

# DETECTION OF ENVIRONMENTAL ACID PENETRATED IN FRP USING OPTICAL FIBER

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## Abstract

*Polymers and their composites are widely used as corrosion resistant materials in chemical plants. It is required to establish a health monitoring method for chemically exposed fiber reinforced plastic (FRP) structures. In this paper, a health monitoring technology that could simply detect the penetration of corrosive environment solution into plastics by using a pH indicator was proposed. At first, several kinds of pH indicator were tested for detection of organic acid penetration into amine cured epoxy resin (EP). From the result of simple immersion test, it was found that bromothymol blue (BTB) and bromophenol blue (BPB) were available for detecting the penetration of chloroacetic acid. Then, two optical fiber sensors thin enough to embed between FRP laminates were made using BTB and BPB, respectively. Samples with sensor were exposed to one-side immersion test. Both showed response, however, especially BPB sensor showed more significant result.*

## 1 Introduction

These days, composite materials are used widely as engineering structures, and many researchers are dealing with health monitoring to detect a mechanical damage of composite structures in fields of aerospace or civil engineering. Although there are various unique methods of health monitoring, optical fiber sensors have still attracted major attention (e.g. Haga, *et al.* [1]). Optical fiber sensors embedded in matrix resin can monitor internal strain, microcracks or interlaminar fractures of fiber reinforced plastic (FRP) laminates.

Nowadays, not only aerospace or civil engineering, chemical plants also use composite materials for anticorrosion apparatus (e.g. storage tank or distillation tower) and the corrosion

monitoring is very important for these apparatus because the corrosion behavior of composite materials is very complicated. There are, however, few applications of optical fiber sensors used for monitoring of chemical change. Doyle, *et al.* [2] reported that optical fiber sensors embedded in epoxy resin could monitor a curing process by the measurement of the spectrum. Kosaka, *et al.* [3] reported the monitoring of resin curing process by using fiber Bragg grating, that can detect the strain involved with curing shrinkage. Li, *et al.* [4] manufactured an optical fiber corrosion sensor, whose core was exposed and electroplated with Fe-C alloy. When it was immersed in a corrosive environment, the Fe-C alloy corrodes, refractive index of the sensor changes, and the intensity of output signal would increase. The sensor demonstrated a good performance for sensing corrosion phenomena.

The authors have studied degradation/corrosion behavior of thermosetting resin [5] and proposed the health monitoring of chemical degradation [6, 7] based on the behavior.

In this study, epoxy resin containing pH indicator was proposed as corrosion sensor embedded in FRP specimen to detect the penetration of organic acid. Differ from inorganic acid, organic acid penetrates gradually into the resin [8, 9] and the focus is that whether corrosion sensor can detect the gradual penetration or not. For on-line monitoring system, optical fiber and spectrophotometer was used. The possibility of practical application of these corrosion monitoring systems was discussed.

## 2 Experimental Details

### 2.1 Materials

In this study, amine cured epoxy resin (EP) was used. The resin, EPOMIK R-140 (Mitsui Chemicals, Inc.) and the hardener, Jeffamine D-230 (Mitsui-Texaco Chemicals Co., Ltd.) were mixed.

The mixture was cast into 2 mm plate and cured. The curing condition was 12 hours at 70 °C and 12 hours at 100 °C. The cured plate was then cut into the specimen. The size of the specimen was 60×25 (mm). Several kinds of pH indicators were examined for these resin system as previous study [6, 7]. From these results, methyl red (MR), bromothymol blue (BTB) and bromophenol blue (BPB) were selected to make up the pH sensors. Each pH indicator was dissolved in ethanol until saturation. 4 ml of BTB and BPB solutions were added into the 133g uncured resin (100g EP resin + 33g hardener), respectively.

Then, the optical fiber sensor, which is thin enough to be embedded between layers of FRP, was tired to be manufactured. Fig. 1 shows the appearance of the optical fiber sensor module embedded in glass-mat reinforced EP. A plastic optical fiber (Eska SH4001: Mitsubishi Rayon Co., Ltd.) was put between two glass cloths and the cloth was impregnated by chemically stable vinyl ester resin (Ripoxy R-804: Showa Highpolymer Co., Ltd.). Then the slit was introduced by mechanical process and the slit was filled with the pH indicator containing EP. The thickness of the sensor module was as same as the diameter of the optical fiber. The whole module was put between two glass mats and the mat was impregnated by EP.

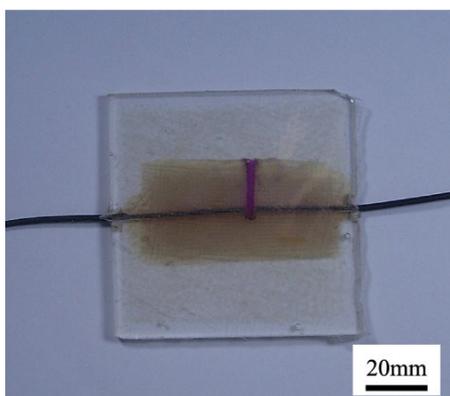


Fig. 1 Photograph of optical fiber sensor embedded in FRP specimen.

## 2.2 Testing Methods

Each specimen was immersed into 3 environmental liquids; deionized water, 10 wt% sulfuric acid, and 0.5 mol/l chloroacetic acid. Every environmental liquid were kept at 50 °C.

After immersion, appearance observation, optical microscope observation, scanning electron microscopy (SEM) investigation, energy dispersion

X-ray system (EDS) for element distribution analysis, spectrophotometer analysis and IR analysis were performed.

For optical fiber sensors embedded specimens, one-side immersion test was performed. The one side of FRP sample was contacted to environmental liquid at 50 °C. Fig. 2 shows the experimental setup of one-side immersion test. Glass vessel was attached to one-side of FRP specimen by clamp and inside of the vessel was filled with 0.5 mol/l chloroacetic acid. The vessel was covered with heater and kept at 50 °C. Both end of the optical fiber was connected to spectrophotometer and the visible spectrum was measured.

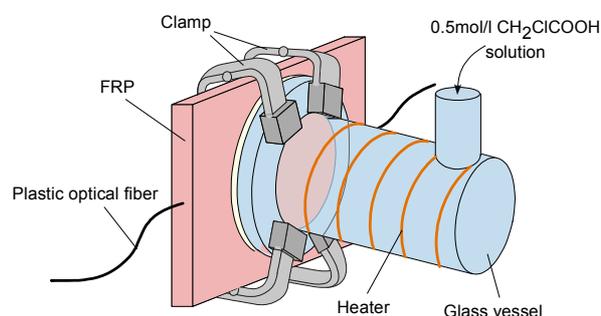


Fig. 2 Schematic view of experimental setup for one-side immersion test.

## 3 Results and Discussion

### 3.1 Examination of pH indicator for detection of penetration of environmental liquid

At first, specimens containing MR were immersed and investigated. Fig. 3 shows the result of immersion test.

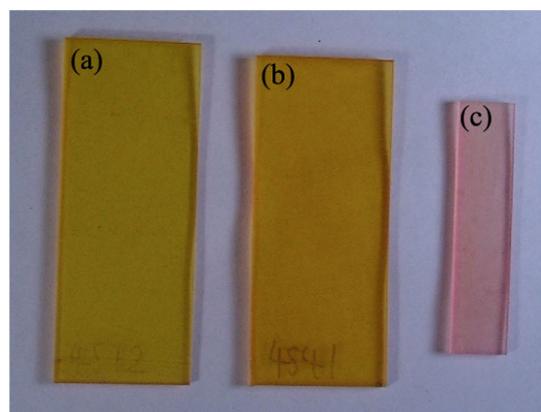


Fig. 3 Photograph of the specimen containing MR (a) before immersion (b) 1000 h immersed in chloroacetic acid (c) 1000 h immersed in sulfuric acid.

After 1000 hours immersion in sulfuric acid, the color of specimen changed from yellow to red. However, after 1000 hours immersion in chloroacetic acid, no color change was observed.

From this result, it was found that MR is not proper to detect the penetration of organic acid. Therefore, MR was excluded from this study hereafter.

Neat resin specimen, BTB containing specimen and BPB containing specimen were immersed in deionized water. The weight change of each specimen is shown in Fig. 4.

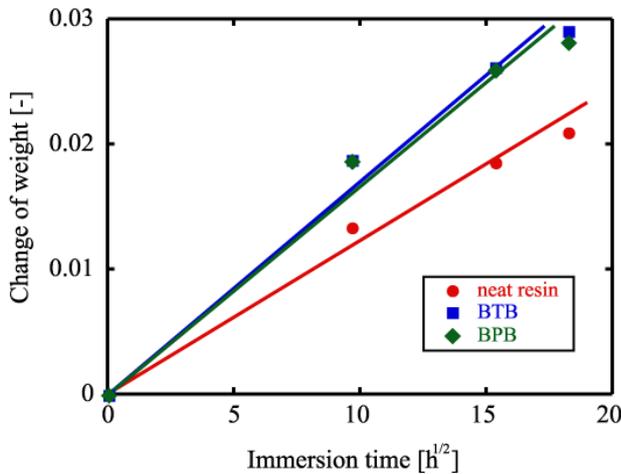


Fig. 4 Weight change of specimens immersed in deionized water.

The weight of specimens were increased proportionally to square root of time by immersion in water, that is to say, water penetrates into the specimen according to the Fick's Law.

Fig. 5 shows the appearance of neat resin specimen, the specimen containing BTB, and the specimen containing BPB immersed in deionized water. From this figure, no color change had observed in each specimen.

From these results of Figs. 4 and 5, it is said that no color change occurs in BTB, BPB and EP resin itself by penetration of water.

Then each specimen was immersed in sulfuric acid. Fig. 6 shows the appearance of each specimen. Neat resin does not change its color by immersing in sulfuric acid. The color of the specimen containing BTB changed from yellowish green to yellow in early period. The specimen containing BPB showed color change from bluish purple to yellow by immersion in sulfuric acid.

This difference of color change behavior is caused by the difference of pH range for color change. BTB changes its color at the pH range of 6-8 and BPB changes at the pH range of 3-5. The specimen before immersion is almost neutral or a little alkaline. Therefore, the initial color of the specimen containing BTB is yellowish green and the specimen containing BPB is bluish purple and both specimen changes color to yellow by immersing in sulfuric acid.

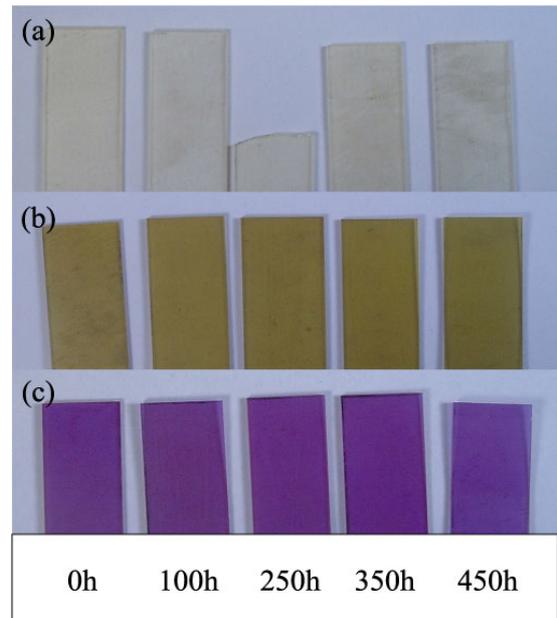


Fig. 5 Photographs of specimen immersed in water (a) neat resin (b) resin containing BTB (c) resin containing BPB.

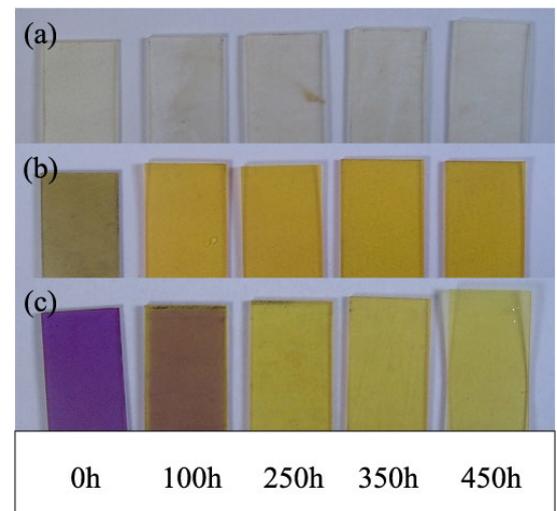


Fig. 6 Photographs of specimen immersed in sulfuric acid (a) neat resin (b) resin containing BTB (c) resin containing BPB.

Afterwards, each specimen was immersed in chloroacetic acid. The appearance of each specimen was shown in Fig. 7. In this figure, no color change was observed a neat resin specimen. Similar to sulfuric acid, EP resin itself does not change its color by immersion in chloroacetic acid.

The specimen containing BTB changed its color from yellowish green to yellow and the specimen containing BPB changed its color from bluish purple to yellow by immersion in chloroacetic acid.

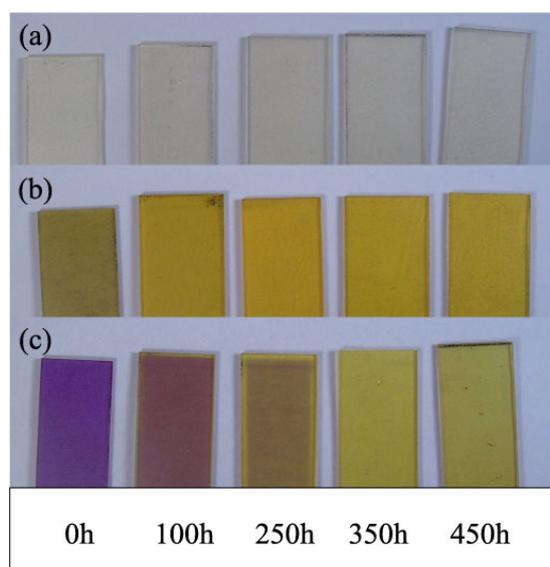


Fig. 7 Photographs of specimen immersed in chloroacetic acid (a) neat resin (b) resin containing BTB (c) resin containing BPB.

Then, before and after the immersion test in chloroacetic acid, the cross section of the specimen containing BTB and the specimen containing BPB were observed by optical microscope and SEM and analyzed “Cl” element distribution by EDS. Results of each specimen was shown in Figs. 8 and 9, respectively. The red line in “EDS” column shows the line profile of Cl element along the depth direction, corresponding to the relative quantity of Cl element existence.

In previous work [8, 9], it was found that inorganic acid penetrates into resin stepwise and organic acid penetrates into resin with concentration gradient. In this study, from the line profile of Cl element in Figs. 8 and 9, it can be said that the chloroacetic acid penetrates into EP resin with concentration gradient.

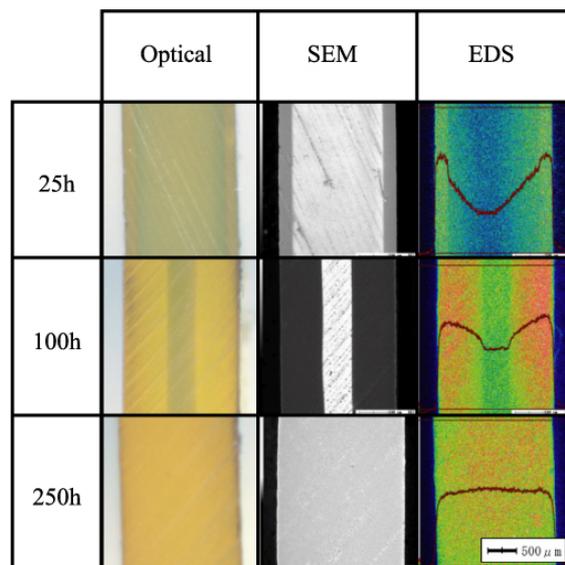


Fig. 8 Photographs of cross section of the specimen containing BTB after immersing in chloroacetic acid.

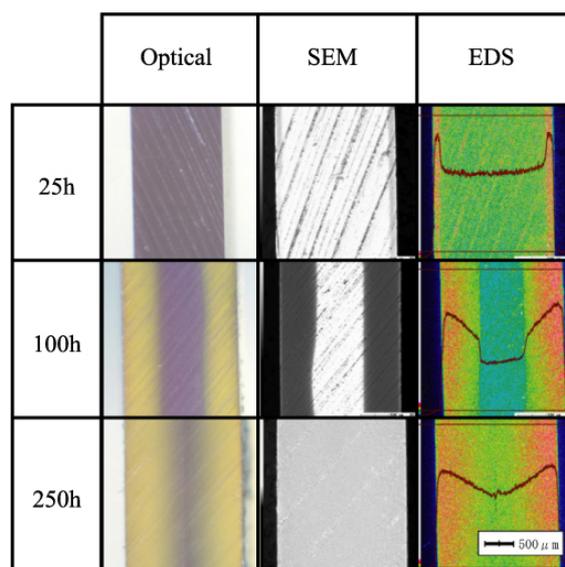


Fig. 9 Photographs of cross section of the specimen containing BPB after immersing in chloroacetic acid.

Both in Figs. 8 and 9, the color changed area observed by optical microscope is recognized and the boundary of color change corresponding to the penetration front of environmental liquid investigated by EDS analysis. However, the specimen containing BTB shows clearer penetration front than the specimen containing BPB similar to stepwise penetration. This difference might be caused by the difference of pH range for color change between BTB and BPB. BTB changes its color around pH range of 6-8, the color of specimen

changes with a little penetration of chloroacetic acid and BPB changes its color around 3-5. The latter needs some quantity of penetration of chloroacetic acid to change the color of specimen.

From the results above, BTB and BPB were selected to establish optical fiber sensor.

**3.2 Evaluation of thin optical fiber sensor embeddable between laminates of FRP shell**

At first, the spectra of BTB and BPB solution were measured by spectrophotometer. Each chart is shown in Figs. 10 and 11, respectively.

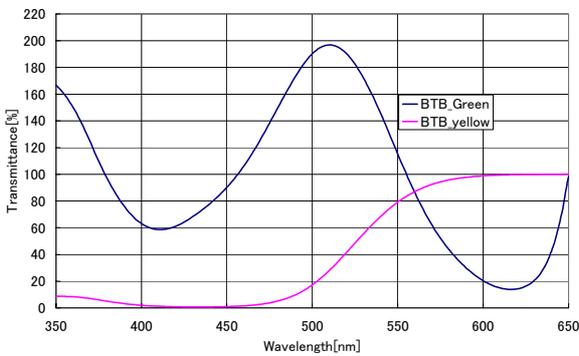


Fig. 10 Spectrum of BTB solution at neutral and acidic state (blue line: neutral state, red line: acidic state).

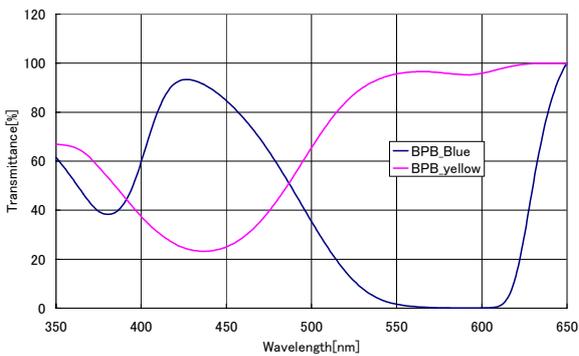


Fig. 11 Spectrum of BPB solution at neutral and acidic state (blue line: neutral state, red line: acidic state).

In each spectrum, the transmittance of 500 or 420 nm at neutral state decreases at acid state and the transmittance of 600 nm appeared. Therefore, the change of transmittance of 450-500 nm and 600 nm regions were noticed hereafter.

Then, the FRP specimens with the embedded optical fiber sensor using BTB and BPB (shown in Fig. 1) were exposed to one-side immersion of

chloroacetic acid (shown in Fig. 2), respectively. Obtained spectra of each sensor are shown in Figs. 12 and 13, respectively.

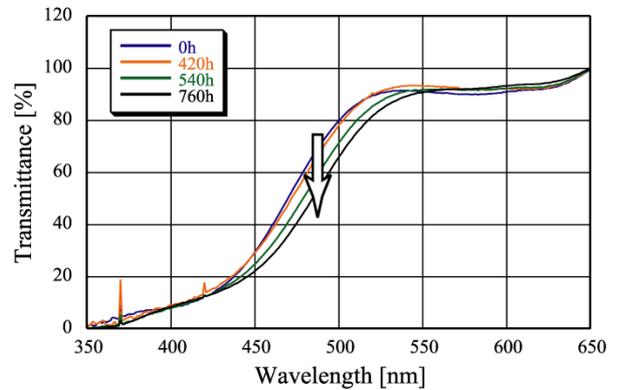


Fig. 12 Visible spectrum of the optical fiber sensor containing BTB immersed in chloroacetic acid.

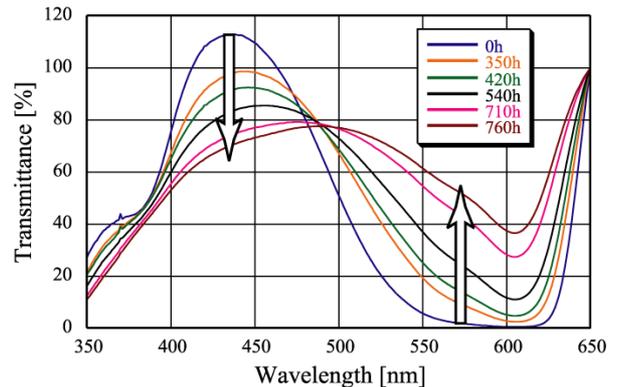


Fig. 13 Visible spectrum of the optical fiber sensor containing BPB immersed in chloroacetic acid.

Before immersion, the spectrum of BTB sensor is similar to the spectrum of BTB solution at acidic state because of the pH range for color change. By immersing in chloroacetic acid, the spectrum of BTB sensor shows a little transition of the decrease near 500 nm. On the other hand, the spectrum of BPB sensor before immersion is similar to the spectrum of BPB solution at neutral state. And the spectrum of BPB sensor shows a large change of decrease of 450 nm and the increase of 600 nm. After immersion, the spectrum of BPB sensor is similar to the spectrum of BPB solution at acidic state.

Comparing these results, it can be said that the BPB sensor is more useful to detect the penetration of organic acid for significant transmittance change at two wavelengths because the effect of some noise

can be reduced by monitoring two transmittance changes simultaneously.

In previous work [7, 10], the shape of sensor module was cylindrical and only simple immersion test into solution was performed. In this study, the shape of sensor module was thin plate that can be embedded between FRP laminates and was able to detect the penetration of organic acid with concentration gradient.

#### 4 Conclusions

The EP resin specimens containing several pH indicators were made and tested. Among a number of pH indicators, especially BTB and BPB showed good result for both sulfuric acid and chloroacetic acid.

The optical fiber sensor, which is thin enough to embed between layers of anti-corrosive FRP application, was manufactured. The slit of the optical fiber was filled with BTB and BPB containing EP resin, respectively.

Each sensor showed response, however, especially BPB sensor showed more obvious result.

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