Figure 5. When corrosion reached at some depth, the blister was generated at an interface between corroded layer and non-corroded part, namely resistance for diffusion of liquid through the corroded layer was decreased by the blister formation. Considering from Figures 4 and 5 corrosion model of resin was shown in Figure 6. At first the liquid diffused into the resin obeying Fick's law and gradually corroded layer was formed (stage1). Then the blisters were generated and growth by swelling pressure beneath the corroded layer (stage 2), and after the collapsing of grown blister, then the corrosion of stage3 started again.

It was found that the blister formation gave the abrupt increase of corrosion depth and the decrease of strength of GFRP due to the penetration of liquid through resin-fiber interface as shown in Figure 1 (step **IV**) and Figure 4 (stage 2).

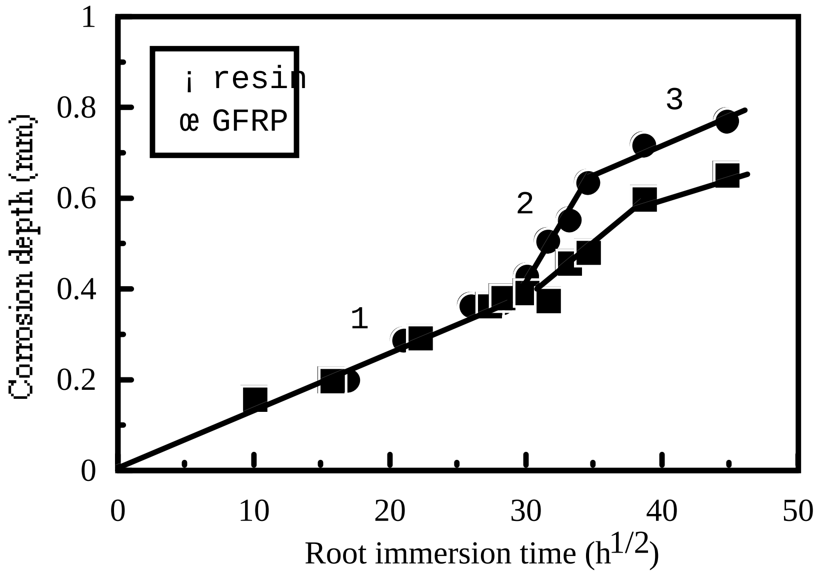

Figure 4: Corrosion depth vs. root immersion time for resin and GFRP.

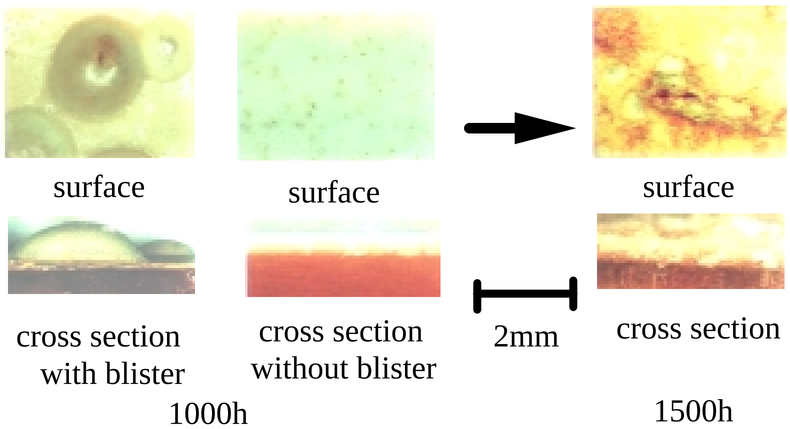

Figure 5: Change of specimen appearance.

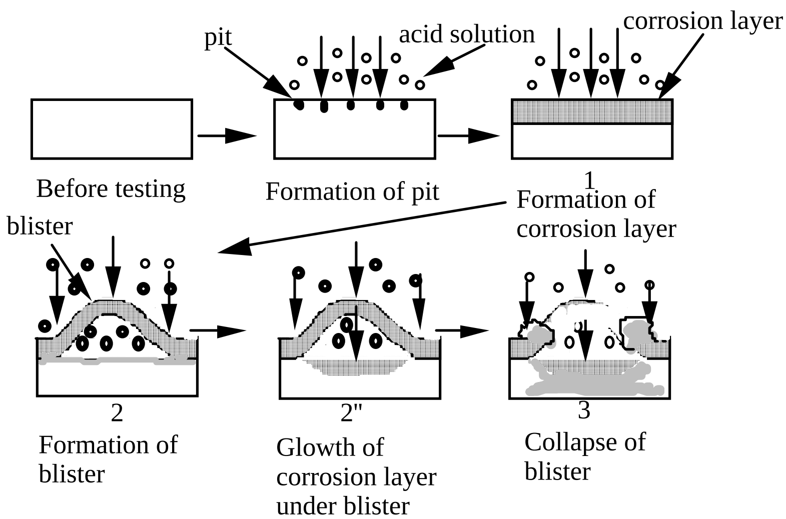

Figure 6: Corrosion model with pit and blister formations for resin.

4. THE EFFECT OF RESIN ADDITIVES ON CORROSION BEHAVIOR

To clarify the formation of pit and blister, the effect of resin additives shown in Table 1 was investigated. Figure 7 shows the effect of additive contents on the variation of flexural strength and number of pit with immersion time. The higher initiator and plasticizer contents, the faster the decrease of resin strength due to the abrupt increase of pit.
Figure 8 shows the effect of resin additives on corrosion depth with immersion time. Corrosion depth increased linearly with root immersion time, and the higher content of plasticizer resin showed faster corrosion than others. Corrosion depth of the resin with initiator content of 0.05 phr 1.07 phr changed with three stages as same behavior as the standard resin specimen. But the corrosion depth increased remarkably in high contents of initiator at stage 2 comparing with ones.
Figure 9 shows the specimen surface of before and after immersion for 0.05phr and 1.07phr initiator involved resins. It was confirmed that blisters were generated only for highly contented specimens.
Consequently, when initiator and particularly plasticizer contents increased, pits, blisters and therefore corrosion depth also increased. On the other hand, the corrosion behavior was little affected by the content of catalyst.

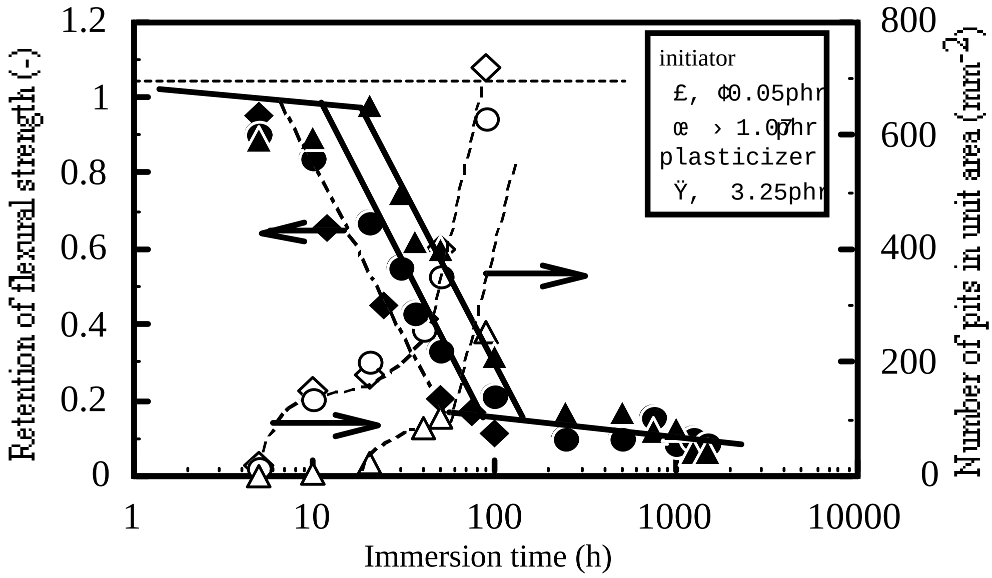

Figure 7: Effect of additive contents on flexural strength and number of pit.

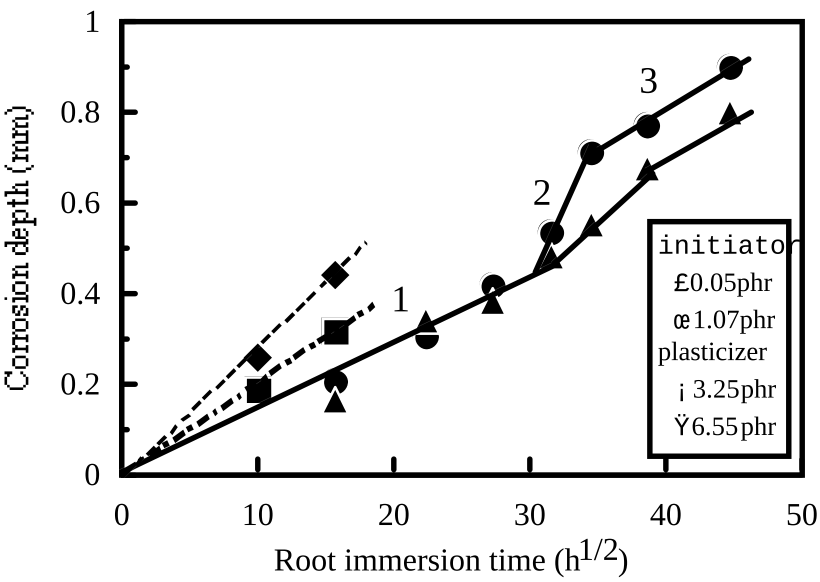

Figure 8: Effect of additives content on corrosion depth.

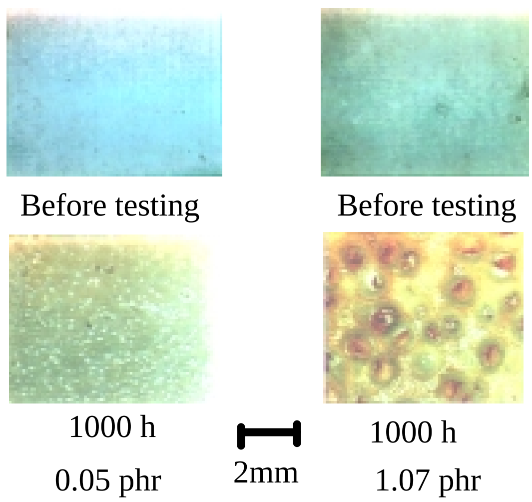

Figure 9: Appearance of specimen surface of resin with 0.05 phr and 1.07 phr initiator.

5. CONCLUSION

The corrosion behavior of and mechanism of resin and GFRP was investigated in nitric acid solution. The resin was degraded with the four process of pitting, hydrolytic corrosion and blister generation at the interface between corroded layer and non-corroded part interface. And the degradation of GFRP occurred by the mechanisms of hydrolytic corrosion of the resin, blister generation and the resin-glass fiber interfacial corrosion. The form of corrosion was confirmed to be the 'corroded layer forming type' by IR analysis, microscopic observation and change of corrosion depth. The cause of pit formation was examined and plasticizer included in initiator was found to play the major role for it. Moreover, degradation model with pit and blister formation was discussed.

Consequently, the degradation caused by the cooperative action of chemical corrosion and physical blister formation, should be considered in designing the corrosion resistance equipment and estimate its residual life.

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