EFFECT OF MATRIX TYPE ON CORROSION MECHANISM OF GRP COMPOSITE IN ACIDIC ENVIRONMENT

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Abstract
In this study the corrosion mechanism of GRP composites were investigated for different resin types. Composite with the epoxy and polyester resin were immersed in acid sulfuric media and strength degradation of specimens were obtained and compared for different immersion times. The corrosion mechanism of GRP composites was investigated using the SEM and EDX methods. Moreover, the acid penetration depth in composite cross section was investigated for the different resin type composites based on the corrosion mechanism of glass fiber. Finally, the fracture surface of the intact and degraded specimens was studied and the comparison was performed between the samples with epoxy and polyester resin. The results showed that E-glass/epoxy composite is more corrosion resistant than E-glass/polyester composite in acidic media. The acid penetration rate into the composite cross section is rather for E-glass/polyester composite.

1 Introduction
GRP composites have been widely used in industrial applications. Most promotion has been made in the case of composite pipeline, storage tanks and fluid handling equipments. Most application of composites area, are in the off-shore oil and gas industry, where the replacement of heavy metal pipelines by lighter composites, causes reduction in the cost manufacturing. In the most of uses in petroleum and oil and gas industry, composite materials are under the attack of corrosive environments. To suppression the corrosion upkeep and damage, many researches were accomplished in the field of composite stress corrosion cracking. Major surveys were about to answer first of all, the effect of vital parameters in corrosion process and second of all, the methods of increasing the composite corrosion resistance. For the first question, it can be mention to research about the effect of corrosive environment temperature [1], matrix toughness [2] and manufacturing process effect on composite stress corrosion [3]. Use of E-CR glass instead of E-glass fiber and resin corrosion resistant coatings is examples of composite corrosion resistance improvement [4]. Effect of matrix type on the stress corrosion behavior of GRP composites have been studied before using the Acoustic Emission experiments [5]. But, the corrosion and crack formation mechanism of composite is still unclear. To support the composite against the corrosive media, it is needed to attain the stress corrosion mechanism in composite structures during the time.
In this study the corrosion mechanism of GRP composites were investigated for epoxy and polyester resin types. Composite samples were immersed in acid sulfuric media and strength degradation of specimens were obtained and compared for different immersion times. The fracture surface of GRP composite due to stress corrosion and mechanically over loaded conditions have been studied before. However, the crack formation and corrosion mechanism of fiber in composite is still unclear. In this study, the corrosion mechanism of GRP composites was investigated using the SEM (scanning electron microscopy) and EDX (Energy Dispersive X-ray) methods. Moreover, the acid penetration depth in composite cross section was investigated for different resin type composites, based on the corrosion mechanism of glass fiber. Acid penetration depth at any corrosion time in composite is an effective parameter in corrosion lifetime design. Moreover the glass fiber ion depletion for fiber filament and composite were evaluated. Finally, the fracture surface of intact and degraded specimens was studied and the comparison was performed between the samples with epoxy and polyester resin.

2 Experiments procedure
The unidirectional E-glass/epoxy and E-glass/polyester composites with the fiber volume fraction of 50 were immersed in 5%Wt sulfuric acid for different immersion times. The samples then were removed from the acid solution, were washed by distilled water, and were dried in air. The strength degradation of the samples was studied using the ASTM D3039 standard test method. The acid penetration depth into the E-glass/polyester composite thickness was determined based on the corrosion of the E-glass fiber. Moreover, the results were compared by the similar data of the mechanism E-glass/epoxy composite [6]. Finally, the SEM and EDX results were used to investigate the fracture mechanism of the samples.

3 Acid penetration depths
Acid penetration in the composites does not cause obvious changes in the brightness and contrast of composites. It means that the penetration of acid in the composites cannot be detected visually. Therefore, The EDX analysis is selected to study the corrosion process in the composites. The corrosion in the composites is mainly affected by corrosion of fibers. Thus, this method is based on the corrosion mechanism of glass fibers. Leaching of the non-siliceous ions from the E-glass fiber has been mentioned in various studies. It was mentioned in the reference [6] that about the 30% Wt of the fiber is consisted of the oxide of the Al and Ca ions. These percentages were decreased to the 21% and 22% respectively after 200 h immersion time. By increasing the immersion time, some deposits with high amount of Fe ion is formed along the fiber surface. In order to investigate the acid penetration depth along the composite thickness, various points of the Longitudinal and transverse composite cross section were studied using the SEM and EDX method. Therefore, the cross section of the samples were washed using the ultrasonic bath to remove the surface deposits. Then the EDX analysis of different points was studied according to the corrosion mechanism of the E-glass fiber. Since this study is statistical, the accuracy of the analysis could be increased by selecting the more investigated points. As an example the EDX results of the shown points on Figure 1 for the cross section of E-glass/polyester composite after 24 h immersing in acid, were displayed in the table 1.
Figure 1. The SEM images of transverse section of a degraded composite after 24 h immersion time.

<table>
<thead>
<tr>
<th>Related Fig.</th>
<th>Element content (%) of marked points</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mg</td>
</tr>
<tr>
<td>1-1</td>
<td>3.15</td>
</tr>
<tr>
<td>1-2</td>
<td>2.85</td>
</tr>
<tr>
<td>1-3</td>
<td>1.70</td>
</tr>
<tr>
<td>1-4</td>
<td>2.11</td>
</tr>
</tbody>
</table>

Table 1. The EDX results of marked points on figure 1.

The results showed that the acid penetration depth is about 33% in the composite cross section. The acid penetration rate into the E-glass/epoxy and E-glass/polyester composite cross section during immersion time is shown in the Table 2. The results showed that the acid penetration depth rate is rather for the E-glass/polyester composite.

<table>
<thead>
<tr>
<th>Immersion Time (h)</th>
<th>Acid Penetration Depth in Composite Thickness (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>48</td>
<td>40</td>
</tr>
<tr>
<td>96</td>
<td>64</td>
</tr>
<tr>
<td>192</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 2. Results of the acid penetration depth
4 Results and discussion

The tensile strength degradation of the composite versus immersing time in the acid solution was displayed in the figure 2. The results showed that the E-glass/epoxy composite, which have tensile strength approximately the same as the E-glass/polyester, maintained its specification more than the other did. The strength amount of the E-glass/polyester composite was slightly less than the E-glass epoxy samples, after 192h of the corrosion time. However, the mechanical properties of the E-glass/polyester were decreased by the higher rate. The fracture cross sections of the E-glass/polyester samples affected by the corrosive media and mechanical loading were depicted in figure 3. It is shown on the figure 4 that the fracture surfaces of the intact composites are approximately the same for two different resin types.

Figure 2. The Strength behavior of composites versus immersion time

Figure 3. The fracture cross sections of the E-glass/polyester samples affected by the corrosive media (figure 3.1) and mechanical loading (figure 3.2)
After 96 h of corrosion time the fracture surface of E-glass/Polyester exhibits a smooth and mirror like planar surface (figure 5.1), while the fracture surface of E-glass/Epoxy seems an irregular and rough structure (figure 5.2). In figure 6 the damage on the fibers of the fracture surface of E-glass/Polyester after 192 h of immersion time is shown.
5 Conclusions

1- The strength of the both composites, which were made by epoxy and polyester resins, were approximately equal for intact samples and samples after 192h corrosion time. However, the properties degradation of the E-glass/polyester composite is more severe than that of E-glass/Epoxy.

2- The penetration rate of the 5%Wt sulfuric acid was rather for the E-glass/polyester composite. This could be seen in the EDX results of the E-glass/polyester samples.

3- The fracture surfaces of the both intact samples were the same. However the smooth and mirror shape fracture surfaces were created rather in the E-glass/polyester composite samples. After 192 h corrosion time, the fiber damage was obvious in the fracture surface of the E-glass/polyester composite samples.

References