



MECHANICAL PROPERTIES OF HEAT RESISTANT COMPOSITE USING TG-LESS EPOXY RESIN AS A MATRIX

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Abstract

In recent years, a high heat-resistant FRP whose matrix is T_g -less epoxy resin has been investigated. While the GFRP using T_g -less epoxy resin as the matrix exhibited good mechanical and heat-resistant properties, the CFRP using T_g -less epoxy resin as the matrix did not. The cause of that problem was considered that the curing of T_g -less epoxy resin was inhibited by an acidic compound adhered on the surface of the carbon fibers. In this study, several treatments for carbon fiber fabrics were investigated. The most effective treatment was immersing carbon fibers into a thin alkali solution to neutralize the acidic compound. The bending modulus of the T_g -less CFRP obtained at 300 maintained more than 80% of that at room temperature and the bending strength maintained approximately 200 MPa at 300 . Further, the creep compliance of the T_g -less CFRP did not change up to 100 h even at an elevated temperature such as 170 .

1 Introduction

Fiber reinforced plastics (FRPs) are used in various fields requiring a performance of a light-weight because of their superiority of high specific strength and modulus. However, there are several issues such as thermal deformation resistance, economy and molding process, before FRPs are applied as the heat resistant materials to the fields of general vehicles or constructions. Polyimide has been developed as heat-resistant resin for the aerospace material, but a molding cost of FRP is too high to use it as general structural materials.

Recently, T_g -less epoxy resin is developed [1]. Its elastic modulus does not drop under a high temperature due to using potassium carboxylate salt as a catalyst. The T_g of normal epoxy resin is about

100 ~ 140 . On the other hand, a storage modulus of T_g -less epoxy resin does not drop under a higher temperature over 200 as shown in Fig.1.

If this T_g -less epoxy resin has sufficient capabilities for a matrix of FRP with the same molding process as ordinary epoxy resins, the FRP using T_g -less epoxy resin can be applied to the various fields of vehicles or constructions as a heat resistant composite.

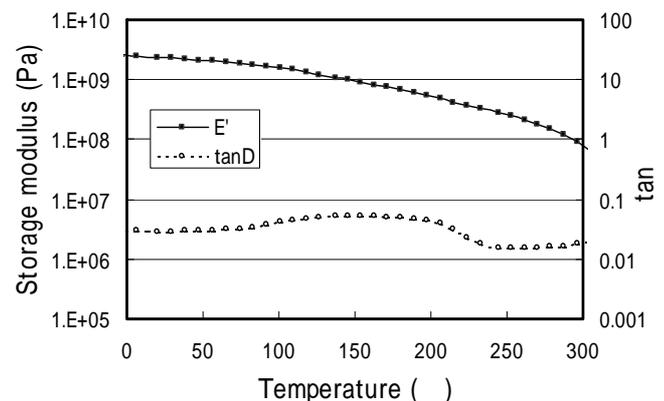


Fig.1 Viscoelasticity of T_g -less epoxy

However, we found that the carbon fiber reinforced plastic (CFRP) using T_g -less epoxy resin as the matrix did not have the expected mechanical or heat-resistant properties. This problem seemed to be associated with the inhibition of curing of the T_g -less epoxy resin near the surface of carbon fiber fabrics. So, the first purpose of this study is to find some methods to overcome this difficulty. Fortunately, we could get two effective methods related to the treatment of the surface of carbon fibers, which will be discussed in this paper.

Another purpose of this study is to evaluate the mechanical properties, such as bending and creep properties under high temperatures, of T_g -less CFRPs by using the prescribed method in JIS.

2 Inhibition mechanism of polymerization of T_g -less epoxy resin

Because T_g -less epoxy resin undergoes curing by the mechanism based on anionic polymerization, as shown in Fig. 1, it would be subject to inhibition by acidic species. According to Fig. 2, the inhibition mechanism is thus represented as follows. The propagating chain end (**1**) is the ion pair of an epoxide anion and a potassium cation, which is generated by the nucleophilic addition of a potassium carboxylate to an epoxy group.

As soon as the propagating chain end (**1**) contacts with a carboxylic acid as a foreign material, a stable salt is formed between the carboxylic acid and the potassium cation. And then, the active oxide anion of **1** becomes an alcoholic hydroxyl group to get deactivated. This hydroxyl group could not nucleophilically attack epoxy monomers any longer, and that results in the termination of anionic polymerization.

On the other hand, we have ascertained that some acidic compounds adhere to the surface of carbon fibers through another investigation. This fact is consistent with that an emulsion consisting of an epoxy resin and a carboxylic acid is usually used as a sizing agent for carbon fibers.

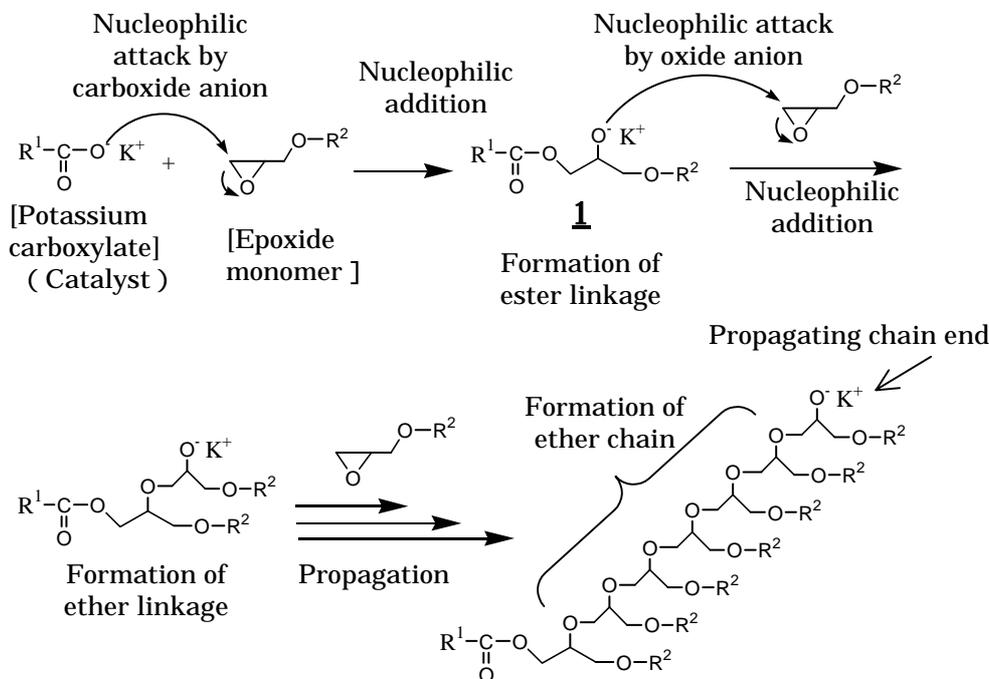


Fig. 1 Polymerization mechanism of T_g -less epoxy resin catalyzed by potassium carboxylate.

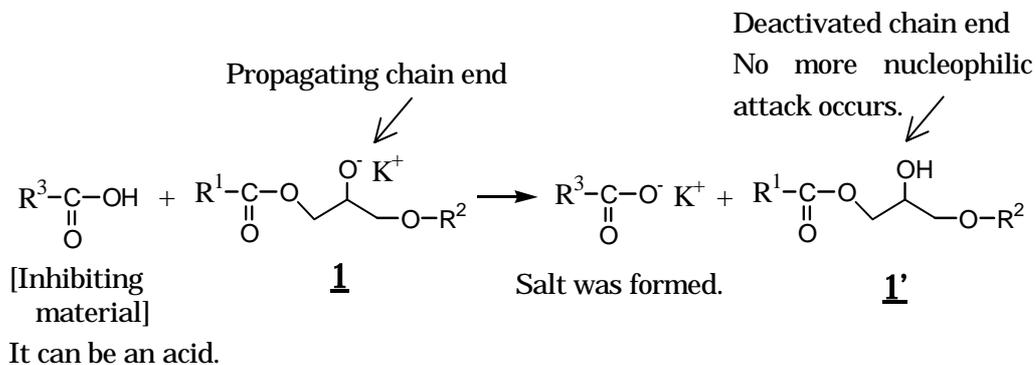


Fig. 2 Inhibition mechanism of polymerization of T_g -less epoxy resin by acids.

Therefore, it is very likely that the acidic compounds adhering to the surface of carbon fibers inhibit the curing of T_g -less epoxy resin based on anionic polymerization when a CFRP is manufactured by using T_g -less epoxy resin and carbon fiber fabrics.

3 Experimental methods

In this section, the matrix resin used for the FRPs, preparation methods of the FRPs, and the procedures for some characteristic evaluations of the FRPs are described.

3.1 Matrix resin

Liquid uncured T_g -less epoxy resin (viscosity 80 mPa·s at 80 °C, prepared based on the previous report [2]) was used as the matrix resin. Fig.3 shows the dependence viscosity of T_g -less epoxy resin on temperature. The gel time is shown in Fig.4. As these data indicate, T_g -less Epoxy Resin is low-viscosity of less than 100mPa·s even if heating at 80 °C. Additionally, it has long pot life of more than 100min at 80 °C. Therefore, we think that this T_g -less epoxy resin is applicable to various molding methods, such as Resin Transfer Molding (RTM).

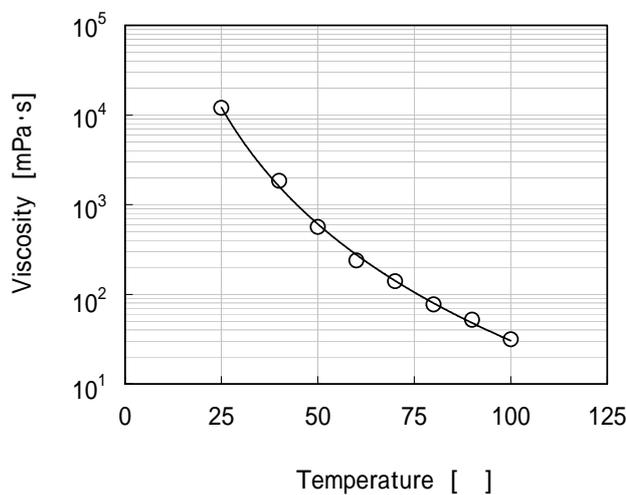


Fig.3 Viscosity of T_g -less Epoxy Resin

Carbon fiber fabric (TORAYCA CO6347 made by Toray Industries Inc.) and glass fiber fabric (Glass Cloth WF230 made by Nitto Boseki Co., Ltd.) were used as the reinforcements. The specification for each fiber fabric is shown in Table 1.

3.2 Preparation of FRP

The prepreg was prepared by the following method. In order to examine the different surface treatments of reinforcing fibers, two types of GFRP specimens and five types of CFRP were prepared. They are listed in Table 2. In the specimen of No.4, the carbon cloth was soaked in acetone for two days in order to wash the sizing agent off from the surface of the carbon fibers prior to impregnation of T_g -less epoxy resin. In the specimens of No.5~7, the carbon cloths were passed through alkali solution in 30 seconds in order to neutralize carboxylic acid of the sizing agent covering on the carbon fibers prior to impregnation of T_g -less epoxy resin.

In addition, the prepreg was pressed at 180 °C for 2 hours under the pressure of 1.0 MPa by using the plane metal mold, and fiber content (V_f), which was determined from the weight content and the specific gravity of T_g -less epoxy resin, was 43-44 vol%. The numbers of the plies of the FRPs were 9 or 11 (see Table 1).

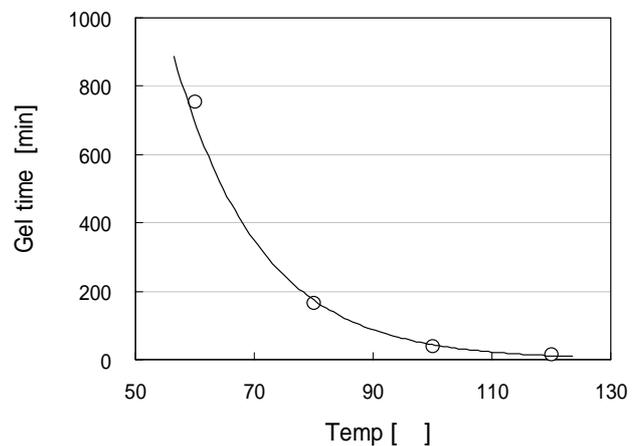


Fig.4 Gel time of T_g -less Epoxy Resin

Table1 Specification of the fiber fabrics

Test piece	Reinforcements			Content of reinforcement	Number of plies	Thickness (mm)
	Weave	Weight (g/m ²)				
CFRP	Carbon fiber fabric TORAYCA CO6347	2x2Twill	198	44	9	2
GFRP	Glass Cloth WF230	Plain	203	43	11	2

The molding process of T_g -less FRPs is shown in Fig.5. T_g -less FRPs could be molded by using the same process as in the case of molding an ordinary FRP. Therefore, it is considered that any additional costs are not necessary for the molding of T_g -less FRPs.

Table 2 Specification of test specimens

	Reinforcing fiber	Coupling agent	Acetone wash	Alkali treatment
No.1	Glass fiber	Epoxy-silane	-	-
No.2	Glass fiber	Amino-silane	-	-
No.3	Carbon fiber	-	none	none
No.4	Carbon fiber	-	2days	none
No.5	Carbon fiber	-	none	1%
No.6	Carbon fiber	-	none	0.1%
No.7	Carbon fiber	-	none	0.02%

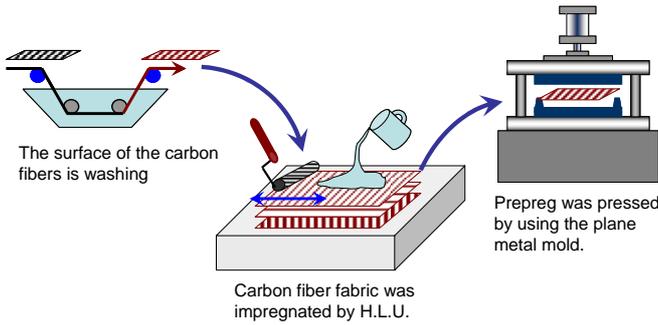


Fig.5 Molding process of T_g -less FRPs

3.3 Characteristics of the FRPs

3.3.1 Bending strength and modulus

To characterize the obtained T_g -less FRPs, we carried out three-point bending tests by using a universal test machine (autograph AG-I made by Shimadzu Co. Ltd.) with a heat chamber based on JIS K7198. The specimens were 2mm thickness, 15mm width, and the test span was 80mm. The crosshead speed was set to 5mm/min and the testing temperatures were room temperature (about 25 °C), 100, 150, 200, 250 and 300 °C. The specimens were held at each testing temperature for 30 minutes before the start of test.

The bending stress (σ_b) and bending modulus (E_b) were calculated from the following equations:

$$\sigma_b = \frac{3P_{\max}L}{2bh^2} \quad (1)$$

$$E_b = \frac{L^3}{4bh^3} \left(\frac{P}{\delta} \right) \quad (2)$$

,where P_{\max} is the maximum load, and P/δ is an initial gradient of the test load-displacement curve.

3.3.2 Dynamic viscoelasticity

The dynamic viscoelastic properties were measured under the air atmosphere from room temperature to 300 °C (2 °C/min) by using a DMS (EXSTAR6000; Seiko Instruments Inc.). The 3-point bending method was adopted and the distance (L) between supports was 40 mm, and the frequency was 1 Hz. The dimensions of the test piece were (b) 10 mm width, (l) 60 mm length and (t) 2 mm thick. The R , which is defined as the ratio of the storage modulus at 250 °C to that at 25 °C was obtained according the following equations:

$$R = \frac{E'_{250}}{E'_{25}} \times 100 \quad [\%] \quad (3)$$

,where E'_{25} and E'_{250} are the storage modulus at 25 °C and that at 250 °C, respectively.

3.3.3 Immersion tests

The resistance to acid and alkali of T_g -less FRPs were evaluated through the immersion tests. The test pieces were immersed into 10% sodium hydroxide solution or 10% sulfuric acid at room temperature. The dimensions of the test pieces were 15 mm width, 15 mm length and 2 mm thickness.

The W_R , which is the rate of weight change, was calculated from the following equation:

$$W_R = \frac{(W - W_{\text{initial}})}{W_{\text{initial}}} \times 100 \quad [\%] \quad (4)$$

,where W_{initial} and W are the weight of test pieces before and after immersion, respectively. The tests were carried out up to 110 days.

3.3.4 Creep test

The long-term heat-resistant property was evaluated through the bending creep tests. The dimensions of the test pieces were 15 mm width,

100 mm length and 2 mm thickness. The tests were carried out at room temperature (about 25 °C), 100, 170 and 200 °C by using a creep testing machine (CP5-L-200 type made by Orientic Co., Ltd.). The 3-point bending method was adopted and the distance (L) between supports was 80 mm. The test load (F) was 10% of the bending strength at room temperature (about 25 °C) in each test pieces. The bending stress (σ_b) and the creep strain (ε_t) were calculated from Equation 1 and:

$$\varepsilon_t = \frac{6d_t h}{L^2} \quad (5)$$

$$D_c = \frac{\varepsilon_t}{\sigma_b} \quad (6)$$

,where F and d_t are the test load and creep deflection, respectively. The tests were carried out from 10 seconds to 100 hours, and the displacement of the load point was recorded.

4 Results and discussions

4.1 The state of impregnation

Fig. 6 shows a SEM observation of the cross section of T_g-less CFRP using the carbon fiber fabrics treated with 0.02% alkali solution (No.7). Voids or unfilled parts were hardly observed in the cross section of T_g-less CFRP, and that seemed to be attributed to the low viscosity of T_g-less epoxy resin before curing. The states of impregnation of T_g-less CFRPs (No.3, No4 and No.6) were excellent as well as No.7.

However, in the cross section of T_g-less CFRP using the carbon fiber fabrics treated with 1.0% alkali solution (No.5), a lot of bubble-shaped parts were observed in the interface between the fiber and resin. The constituent of the parts was measured by elemental analysis using EDS (Energy Dispersive X-ray Spectrometer). Fig. 7 shows the SEM observation and elemental analysis result for the cross section of No.5. As shown in Fig. 7, the EDS chart of the bubble-shaped parts clearly indicated the existence of potassium. That means the excess potassium hydroxide deposited in the interface between the fiber and resin. The weakened bonding strength of the CFRP (No.5), discussed in 4.2, is considered a cause of this deposited potassium hydroxide. This result shows that the maximum concentration of an acceptable potassium hydroxide solution might be lower than 0.1%

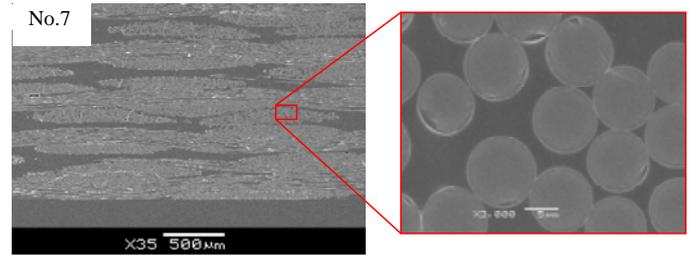


Fig.6 SEM observation of cross section (No.7)

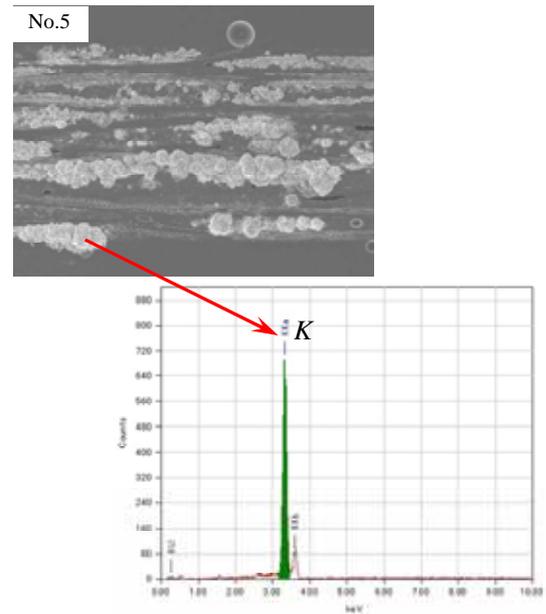


Fig.7 SEM observation of cross section (No.5) and EDS for the bubble-shaped part

4.2 Bending strength and modulus

The results of three point bending test at higher temperatures are shown in Fig.8 and Fig.9. The all of bending moduli at 300 maintained more than about 80% of that at room temperature except in No.5. The GFRP and CFRP using T_g-less epoxy resin as the matrices exhibited high potential of flexural rigidity even at elevated temperature. However, the bending strength tended to become lower as temperature increased.

In the case of CFRP, some differences in bending properties were observed. The strength of No.3 specimen using the untreated carbon fiber fabrics dropped over the temperature of 100 . On the contrary, the strength of No.4 specimen using the carbon fiber fabrics washed with acetone gradually dropped with an increase of the temperature. As an easier method, No.6 and No.7 specimens using the carbon fiber fabrics treated with alkali solution also exhibited the higher strength holding rate at the

elevated temperatures. From the result of the bending test, the treatment of the carbon fiber surface is important. The reduction of the bending strength depending on the different treatment is considered to connect with the sizing agent covering on the carbon fibers. The sizing agent for carbon fibers generally includes carboxylic acid. This acid is likely to inhibit the anionic polymerization of T_g -less epoxy resin on the interfacial surface of the carbon fibers, as described above. Therefore the washing or neutralization of the sizing agent on the carbon fibers was effective. However, too dense alkali solution brought about a reverse effect. The white powder of alkali deposited on the surface of the carbon fibers, or a lot of bubble-shaped parts were formed in the interface between the fiber and resin in the case of the treatment with 1% alkali solution. That should make the bending strength of CFRP lower.

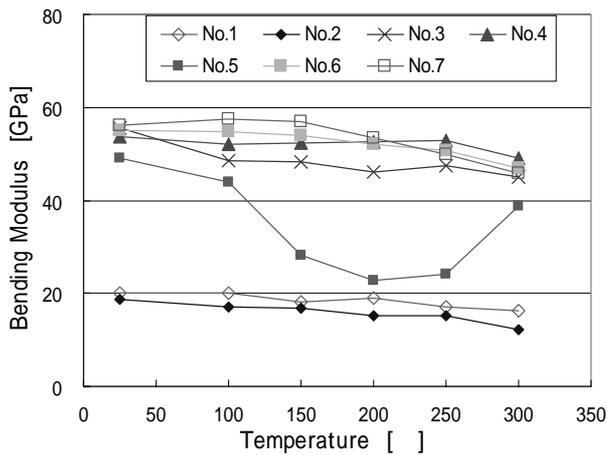


Fig. 8 The temperature dependences of flexural moduli for the various CFRPs

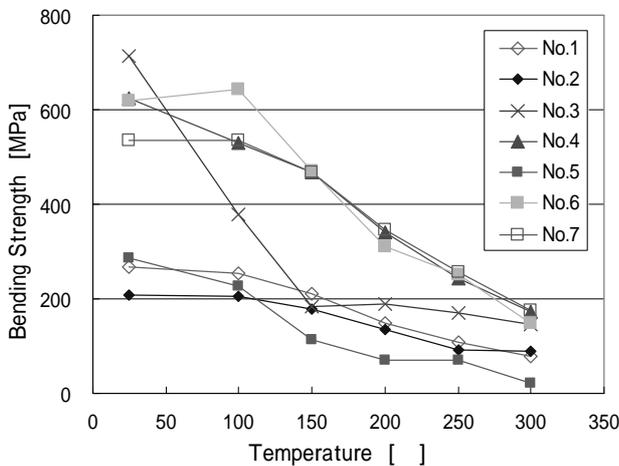


Fig. 9 The temperature dependences of bending strength for the various CFRPs

4.3 Dynamic viscoelasticity

Dynamic viscoelasticities of CFRPs (No.3 ~ No.7) are shown in Fig.10. The storage modulus (E') and the $\tan \delta (=E''/E')$ were almost constant up to 300 °C except in No.5. The storage modulus (E') of No.3 was decreased with increasing temperature. This could be caused by unpolymerized interfacial surface of the carbon fibers, which would relate to the low bending strength and modulus of No.5.

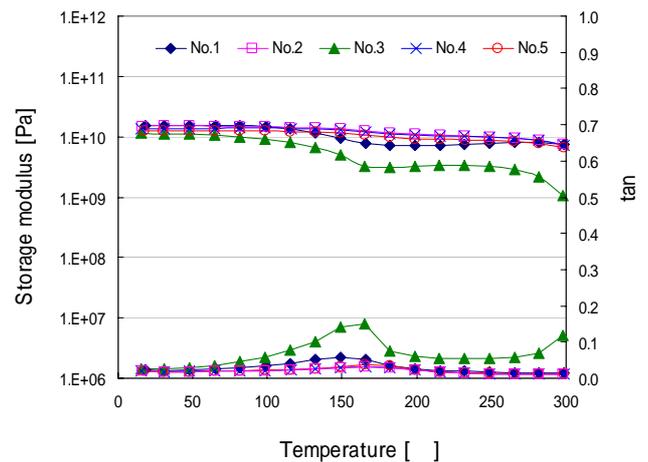


Fig.10 Dynamic viscoelastic behavior of the various CFRPs

Table 3 R value and peak of tan

	No.3	No.4	No.5	No.6	No.7
R [%]	49.9	66.8	27.7	71.7	68.6
tan (max.)	0.0592	0.0328	0.1702	0.0323	0.0396

4.4 Immersion tests

The resistance to acid and alkali of CFRP using the carbon fiber fabrics treated with 0.02% alkali solution (No.7) are shown in Fig.11. In this figure, no more change in the weight of test pieces was observed after immersion for 1 week. That suggest that any hydrolysis caused by acid or alkali did not occur in the resin matrix during the immersion. So, it is concluded that the CFRP (No.7) has excellent corrosion resistance to both acid and alkali. This could be caused by the fact that the cured T_g -less resin consists of only aromatic backbones and alkyl ether linkages forming cross-linking networks that cannot be subject to hydrolysis by acid or alkali.

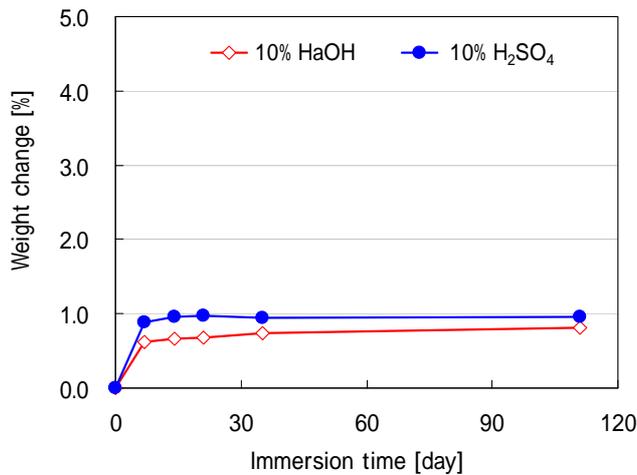


Fig.11 Immersion test results

4.5 Creep test

The results of the bending creep tests for the CFRP (No.7) at room temperature (about 25 °C), 100, 170 and 200 °C are shown in Fig.12. Any creep did not occurred at room temperature (about 25 °C), 100, 170, but did at 200 °C. The increase in creep compliance during the aging at 200 °C may be caused by pyrolysis of T_g-less epoxy resin because the dynamic viscoelastic tests have clarified that T_g-less CFRP exhibited extremely few viscosity properties even at that high temperature such as 200 °C.

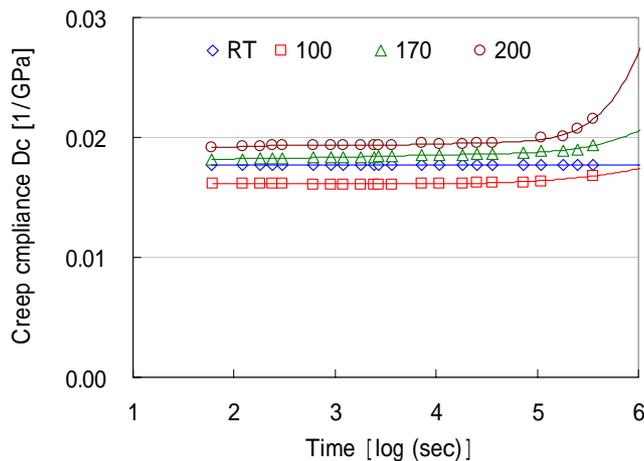


Fig.12 Changes in creep compliance for the CFRP (No.7) at room temperature and higher temperatures

5 Conclusions

T_g-less epoxy resin could be used as the matrices of both GFRP and CFRP by using the same molding process as in the case of an ordinary FRP.

The bending moduli of the T_g-less FRPs at 300 °C maintained more than approximately 80% of that at room temperature. In the case of CFRP, the surface treatment of the carbon cloth with thin alkali solution was an easier treatment and showed the most effective for maintaining the bending strength at the higher temperature.

The results of the bending creep tests suggested that creep compliance of T_g-less CFRP began to increase above 170 °C. This increase in creep compliance may be caused by pyrolysis of T_g-less epoxy resin. Therefore, the investigation to improve the long-term heat-resistant property or anti-pyrolysis property of T_g-less resin should be performed for the next step.

References

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