

Fundamental study on the effect of water absorption in epoxy adhesive used in CFRP-steel joints

Kyushu University Student Member ○Jiajing XIE
Kyushu University Fellow Member Shigenobu KAINUMA

Kyushu University Regular Member Muye YANG

1. Introduction Recent years, CFRP was usually used to reinforce the steel structures. One major drawback when it comes to using CFRP composites for strengthening and repairing steel structures is the lack of knowledge relating to the long-term performance and durability properties of CFRP/steel bonded joints. Particularly, adhesive degradation is the most widely concerned problem. Adhesive bonding has distinct advantages compared with mechanical fastening techniques, such as easier assembly, cost efficiency, and more uniform stress distribution. However, a number of environmental parameters such as moisture and UV radiation, are known to affect the durability and deterioration characteristics of the CFRP strengthened steel structures. A review of the literature reveals that moisture is the most problematic substance when it comes to the durability of adhesive joints with FRP and metallic adherents [1]. Epoxy resin (ER) as a most common type of polymer adhesive, is susceptible to the ambient humidity, and moisture diffusion can alter their thermo-physical, mechanical, and chemical characteristics [2,3]. The modulus and strength of adhesives are also known to deteriorate as a consequence of moisture ingress. In this study, moisture test was used to the influence of the environment on the water absorption rate. The DSC test and FTIR test were used to investigate the effect of water on the internal structure after the resin absorbed water.

2. Test method In this test, all the specimens were made by epoxy adhesive (Araldite® 420), the dimension of specimens were 50×50×1 mm, made by steel mold base. They were cured under 60°C and 45%RH for 2 hrs. After curing finished, all the specimens were put in a thermo-hygrostat under 60°C and 30% RH for 12 hrs to dry. Then specimens were exposed to five environments: 1) Atmosphere of 50°C and 50% RH; 2) 23°C distilled water; 3) 23°C 3.5 mass% NaCl solution; 4) 50°C distilled water; 5) 50°C 3.5 mass% NaCl solution. The test conditions were referred to JIS-K7092. There were three same samples tested in each kind of test environment. All specimens were weighed using a scale with an accuracy of 0.01 mg. To measure the weight changing according to time, specimens were taken out from the test environments after a decided exposure period (t) about 2, 4, 8, 12, 24, 48 and 72 hrs, wiped using a dry cloth and weighed immediately. The specimens were then returned to the test environments for continuing exposure. The moisture uptake (M_t) for each specimen was calculated using Eq. (1):

$$M_t = \left(\frac{W_t - W_0}{W_0} \right) \times 100 \quad (\%) \quad (1)$$

where: W_0 is dry weight of specimens; W_t is weight after absorbed water of specimens.

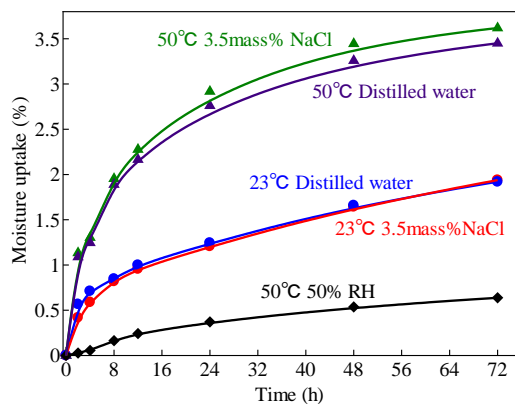


Fig.1 Moisture uptake in ER

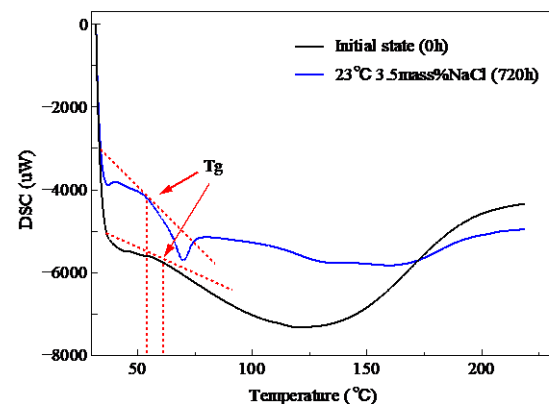
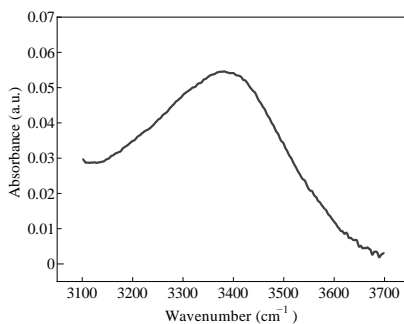
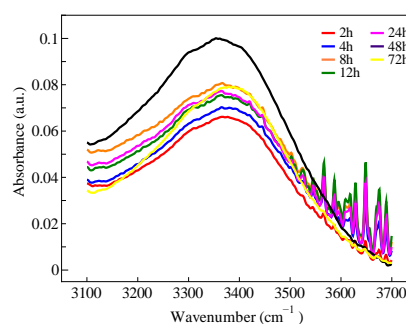


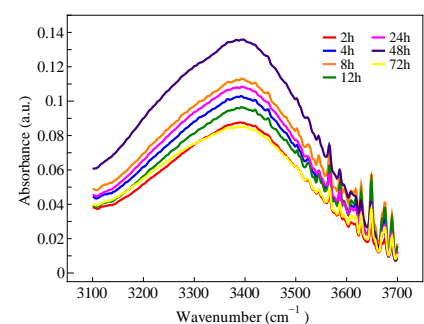
Fig.2 DSC result



(a) Dried specimen (0 hr)



(b) Atmosphere (50°C, 50%RH)



(c) Immersion in Distilled water (23°C)

Keywords: Epoxy adhesive, Moisture diffusion, Environmental degradation, CFRP-steel joint

Contact address: 744 Motooka, Nisi-ku, Fukuoka, 819-0395, Japan, Tel: +81 92-802-3392

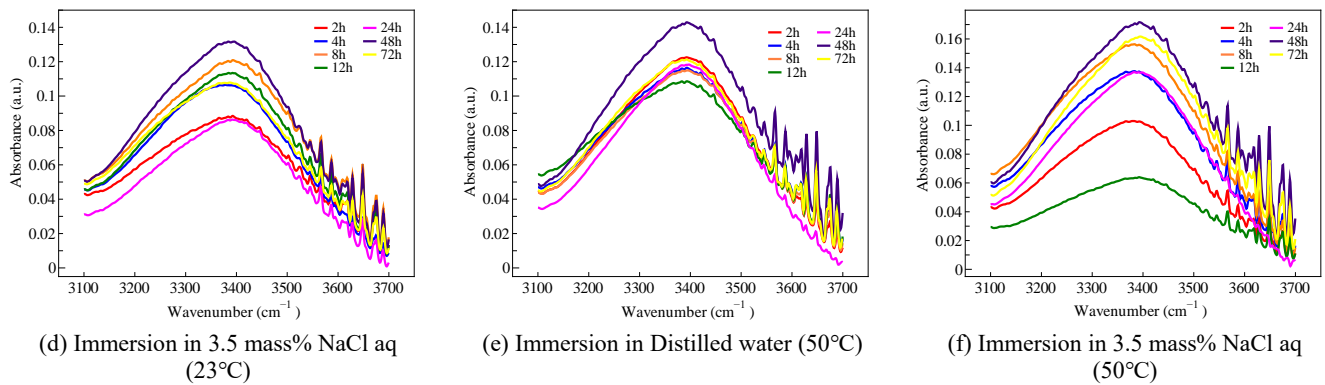


Fig.3 Test results of FTIR-ATR

After specimens tested for 2, 4, 8, 12, 24, 48 and 72 hrs, Fourier transform infrared spectroscopy – attenuated total reflectance (FTIR-ATR) were performed. The test was carried out for a wavenumber (cm^{-1}) between 3100 and 3700 (cm^{-1}), which corresponds to O-H groups. After FTIR analysis, the specimens were immediately returned to the test environment for continuing exposure. To analyze the effect of water absorption on the internal structure of the ER, we measured the glass transition temperature (T_g) of two specimens using a high sensitivity differential scanning calorimeter (DSC). One specimen is in the initial dry condition, and another one is immersed in 23°C 3.5 mass% NaCl aq for 700 hrs. The DSC test was carried out for a temperature between 30 and 230 ($^{\circ}\text{C}$) and the program speed is 0.01-100 $^{\circ}\text{C}/\text{min}$.

3. Test results The mean value of the moisture uptake (M_t) of each group was calculated as shown in Fig.1. From the obtained M_t of the specimens according to time, atmosphere and immersion environments showed considerable difference to the water absorption, that the water absorption in the atmospheric environment is about one-seventh of that in solution environment after 72 hrs. For the immersed specimens, their water absorption rates were all rapidly increased from 0~12 hrs, whereas after 12 hours, their water absorption rate gradually slowed down and the inner free water tended to be saturated. Moreover, for the cases of different electrolytes (distilled water; 3.5 mass% NaCl aq) performed under the same temperature, various electrolyte concentrations almost would not affect the water absorption of the adhesive. The difference in concentration has no effect on water absorption rate and capacity. However, for the cases under different temperatures, even the same electrolyte would lead to multiple differences in water absorption. It was indicated that the accumulated water environment and temperature are the main control factor of EP water absorption, and the higher temperature significantly accelerated water absorption speed.

The DSC results was shown in Fig.2. The specimens exposed to the atmospheric environment has a higher T_g than the specimen in the NaCl aq environment. After absorbed water, there were two kinds of water called free water and bound water in the aging ER specimens. Free water occupy free spaces of the polymer, resulting in material plasticization, bonded water has more hydrogen bonds to the resin than free water, resulting in this case in swelling, plasticization and decreasing both strength and glass transition temperature. In this test, the specimen in NaCl aq environment has more bound water than specimen in initial state. As time increased water were absorbed into the specimen, the bounds water were increased. They act as a plasticizer and are responsible for T_g decreasing. These bounds disrupt Vander Waals initial forces between the polymer chains and the hydrogen bonds resulting in chain segment mobility increment.

The content of free O-H groups has an increasing tendency with the increase of immersion time as shown in Fig.3. In the 48th hour, the amount of O-H groups reached the peak. In the period of 8 to 12 hrs, the peak value of O-H groups were all decreased as shown in Fig.3(b) to Fig.3(f). It may be that a part of the free O-H groups had combined with the molecules of the adhesive material so that a part of free water became bound water. This change may have a series of effects on the mechanical properties and electrical resistance of the material, this will be verified in subsequent experiments.

4. Conclusion 1) The epoxy resin shows different water absorption behavior in the atmospheric and immersion environments, while the temperature would largely affect the moisture uptake in adhesive plate. 2) During the immersion process, a part of the free water combined with the molecules inside the adhesive material to become bound water. 3) Water absorption lead to an increase in bound water content, they act as a plasticizer and are responsible for glass transition temperature (T_g) decreasing.

References

- 1) P. Galvez, J. Abenojar, M.A. Martinez, Effect of moisture and temperature on the thermal and mechanical properties of a ductile epoxy adhesive for use in steel structures reinforced with CFRP, Composites Part B: Engineering 176 (2019) 107194.
- 2) J. Zhou, J.P. Lucas, Hygrothermal effects of epoxy resin. Part I: The nature of water in epoxy, Polymer 40 (1999) 5505–5512.
- 3) M. Heshmati, R. Haghani, M. Al-Emrani, Effects of moisture on the long-term performance of adhesively bonded FRP/steel joints used in bridges, Composites Part B: Engineering 92 (2016) 447–462.