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Revised

Degradation Behavior of Epoxy Lining Materials under Corrosive Conditions Intended for Biomass Gas Plant

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ABSTRACT

Methane fermentation facilities treating agricultural biomass and raw garbage are constructed to produce biofuel gas. Biomass storages are in serious corrosive condition which contains sulfuric acid and various organic acids. Thus in this severe environment, even epoxy resin used as lining to protect base-structure is fairly degraded.

Corrosion behavior of epoxy resin by sulfuric acid, organic acids and mixture of these environments has been researched and reported. According to these researches, initially water penetrates into resin. Both sulfuric acid and acetic acid also penetrates into resin and accelerates penetration each other. That is, the synergy effect was confirmed. Also, it was confirmed that the third organic acid component also accelerates degradation of epoxy resin. In this research, the corrosion behavior in environments which include sulfuric acid, acetic acid, and n-butyric acid as the third component was studied in detail.

Keywords

Corrosion, Lining, Epoxy resin, Biomass gas plant, Sulfuric Acid

INTRODUCTION

Generally concrete degradation by acid is serious problem. For example, in the geothermal industry, concrete in cooling towers is degraded by sulfuric acid produced by sulfur oxidizing bacteria (Berndt, 2011). Similar degradations also happen in sewer pipelines (Dierks, 1991). Lining materials to protect sewer pipes has been researched (Masuda, 2008). However, not only sulfuric acid but acetic acid penetrate into mortar and degrades reinforcing steel (Oueslati, 2012). In contact with an acetic acid solution, concrete will undergo an acid-basic reaction leading to the formation of soluble salts in water (Bertron, 2005).

Methane fermentation facilities treating agricultural biomass and raw garbage are constructed to produce biofuel gas. Biomass storages are in serious corrosive condition for not only concrete structure but also polymeric lining materials to protect base-structure, since it contains sulfuric acid and various organic acids, such as acetic acid, n-butyric acid, n-valeric acid, propionic acid and lactic acid. Thus in this severe environment, even epoxy resin is fairly degraded. When an epoxy liner for concrete is corroded, protection ability of liner may be decreased and adhesive strength of the liner will decrease after long usage.

Corrosion behavior of epoxy resin by sulfuric acid (Hiramoto, 2003), acetic acid (Kubouchi, 2005) and mixture of these environments has been researched and reported. According to these researches, initially water penetrates into resin. Especially high concentrated acetic acid fairly accelerates swelling because acetic acid has high affinity to epoxy resin. Both sulfuric acid and acetic acid also penetrates into resin and accelerates penetration each other. That is, the synergy effect was confirmed. As a result of elemental analysis on cross-section of specimen, it was confirmed that sulfur element distribution is step-like. Also, the research in the corrosive environment which includes the third component was conducted, and it was confirmed that the third component also accelerates degradation of epoxy resin (Sharmin, 2011). In any case, penetration depth is proportional to root of immersion time. For temperature effect, Arrhenius relation is recognized. About concentration, the higher the concentration, the more rapidly acids penetrate, however when sulfuric acid concentration is higher than 10mass%, penetration ratio is reduced due to osmotic pressure (Masuda, 2008). In this research, the corrosion behavior in environments which include sulfuric acid, acetic acid, and n-butyric acid as the third component will be studied in detail.

EXPERIMENTAL

Materials

Bisphenol F type of epoxy resin and amine hardener (DBS) were used in this work. Table 1 shows information of hardener and the mass ratio. Main component of hardener; DBS is diamino diphenylmethane which is one of aromatic amine.

Table 1: Component of curing agents

Hardener	Composition	Hardener/resin ratio
DBS	Diamino diphenylmethane/Benzylalcohol/ Salicyclic acid=(2mol/0.76mol/0.2mol)	45 phr

Samples preparation method

After mixing the bisphenol F type epoxy resin and curing agent according to the mass ratio shown in Table 1, it was degassed in vacuum desiccator for 5min. Then epoxy resin was cured at 40˚C for 24 hours and post curing was conducted at room temperature for 1 week. The cured epoxy resin was cast to 2 mm thick plate and cut into 25 mm wide and 60 mm long pieces. The final dimension of the specimen was 60 mm x 25 mm x 2mm.

Corrosion test

Before immersion, mass of each specimen was measured. Then specimens were immersed in mixture of sulfuric acid, acetic acid and n-butyric acid as environmental solutions. Information of acid mixtures is given in Table 2. The temperature was kept at 70˚C during environmental solution immersion test. Specimens were fixed with Teflon tube holders and immersed in solutions. Specimens were taken from the environmental test vessel after certain time and wiped off carefully. Then specimens were kept in laboratory atmosphere for 1 hour and the mass of specimens was measured. This mass is defined as “wet mass” taken as an average value of four test samples. From mass data of specimens before and after immersion, mass change was investigated. Degradation was evaluated by analysis based on visual observations on surface, scanning electron microscope (SEM) observations and elementary analysis by using energy dispersion spectroscopy (EDS) on cross-section of specimens.

Table 2. Information about contents of acid mixtures

Mixtures	Contents
1. Acid mixture A	10% sulfuric acid +5% acetic acid
2. Acid mixture B	10% sulfuric acid +5% acetic acid +5g n-butyric acid
3. Acid mixture C	10% sulfuric acid +5% acetic acid +10g n-butyric acid
4. Acid mixture D	10% sulfuric acid +5% acetic acid +15g bromobutyric acid

RESULTS

Visual observation

Changes in the appearance of the specimens immersed in acid mixture A solution at 70˚C were shown in Figure 1.1. Sample color turned to greenish and darkish. Due to presence of acetic acid, samples became soft after 100 hours.

Changes in the appearance of the specimens immersed in acid mixture C solution at 70˚C were shown in Figure 1.2. Same as immersed in acid mixture A, sample's color turned to greenish and darkish. All of the other specimens showed same color change immersed in acid mixture B and D.

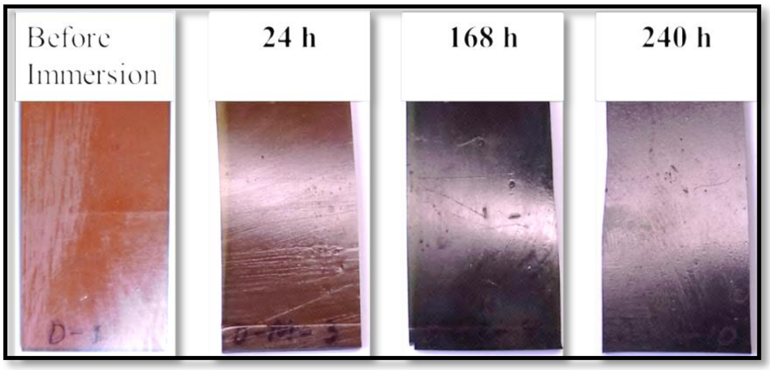


Figure 1.1. Photos of specimens before immersion and after immersion in acid mixture A (10%sulfuric acid +5% acetic acid) at 70°C

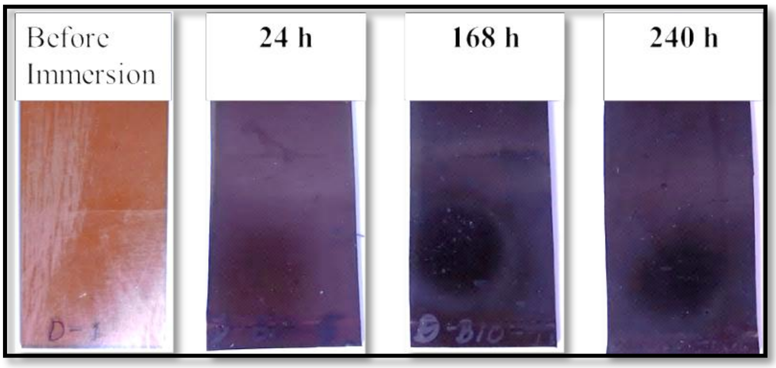


Figure 1.2. Photos of specimens before immersion and after immersion in acid mixture C (10%sulfuric acid +5% acetic acid +10g n-butyric acid) at 70°C

Mass change observation

In order to study the effect of mixture of inorganic and organic acid solutions on corrosion behavior, mass changes were examined.

First, samples were immersed in acid mixture A at 70˚C. As shown in Figure 2.1, mass change is proportional to root immersion time, therefore it can be said that samples showed fickian behavior. Fickian behavior is derived by Fick's second law.

Next, in order to study the effect of n-butyric acid as the third component of mixture of inorganic and organic acid mixture solutions on corrosion behavior, samples were immersed in acid mixture B, C and D at 70˚C. Mass change of D conditions plotted on root immersion time is shown in Figure 2.1. In these conditions samples shows proportional tendency same as immersed in A.

For comparison of degradation behavior, the mass changes of samples were investigated after 1 day, 7 days and 10 days shown in Figure 2.2. It shows that the more n-butyric acid contained, the more sample's mass gained. (A~C)

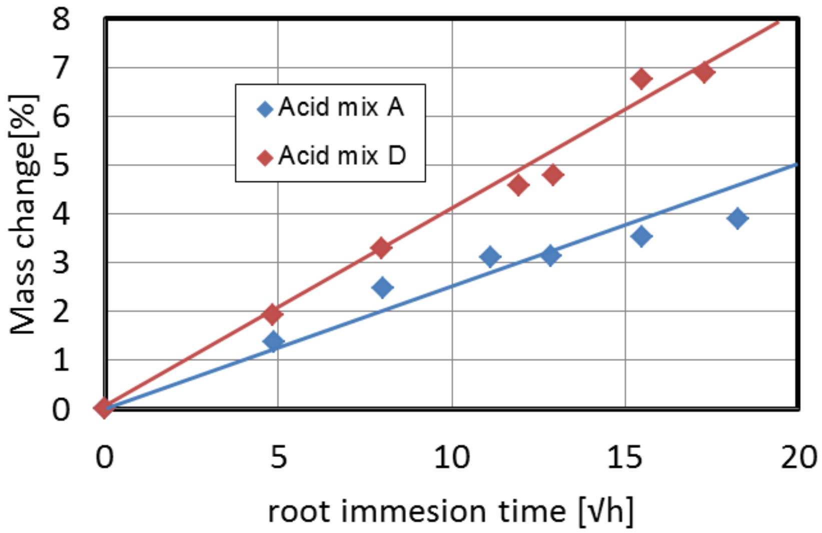


Figure 2.1. Mass change of samples immersed in acid mixture A and D at 70°C

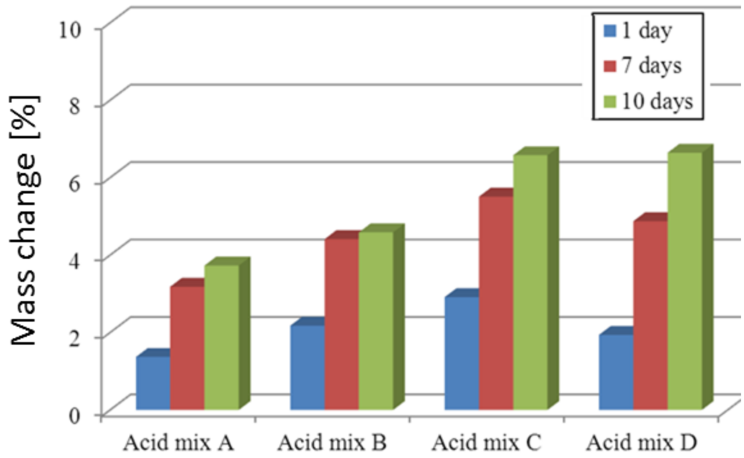


Figure 2.2. Comparison of mass change of samples for acid mixtures at 70˚C

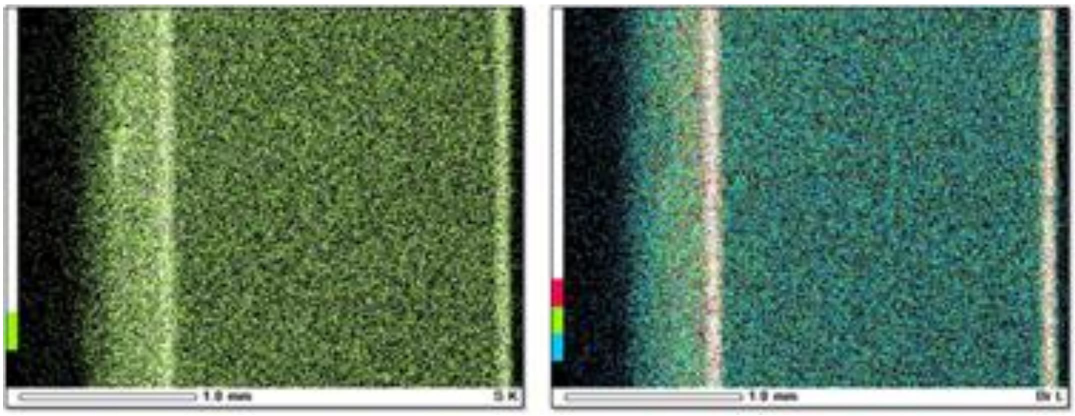
Corrosion mechanism: EDS analysis

In the previous section, mass of penetrant was discussed. In this section, by elemental analysis on cross-section of specimen, distribution of sulfur element and bromine element as a result of acid mixture penetration will be discussed. To inspect organic acid and sulfuric acid penetration into the samples using EDS, samples were immersed in acid mixture D (10% sulfuric acid +5% acetic acid +15g bromobutyric acid) at 70˚C. Figure 3 showed EDS mapping data of penetrated sulfur element (left photographs) and bromine element (right photographs) into samples immersed in acid mixture D after (a) 24h, (b) 168h and (c) 240h.

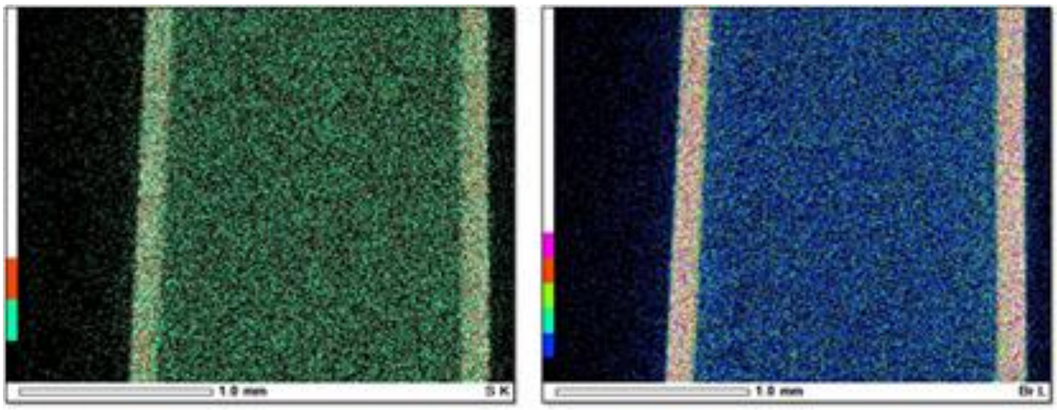
Especially worth mentioning is that both S and Br elements distributed in a step-like pattern. As a result of mass change, fickian behavior was shown, however as a result of EDS mapping, step-like distribution was observed.
In our previous study on immersion in sulfuric acid and acid mixture of sulfuric acid and acetic acid, step-like distribution of S element was observed and we have reported as below. In the case of amine cured epoxy resin samples, the penetrated H_2SO_4 reacted with amine to form amine salts. In addition to this, acetic acid reacted with polymer as acid and solvent. In this period, the acid ion coordinated with the amine group to form amine salt and acetic acid as solvent accelerated acid penetration rate. As a result large amount of acid penetrated. From the result that S distribution was kept step-like while n-butyric acid as the third component was added, it is implied that n-butyric acid didn’t change the mechanism of acid penetration into amine cured epoxy resin.

CONCLUSION

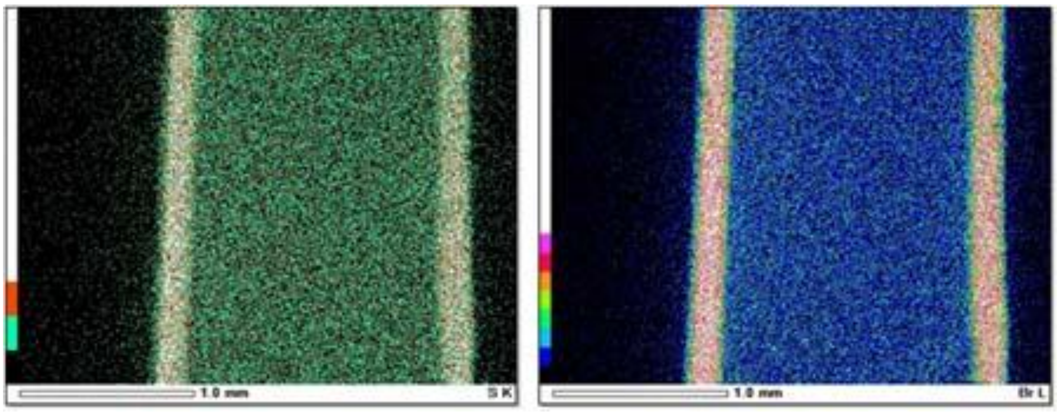
In this study, degradation behavior of amine cured epoxy resins under biomass plant condition has been studied. Amine cured epoxy samples were immersed in different types of organic acid and inorganic acid mixture. Corrosion behavior of the samples has been investigated systematically and penetration behavior of environmental solution into the resin samples as well as mechanism of organic acid and sulfuric acid mixture penetration was discussed.
Mass gain after immersion was investigated. As a result, fickian behavior was observed and adding n-butyric acid in the acid mixture increased mass gain. N- Butyric acid as the third component accelerated the degradation behavior of amine cured samples.
EDS mapping was conducted. As a result, step-like distribution of S and Br element was observed. On the other hand, it was confirmed that step-like distribution of S element was observed. when immersed in sulfuric acid and acid mixture of sulfuric acid and acetic acid. This result indicates that the mechanism of acid penetration was unchanged if third component is added in acid mixture.
In conclusion, n-butyric acid as the third component accelerated the degradation of amine cured epoxy resin, however didn’t change the mechanism of acid penetration into amine cured epoxy resin.



(a) 24h



(b) 168h



(c) 240h

Figure 3. EDS mapping images of penetrated S(sulfur, left photographs) element and Br(Bromine, right photographs) element into samples immersed in acid mixture D (10%sulfuric acid + 5% acetic acid + 15g bromobutyric acid) at 70°C after (a) 24h, (b) 168h, (c) 240h

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