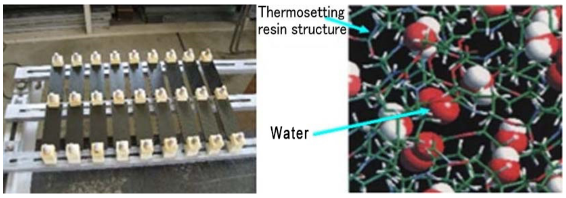
Accelerated Water Absorption Method for Composite Materials



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When developing composite parts, the design is carried out assuming that the strength and stiffness will be reduced after absorbing moisture during long-term operation. However, it is difficult to simulate the moisture absorption conditions at the time of development and evaluation in a short amount of time, and generally moisture absorption is carried out over a long time in a high-humidity environment. This paper presents a new accelerated moisture absorption method for shortening the evaluation period of composite materials.

1. Introduction

In transportation equipment and environmental engineering fields, new composite materials such as epoxy resin composite materials have been more widely used. When exposed to an operation environment for a long time, epoxy resin composite materials absorb moisture in the atmosphere and their strength and stiffness are lowered. Therefore, composite material parts are designed based on the properties in which the predicted reduction of the strength and stiffness due to moisture absorption is taken into account. With such a background, for the development of new resin-based composite material parts, improvement of the accuracy of the technology for evaluating the strength and stiffness after moisture absorption in the operational environment in a short time is required.

This paper reports on the results of configuring and verifying the accelerated moisture absorption conditions of epoxy resin composites with respect to the diffusion of moisture into composite material.

2. Concept of accelerated moisture absorption

For configuring the conditions of the accelerated moisture absorption method, the test and examination were carried out as follows:

(1) Configuring conditions for accelerated moisture absorption
(2) Repeating the accelerated moisture absorption to verify the reproducibility and deterioration

2.1 Necessity of moisture absorption

As described above, epoxy resin composites absorb moisture in the atmosphere until the equilibrium state is reached during long-term operation. Since the moisture absorption increases the mobility of the epoxy resin, the strength and stiffness of the composite material are lowered. Therefore, the design of composite material parts is carried out based on the properties in which the expected reduction of the strength and stiffness due to moisture absorption is included. Specifically, as shown in **Figure 1**, moisture absorption parameters of the composite material are acquired[1] firstly, and the final equilibrium moisture absorption amount in a long-term operation environment (generally the operating temperature of composite parts is assumed to be 80°C or lower) is predicted. Then design data of the composite material part that has absorbed moisture until the equilibrium moisture absorption amount is reached is acquired.

It takes as long as 100 days or more for a large or thick part to reach the prescribed moisture absorption amount, so it is hoped to create a test method to accelerate the absorption of moisture so that evaluation can be performed in a short period of time.

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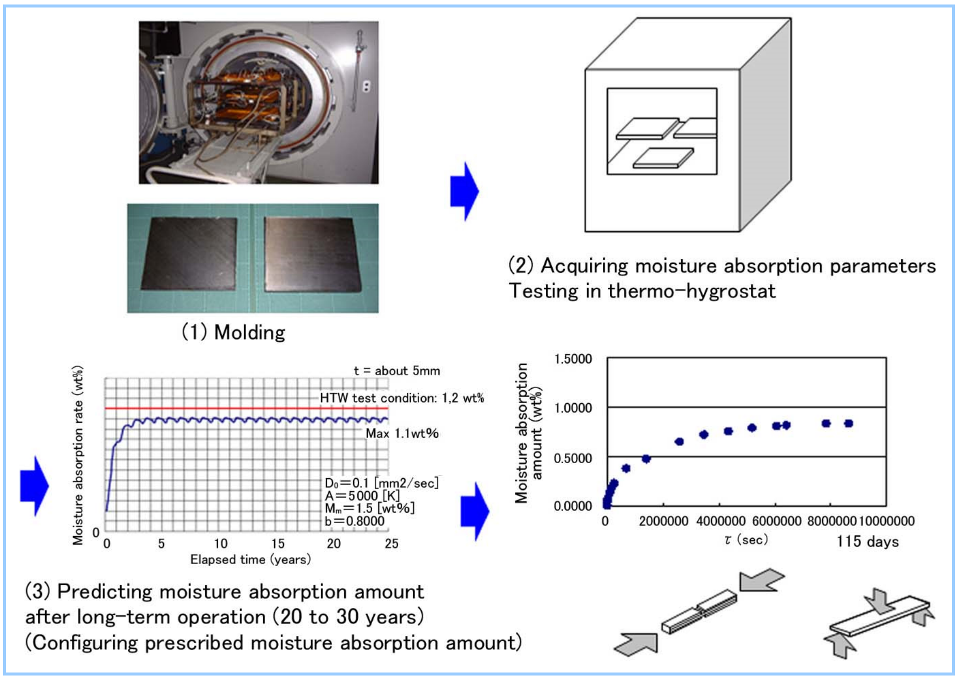

Figure 1 Evaluation flow of moisture absorption effect

2.2 Moisture absorption form

As shown in **Figure 2**, moisture absorption into epoxy resin is caused by the diffusion of water or clusters into the three-dimensional crosslinked structure of the resin. It is assumed that the moisture absorption progresses, diffusing from the surface layer. As shown in **Figure 3**, initially the moisture concentration is high at the surface layer and low at the center of the thickness. However, it is expected that the moisture concentrations in the surface layer and the center will become uniform with the lapse of time.

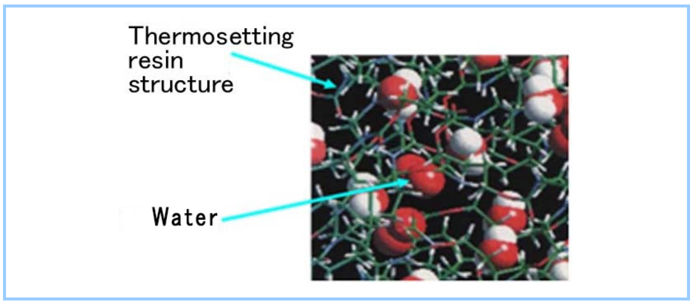

Figure 2 Diffusion of moisture into matrix resin

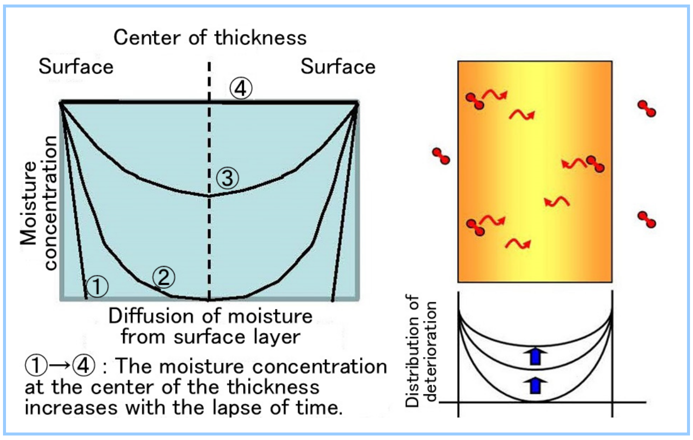

Figure 3 Moisture concentration in thickness direction with regard to moisture diffusion and distribution of deterioration

3. Examination on accelerated moisture absorption

It takes half a month to one month or more for a composite part several millimeters in thickness to reach the equilibrium moisture absorption state at a temperature of 80°C and a humidity of 85%. **Figure 4** shows the moisture absorbing behavior of a specimen about one millimeter in thickness.

To increase the moisture absorption rate, it is necessary to raise the temperature. However, if the temperature is raised to 100°C or higher, the water evaporates resulting in a dry state. To deal with this, an autoclave pressurization system is applied as one method to raise the temperature while keeping the water vapor. The pressurization system has abundant achievements as a method to steam-sterilize foodstuffs and medical equipment, and has high capability and versatility. In this research, an LSX-500 autoclave (AC) device for laboratory sterilization systems owned by the National Institute of Advanced Industrial Science and Technology shown in **Figure 5** was used.

As a specimen, a carbon fiber reinforced epoxy resin matrix composite (CFRP) with a curing temperature of 180°C and a fiber volume fraction (Vf) of about 55% was used.

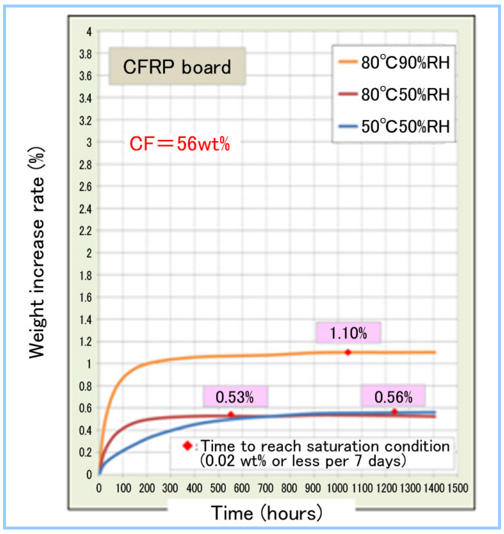

Figure 4 Moisture absorbing behavior of composite material

Figure 5 Autoclave

3.1 Examination of accelerated moisture absorption condition

As an examination of the accelerated moisture absorption condition, the accelerated moisture absorption behavior was evaluated at each temperature. Since the strength property deteriorated at temperatures higher than 120°C, a milder temperature of 120°C was set as the accelerated moisture absorption condition. **Figure 6** presents the results of the moisture absorbing behavior of a CFRP 1.5 mm in thickness. In the case of accelerated moisture absorption at 120°C and 0.2 MPa, the moisture absorption amount is saturated at 60 hours and did not change until 86 hours from a constant value. The reason why the moisture absorption amount decreased at 96 hours has not been clarified. However, after confirming that the CFRP physical properties did not deteriorate, the accelerated moisture absorption time was set to 72 hours. This result corresponds to acceleration that reduces the time required for the achievement of the equilibrium moisture absorption state in an environment at 80°C and 90% RH (about 700 hours) by a factor of 10.

Table 1 shows the results of the infrared absorption detection of absorbed heavy water performed to check the internal diffusion of moisture. The standard peak was set to 1640 cm-1, and the peak 2480 cm-1 derived from heavy water was normalized to test the concentration. It was confirmed that the existing amount of heavy water was almost equal between the surface and the center of thickness and that heavy water permeated internally due to this accelerated moisture absorption condition.

The activation energy of water diffusion in another similar epoxy based CFRP is about 47 kJ/mol. By increasing the temperature from 85°C (reference temperature) to 120°C, acceleration of about 4 times is expected. It is considered that moisture absorption is accelerated by the acceleration of diffusion due to temperature and the increase of moisture concentration (relative humidity 100% RH) in the environment (in the autoclave).

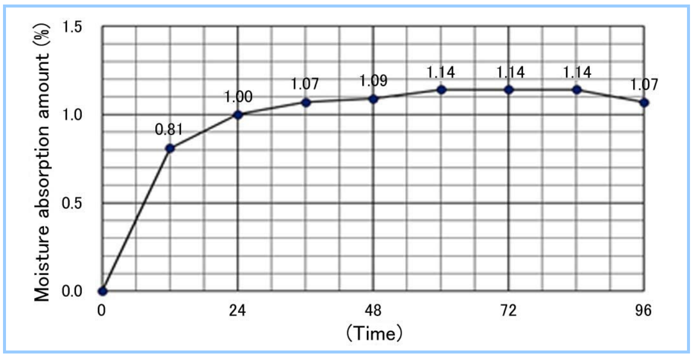

Figure 6 Moisture absorbing behavior under accelerated moisture absorption condition (120°C)

Table 1 Absorbance ratio of heavy water peak

	Average of absorbance ratio (I2480/I1640)
At the surface after accelerated moisture absorption	0.12
At the center after accelerated moisture absorption	0.11

3.2 Reproducibility of accelerated moisture absorption and its effect on CFRP properties

Figure 7 indicates the change in the moisture absorption rate in repeated cycles of accelerated moisture absorption and reduced pressure drying. In this test, the mass of the same sample (n = 3) was measured after the achievement of saturation and absolute drying. Every time the cycle of moisture absorption and drying is repeated, the saturated moisture absorption rate decreased from 1.77% by 0.1%. This is a phenomenon also observed for water-containing substances such as gels. It is thought that when a dry state is reached, the consolidation of molecules progresses in the region of the molecular structure related to moisture absorption and the degree of re-moisture absorption decreases.

Next, the influence on the bending strength of repeated cycles of accelerated moisture absorption and reduced pressure drying was evaluated. A three-point bending test with a span distance of 60 mm was carried out using a specimen of 15 × 100 × 1.5 mm for evaluation. **Figure 8** shows the bending strength in repeated cycles of accelerated moisture absorption and reduced pressure drying. Any change in the strength due to the repeated cycles was not observed, and it was confirmed that deterioration did not occur under this condition.

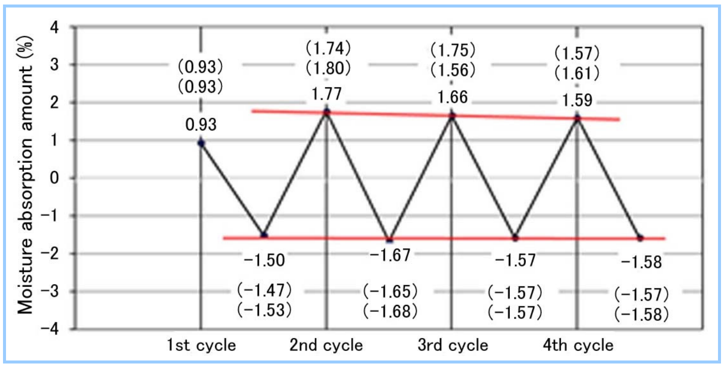

Figure 7 Change in moisture absorption rate in repeated cycles of accelerated moisture absorption (120°C, AC 3 days) and reduced pressure drying (100°C, 3 days)

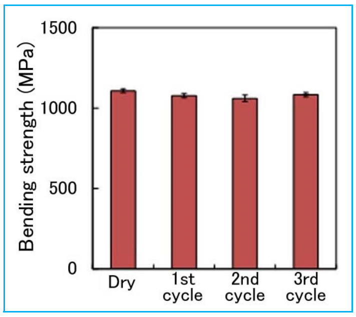

Figure 8 Change in bending strength in repeated cycles of accelerated moisture absorption (120°C, AC 3 days) and reduced pressure drying (100°C, 3 days)

In addition, the influence on the viscoelastic characteristic of repeated cycles of accelerated moisture absorption and reduced pressure drying was evaluated. Firstly, **Figure 9** shows the change in the viscoelasticity characteristic under the condition where the strength decreases (after exposure to 160°C for 7 days). In particular, the loss modulus (modulus of elasticity that responds late to strain change), tanδ (ratio of loss modulus to storage modulus, which increases as viscosity becomes prominent) remarkably appeared. Two peaks were observed in the loss elastic modulus, and at the initial stage the height ratio (ratio of low-temperature peak to high-temperature peak) of the two peaks was almost 1, but under the condition after exposure to 160°C for 7 days, decreasing behavior with respect to the temperature appeared. Regarding tanδ, when the ratio of the two peaks is focused on, the initial value is 0.24. However, under the condition after exposure to 160°C for 7 days, the peak on the low temperature side becomes larger and the ratio changes to 0.54.

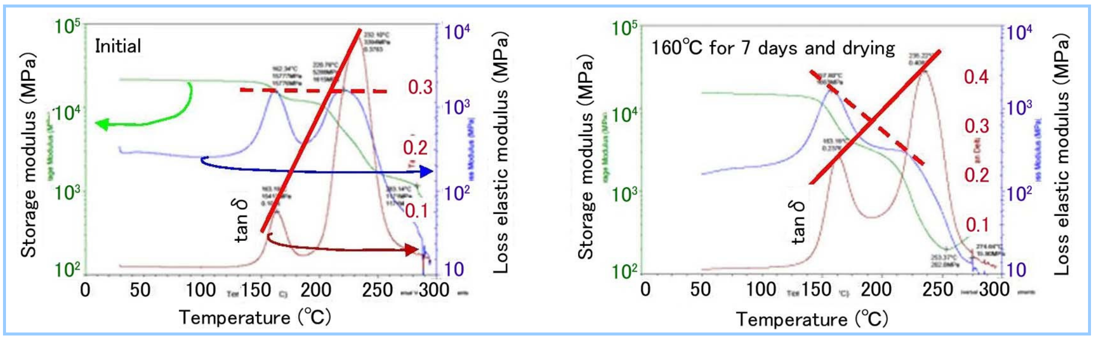

Figure 9 Changes in viscoelastic characteristic after accelerated moisture absorption (160°C, AC 7 days) and reduced pressure drying (100°C, 3 days)

On the other hand, **Figure 10** shows the change of the viscoelasticity characteristic in the repeated cycles (after absolute drying) under the accelerated moisture absorption condition. The peak ratio of the loss modulus is approximately 1 and is not changed by repetition. In addition, the two peak ratios of tanδ are 0.23 to 0.26 even after repeating with respect to the initial 0.24. No change that affects the molecular mobility of the matrix resin has occurred, so it is presumed that the peak positions and the peak ratios of the storage elastic modulus (elastic modulus directly responding to strain change), the loss modulus of elasticity, and tanδ do not change.

Based on the above, it was confirmed that accelerated moisture absorption was possible under the conditions of 120°C and 0.2 MPa × 72 hours, and that no deterioration occurred. On the other hand, before applying the accelerated moisture absorption condition to thick parts that take time to reach the specified amount of moisture absorption, it is necessary to confirm at the coupon level that, with regard to the physical properties after moisture absorption time, there is no change in the strength, viscoelasticity, etc.

This accelerated moisture absorption method is underway toward ISO standardization at the National Institute of Advanced Industrial Science and Technology, and is under discussion in the technical committee established at The Japan Plastics Industry Federation Standards Subcommittee.

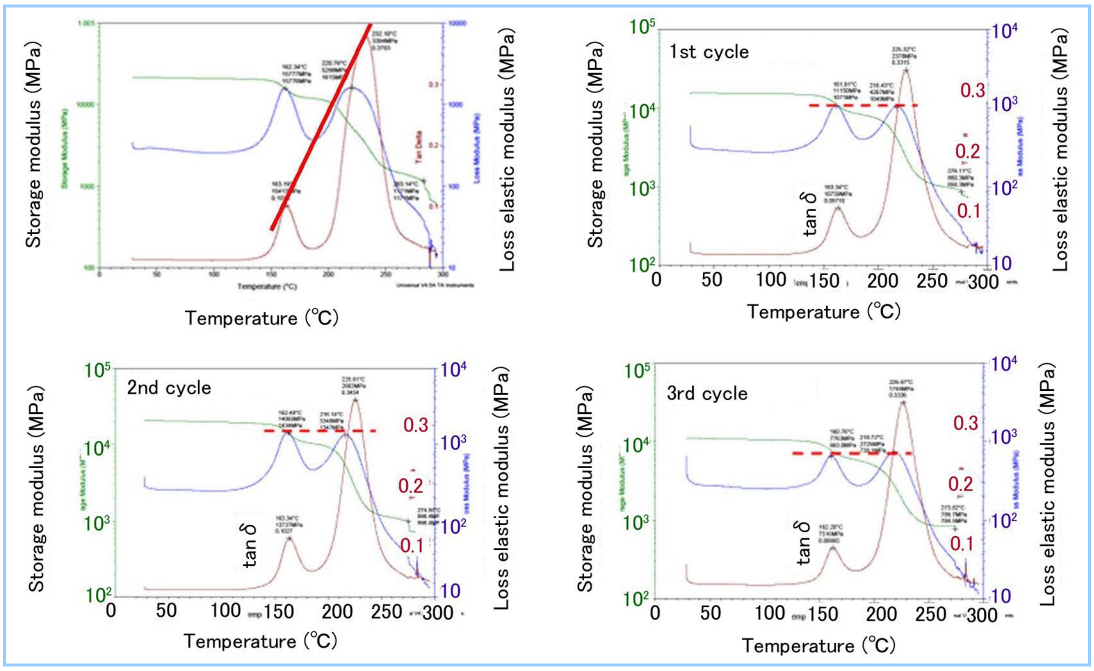

Figure 10 Changes in viscoelastic characteristic in repeated cycles of accelerated moisture absorption (120°C, AC 3 days) and reduced pressure drying (100°C, 3 days)

4. Conclusion

We examined the accelerated moisture absorption method at a level where the physical properties are not affected, and clarified as follows.

- For a part about 1.5 mm in thickness, roughly 10 times accelerated moisture absorption was possible under the conditions of 120°C and 0.2 MPa for 72 hours.
- It was possible to repeat accelerated moisture absorption and drying, and it was verified that there is no influence on the strength and viscoelasticity, and that the conditions do not cause occurrence of deterioration.

We will apply the accelerated moisture absorption method to contribute to the development of new composite material parts and the shortening of the design period. Finally, this research is based on the results of collaborative research with the National Institute of Advanced Industrial Science and Technology, and we appreciate their support.

References

1. Standard Test Method for Moisture Absorption Properties and Equilibrium Conditioning of Polymer Matrix Composite Materials, ASTM D5229/D5229-14, 2014