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Muneaki Yamaguchi <sup>a</sup> , Yuko Tanaka <sup>b</sup> & Katsutoshi Tanaka <sup>c</sup>

<sup>a</sup> Osaka National Research Institute, AIST 1-8, Midorigaoka, Ikeda, Osaka 563, Japan

<sup>b</sup> Osaka National Research Institute, AIST 1-8, Midorigaoka, Ikeda, Osaka 563, Japan

<sup>c</sup> Osaka National Research Institute, AIST 1-8, Midorigaoka, Ikeda, Osaka 563, Japan

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## Effects of coupling agents on dynamic mechanical properties of aged and wet multi-functional epoxy resins cured with acid anhydrides and filled with pitch based carbon short fibers treated with coupling agents

MUNEAKI YAMAGUCHI, YUKO TANAKA and KATSUTOSHI TANAKA

*Osaka National Research Institute, AIST 1-8, Midorigaoka, Ikeda, Osaka 563, Japan*

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**Abstract**—Pitch-based carbon short fibers (PCF) as functional fillers were treated with five types of coupling agents (CA) and were filled with multi-functional epoxy resin (EP) cured with three types of acid anhydrides at 22.2 wt%. The influence of aging and wetting on the dynamic mechanical properties was studied by use of a non-resonant forced-vibration method. The samples were aged at 130°C for 5000 h or wetted in distilled water at 21°C for 5000 h. The longer the aging time, the larger the weight reduction of the aged specimens: the maximum value was 3.6 wt% for 5000 h. The glass transition temperature ( $T_g$ ) for the CA-treated specimens dropped more compared with the untreated specimens (UA). Although CA on the surfaces of PCF was lost by aging, the storage modulus ( $E'$ ) increased at a lower temperature  $-140^\circ\text{C}$  and decreased at higher temperatures (over  $200^\circ\text{C}$ ). The maximum water absorption rate for the wetted specimens was 2.3 wt% and the decrease of  $T_g$  was similar to that for the UA specimens. The value of  $E'$  increased at lower temperatures but decreased at higher temperatures. The influence by both aging and wetting on the mechanical dynamic properties was similar even though the mechanism for each is different.

**Keywords:** Multi-functional epoxy resin; pitch-based carbon short fiber; coupling agent; composite materials; aging and wetting; dynamic mechanical properties.

### 1. INTRODUCTION

The authors have been investigating the filling effect of pitch-based carbon short fibers [1, 2] as functional fibers on the mechanical dynamic properties. All the short fibers filled with polyvinylchloride (PVC) resin with roll mixing and press molding were all broken during the roll mixing but were aligned in the machine direction [3, 4]. The effect of coupling agents for short fibers was also investigated [4].

When multi-functional epoxy resin [5] was chosen as a matrix and cured after mixing with short fibers, these short fibers were not broken [6]. A difference

due to the type of hardeners in affinity between the epoxy resin and short fibers was observed. When short fibers were treated with coupling agents [7], the affinity with epoxy resin increased and the dynamic mechanical properties were also improved [8, 9].

Water-resistance and heat-resistance of short fiber filled multi-functional epoxy resin have been evaluated by measuring the dynamic mechanical properties through aging for up to 5000 h and wetting for 5000 h. The relationship between the state change and the dynamic mechanical properties by aging and wetting was reported previously for matrices (multi-functional epoxy resin) [10] and for materials filled with pitch-based carbon and graphite short fibers [11]. A similar study for materials filled with Aramid short fiber of length 1 mm was also reported [12, 13].

In this paper, multi-functional epoxy resin cured with three types of acid anhydrides filled with pitch-based carbon short fibers at 22.2 wt% treated with five types of coupling agents was aged at 130°C for 5000 h and wetted at 21°C for 5000 h and its dynamic mechanical properties were investigated over a wide temperature range of -150 to +300°C. The results were compared with materials filled with short fibers that were untreated with coupling agents [11] and matrices [10] and the utility of the materials were also evaluated.

## 2. EXPERIMENTAL

### 2.1. Materials

Three types of multi-functional epoxy resin (Table 1) used in the previous reports [6, 8–13] mixed with three types of acid anhydride hardeners (Table 2) were used as matrices (Table 3). As fillers, pitch-based carbon short fibers (abbreviated as PCF, manufactured by Kureha Chemical Inc., Kureha Chop® M-102S) used in the previous reports [6, 8, 9, 11] with a length of 200  $\mu\text{m}$  and a diameter of 11.7  $\mu\text{m}$  were used that had been dried at 105°C/2 h before their usage.

Five types of coupling agents (abbreviated as CA) used in the previous report [8] (Table 4) were also employed. PCF was dipped in 1% tetrahydrofuran (THF) solution of CA for 48 h and was dried at 80°C/48 h after filtering. CA-treated PCF with 22.2 wt% (volume fraction of about 0.18 estimated from the specific gravity of the matrices [12]) was then filled and mixed. Specimens were placed in vessels made of silicone rubber after mixing and degassed under reduced pressure and were heated (Table 3).

Obtained molded plates of 70  $\times$  80 mm<sup>2</sup> and a thickness of 5–6 mm (for naming convention, EP · C cured with a hardener, A, and filled with SG-treated PCF is denoted as EP · C-A-SG) were machined on all the surfaces in order to remove the influence of skin layers [14] and specimens of a thickness of 3 mm, a width of 4 mm and a length of 70–80 mm were made. The specimens were then annealed at 80°C/48 h in order to remove residual strains [6, 8–13].

Processing of the aging and wetting of specimens in order to evaluate heat-resistance and water-resistance was carried out in a manner similar to the previous

**Table 1.**  
Multi-functional epoxy resins

Code	Chemical structure
EP · C	Tetraglycidyl-1,3-bisaminomethylcyclohexane (Tetrad C) <sup>a</sup>
EP · L	Tetraglycidyl-diamino-diphenylmethane (Epikote 604) <sup>b</sup>
EP · Y	Triglycidyl- <i>p</i> -aminophenol (Epikote YX-4) <sup>b</sup>

<sup>a</sup> Supplied by Mitsubishi Gas Chemical Inc.

<sup>b</sup> Supplied by Yuka Shell Epoxy Inc.

**Table 2.**  
Hardeners

Code	Chemical structure
A	1,2-Cyclohexane dicarboxylic anhydride (HHPA)
B	Hexahydro-4-methylphthalic anhydride (MHPA)
C	Methylnadic anhydride (MNA)

**Table 3.**  
Curing conditions

Epoxy resin	Component of hardener (phr)			Curing condition
	A	B	C	
EP · C	134	146	154	Room temp./14 h + 90°C/2 h + 120°C/2 h + 180°C/2 h
EP · L	104 <sup>a</sup>	114 <sup>a</sup>	120 <sup>a</sup>	Room temp./14 h + 100°C/2 h + 180°C/4 h
EP · Y	139 <sup>a</sup>	—	160 <sup>a</sup>	Room temp./14 h + 100°C/2 h + 180°C/4 h

<sup>a</sup> Added N,N'-dimethylbenzylamine by 1 phr as accelerator.

**Table 4.**  
Coupling agents

Code	Chemical structure
SB	N-Benzyl- $\gamma$ -aminopropyl trimethoxysilane (X-12-512) <sup>a</sup>
SG	$\gamma$ -Glycidoxypopyl trimethoxysilane (KBM-403) <sup>a</sup>
SP	N-Phenyl- $\gamma$ -aminopropyl trimethoxysilane (KBM-573) <sup>a</sup>
AL	Alkyl 3-oxobutanoate aluminium diisopropoxide (AL-M) <sup>b</sup>
TA	Isopropyl tri(N- $\beta$ -aminoethyl- $\beta$ -aminoethyl) titanate (KR-44) <sup>b</sup>

<sup>a</sup> Supplied by Shin-Etsu Chemical Co., Ltd.

<sup>b</sup> Supplied by Ajinomoto Co., Inc.

reports [10, 11, 13]. For aging, a gear oven was used at 130°C for up to 5000 h. For wetting, the specimens were immersed in distilled water to remove air attached to the specimens by degassing and were kept at 21°C under atmospheric pressure

for 5000 h. Change of weight for the specimens due to the treatment was calculated from the difference in weight before and after the treatment.

## 2.2. Measurements

Similar to the previous reports [6, 8–13], the dynamic mechanical properties were measured by a Rheovibron DDV-25FP (manufactured by Orientec Inc.). The measuring conditions were: distance between clamps, 52 mm; frequency of 110 Hz; amplitude of  $\pm 10\ \mu\text{m}$ ; heating rate of  $2^\circ\text{C}/\text{min}$ ; temperature range of  $-150$  to  $+300^\circ\text{C}$  with a temperature interval of measuring of  $5^\circ\text{C}$ . An SEM (a JEM-5200 manufactured by Nihon Electron, Inc.) was used to observe the surface and dispersion states of short fibers before and after the aging.

## 3. RESULTS

### 3.1. Dispersion state of carbon short fibers

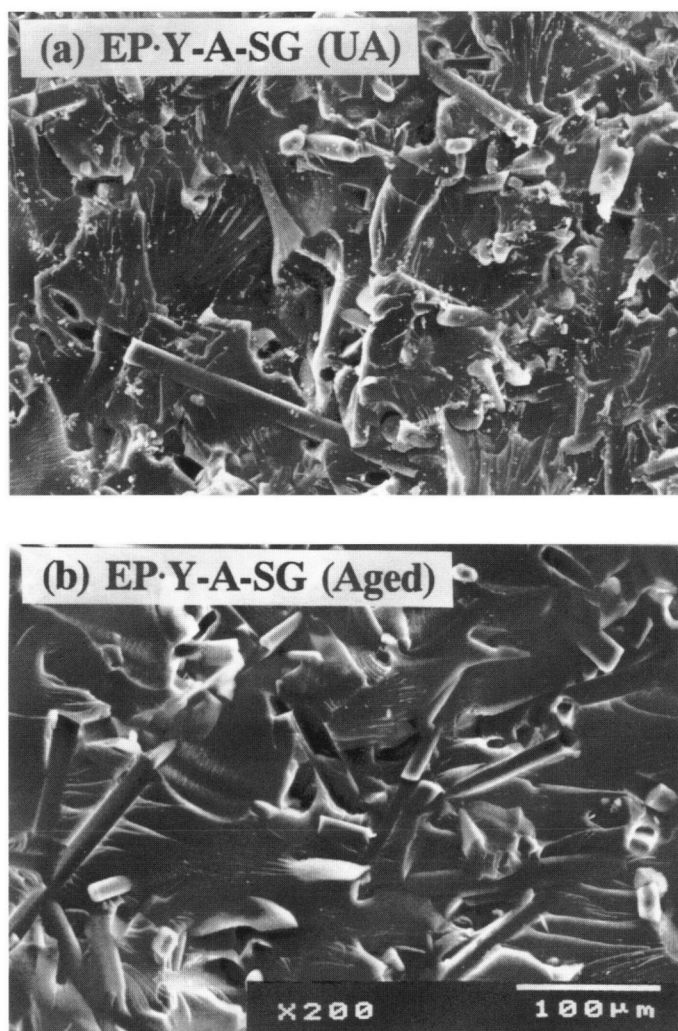
Figure 1 shows SEM photographs of the fractured surfaces of specimens filled with CA-treated PCF after washing. The short fibers in the unaged specimens of EP-Y-A-SG (UA, 0 h, specimens (Fig. 1a) were randomly distributed and the dispersion state did not change after 5000 h of aging (Fig. 1b)) but the EP surface became smoother. A similar tendency for the short fibers in other specimens filled with CA-treated PCF was observed before and after aging.

Figure 2 shows an SEM photograph of the fractured surface of PCF before and after aging. Many pieces of EP were left on the UA specimens surface but the number of EP specimens decreased after aging. The influence by CA and hardeners was small. A similar tendency was observed for the specimens filled with CA-untreated PCF (UT) before and after aging [11].

### 3.2. Influence of aging

**3.2.1. Weight change of samples due to aging.** Table 5 shows decreasing of weight of all the specimens that were aged for 5000 h. The weight decrease rate for these specimens decreased linearly for up to 5000 h over the range of 1.9–3.6 wt%. The values for many CA-treated specimens were larger than those for UT specimens which were 1.3–2.5 wt% [11] and some were more than doubled depending on the combination of EP and hardeners. The values for the specimen treated with Si-based CAs were about the same as those for the specimen treated with AL- and TA-based CA for tetra-functional EP but were smaller for tri-functional EP. The values for the matrices were 1.1–2.8 wt% [10] which were about the same as those for UT specimens.

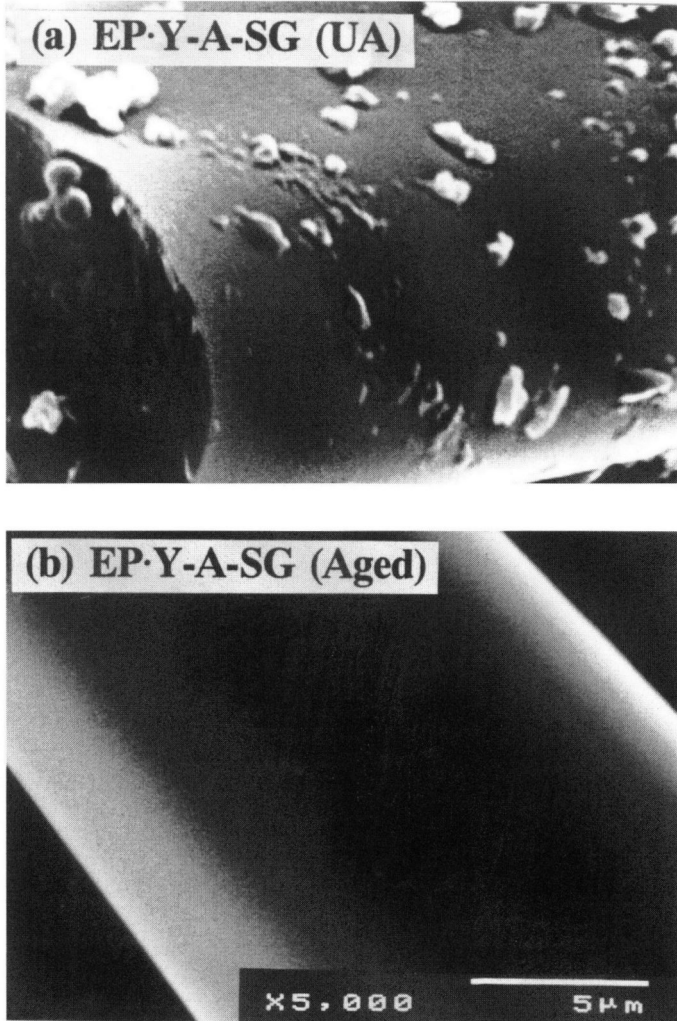
**3.2.2. Temperature dependence of dynamic mechanical properties.** Figure 3 shows the temperature dependence of the storage modulus ( $E'$ ) and  $\tan \delta$  for



**Figure 1.** SEM photographs of fractured surface of EP·Y-A-SG: (a) unaged; (b) aged for 5000 h.

EP·C-A-SG aged for 5000 h. The values of  $E'$  increased more compared with the UA specimens over the temperature range from low to 150°C but they decreased in the higher temperature region. The  $\alpha$ -peak in the high temperature region which indicates the glass transition temperature ( $T_{ga}$ ) of the  $\tan \delta$  curve was shifted to the lower temperature (decreasing) and the lower temperature side became broader. The large broad  $\beta$ -peak of about -20°C spread on the lower temperature side. For other specimens, the values of  $E'$  for EP·L-A-AL were small over the whole temperature range. The shift of  $\alpha$ -peak temperature ( $T_{ga}$ ) for the  $\tan \delta$  curve was small.

Such behavior is due to the fact that disorder of molecular arrangement and unreacted parts disappeared by aging [10, 11, 13] and the temperature dependence of  $E'$  and  $\tan \delta$  for other specimens showed a similar tendency. Such behavior was



**Figure 2.** SEM photographs of surface of CA-treated PCF fibers of EP · Y-A-SG: (a) unaged; (b) aged for 5000 h.

also observed in the previously reported UT specimens [11], the matrices [10] and the AFP filled specimens [13].

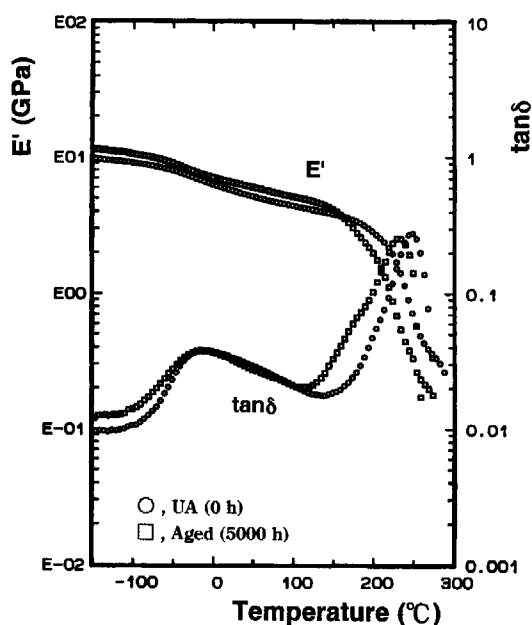
Table 6 shows the difference ( $dT_{ga}$ ) of  $T_g$  between aged specimens for 5000 h ( $T_{ga}(5000)$ ) and UA specimens ( $T_g(0)$ ). The values of  $dT_{ga}$  were in the range of  $-20.0$  to  $-3.5^\circ\text{C}$  and the values of  $T_{ga}(5000)$  for all the specimens were below those for the UA specimens. The decrease in temperature for TA-treated specimen was smaller than those for three types of Si-based CA- and AL-treated specimens. The values  $dT_{ga}$  for the UT specimens [11] were in the range of  $1.0$  to  $-8.5^\circ\text{C}$  and the values for the matrices were  $1.5$ – $8.5^\circ\text{C}$ , all of which increased over a wide range.



**Table 5.**

Decrease of weight (%) of specimens after aging at 130°C for 5000 h

Epoxy resin	Hardener	Coupling agent					
		UT <sup>a</sup>	SP	SG	SP	AL	TA
EP · C	HHPA	2.5	2.8	2.8	3.4	3.0	2.2
	MHPA	1.3	3.5	3.6	3.5	3.6	2.9
	MNA	2.3	3.6	2.5	2.7	2.7	2.6
EP · L	HHPA	1.3	2.1	2.3	2.6	2.3	2.7
	MHPA	1.7	2.8	2.5	2.1	2.4	2.5
	MNA	1.4	—	2.4	—	2.5	—
EP · Y	HHPA	1.4	1.9	2.6	2.5	2.9	3.0
	MNA	1.8	—	2.8	2.5	2.8	2.9

<sup>a</sup> CA-untreated specimen.**Figure 3.** Temperature dependence of dynamic storage modulus ( $E'$ ) and  $\tan \delta$  of unaged and aged EP · C-A-SG specimens.

**3.2.3. Storage modulus.** Figures 4a and b show the ratios of  $E'$  for A- and C-cured specimens to  $E'$  for UA specimens ( $E'_{a,CA}(5000)/E'_{CA}(0)$ ). The values of  $E'_{a,CA}(5000)/E'_{CA}(0)$  were 1.0–1.1 at low temperature ( $-140^{\circ}\text{C}$ ) which were larger than those for the UA specimens (similarly for the B-cured specimens not shown in the figure) and were 0.9–1.1 at room temperature ( $25^{\circ}\text{C}$ ) which were about the same as the UA specimens. At a higher temperature ( $200^{\circ}\text{C}$ ), the values for most specimens were 0.4–0.7 but the values for the EP · C-C specimens

**Table 6.**  
Effect of aging for 5000 h on  $dT_{ga} (T_{ga}(5000) - T_g(0))$  (°C) of CA-treated PCF-filled specimens

Epoxy resin	Hardener	Coupling agent					
		UT <sup>a</sup>	SP	SG	SP	AL	TA
EP · C	HHPA	3.5	−7.5	−13.5	−13.0	−8.0	−4.5
	MHPA	1.5	−11.0	−16.5	−19.0	−15.0	−8.5
	MNA	4.0	−6.0	−5.0	−5.5	−6.5	−3.5
EP · L	HHPA	3.0	−17.5	−17.0	−16.5	−17.5	−20.0
	MHPA	1.0	−11.5	—	−9.0	−11.5	−9.0
	MNA	2.5	—	−15.5	—	−18.0	—
EP · Y	HHPA	2.0	−11.0	−10.5	−14.5	−13.0	−6.5
	MNA	8.5	—	−7.0	−9.0	—	−5.5

<sup>a</sup> CA-untreated specimen.

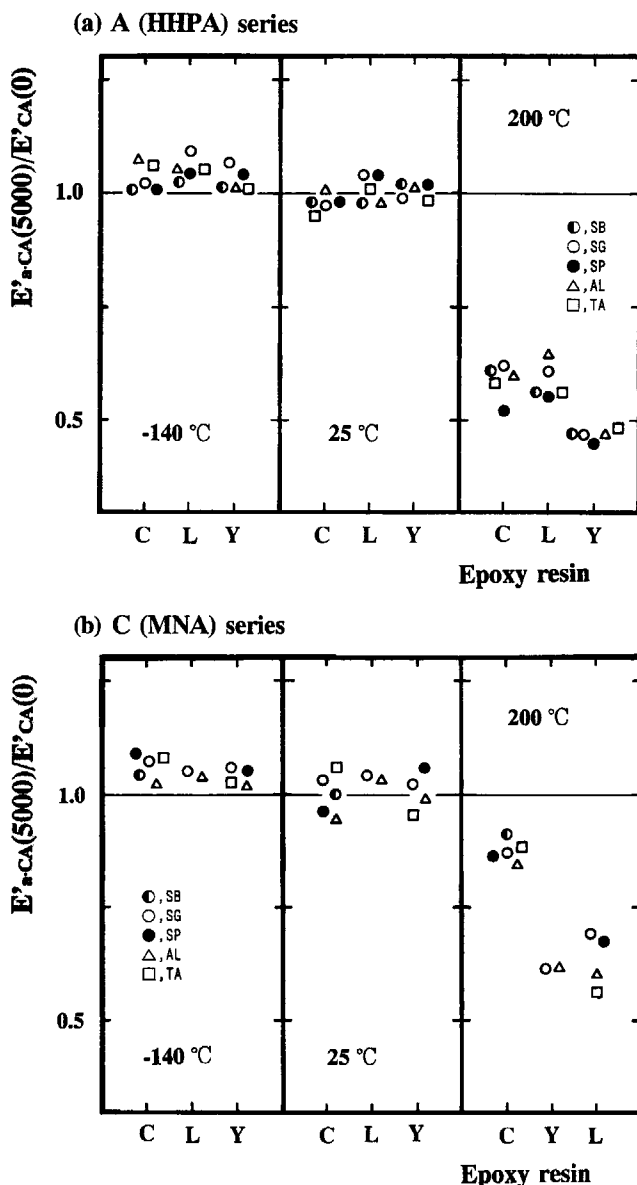
(Fig. 4b) were as large as 0.8–0.9. However, the difference due to the type of CA for all the specimens was small.

*3.2.4. Comparison with storage modulus of matrix.* Figure 5 shows the ratios of  $E'$  for the specimen aged for 5000 h to  $E'$  for the matrix at 25°C ( $E'_{a,CA}(5000)/E'_{a,MAT}(5000)$ ). The values for the CA-treated specimens were 1.2–1.7, which were smaller than those for the UT specimens. The difference among different CA types was small but the values for the silane SG-treated specimens with epoxy groups at the end of molecular were larger than those for the CA-treated specimens with other groups. For the effect of hardeners, the A-cured specimen was more influenced than B- and C-cured specimens.

*3.3. Influence of wetting*

*3.3.1. Weight change of samples due to wetting.* Table 7 shows the water absorption rates for all the specimens which were wetted for 5000 h. The water absorption rates of the specimens were in the range of 1.0–2.3 wt% and the values for tetra-functional EP · C were large while the values for B-cured specimens and TA-treated specimens were smaller. These values were smaller than those for the UT specimens [11] of 1.3–3.7 wt% and the matrices [10] of 1.2–3.0 wt%.

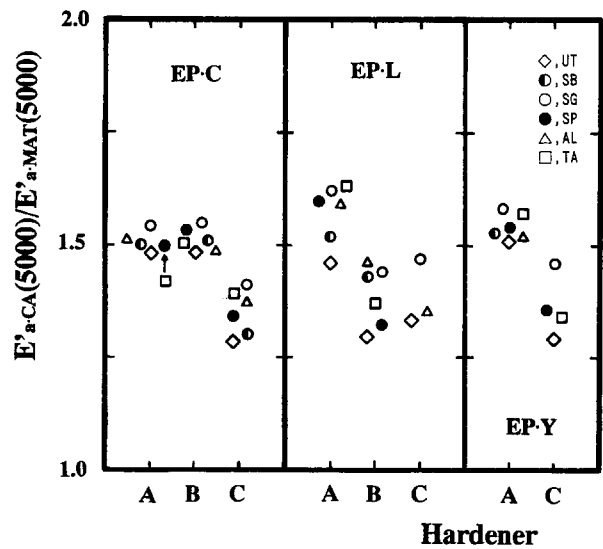
*3.3.2. Temperature dependence of dynamic mechanical properties.* Figure 6 shows the temperature dependence of  $E'$  and  $\tan \delta$  for EP · Y-A-TA which was wetted for 5000 h. The values of  $E'$  slightly increased at lower temperatures but the decrease above room temperatures and especially in the high temperature range was very significant. The  $\alpha$  ( $\alpha'$ )-peak of the  $\tan \delta$  curve was shifted to the low temperature side and a large shoulder ( $\alpha''$ -peak) appeared on the low temperature side [10, 11, 13]. The  $\beta$ -peak at low temperature increased on the low temperature



**Figure 4.** Ratios of dynamic storage modulus ( $E'$ ) of CA-treated PCF filled specimens aged for 5000 h ( $E'_{a \cdot CA}(5000)$ ) and unaged specimens (UA,  $E'_{a \cdot CA}(0)$ ): (a) A (HHPA) series; (b) C (MNA) series.

side as well. In some of the  $\tan \delta$  curves for other specimens, the  $\alpha$ -peak shifted to the low temperature side. Similar behavior was also observed in the UT specimens [11], the matrices [10] and the AFP filled specimens [13].

Table 8 shows the difference of  $T_g$  ( $dT_{gw}$ ) between the wetted specimens for 5000 h and the UA specimens. The values of  $dT_{gw}$  were  $-21.5$  to  $-3.5^\circ\text{C}$  which



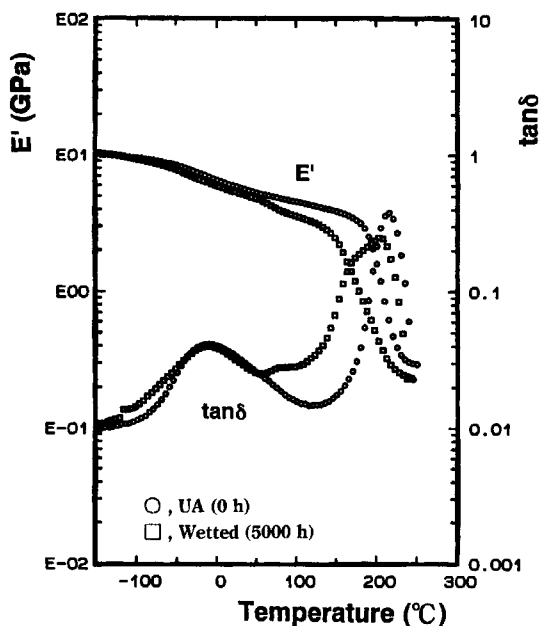
**Figure 5.** Ratios of dynamic storage modulus ( $E'$ ) of CA-treated PCF filled specimens and those of matrices aged for 5000 h,  $E'_{a-CA}(5000)/E'_{a-MAT}(5000)$  at 25 °C.

**Table 7.**  
Absorption of water (%) of specimens at 21 °C for 5000 h

Epoxy resin	Hardener	Coupling agent					
		UA <sup>a</sup>	SP	SG	SP	AL	TA
EP · C	HHPA	3.6	2.0	1.9	1.7	1.9	1.0
	MHPA	3.7	1.3	1.3	1.3	1.3	1.3
	MNA	2.3	1.4	1.6	1.8	1.8	2.3
EP · L	HHPA	1.3	2.1	1.8	1.7	1.9	1.6
	MHPA	2.2	1.3	1.5	1.4	1.6	1.3
	MNA	1.4	—	1.4	—	1.6	—
EP · Y	HHPA	3.1	2.2	2.2	2.1	2.1	2.1
	MNA	3.4	—	1.9	1.9	1.9	1.5

<sup>a</sup> CA-untreated specimen.

were similar to  $dT_{ga}$  for the aged specimens. The decrease was significant for specimens with  $\alpha$ -peaks or shoulders. Although the difference among different CA types was small, the values were particularly small for B-cured specimens. The influence by the types of EP was very evident and the decrease for tri-functional EP was larger than that for tetra-functional EP. The values of  $dT_{gw}$  for the UT specimens were in the range of  $-9.0$  to  $-1.0$  °C [11] and the values for the matrices were in the range of  $-9.5$  to  $-2.5$  °C [10], which implies that the decrease of temperature was small but all the specimens showed decrease.



**Figure 6.** Temperature dependence of dynamic storage modulus ( $E'$ ) and  $\tan \delta$  of unaged and wetted EP·Y-A-TA specimens.

**Table 8.**

Effect of wetting for 5000 h on  $dT_{gw}$  ( $T_{gw}(5000) - T_g(0)$ ) (°C) of CA-treated PCF-filled specimens

Epoxy resin	Hardener	Coupling agent					
		UT <sup>a</sup>	SP	SG	SP	AL	TA
EP·C	HHPA	-2.5	-12.0	-15.0	-13.0	-9.0	-13.0
	MHPA	-1.0	-9.5	-10.5	-12.5	-12.5	-5.5
	MNA	-1.5	-12.0	-11.0	-14.5	-10.0	-14.0
EP·L	HHPA	-1.5	-16.5	-15.5	-17.0	-15.0	-14.5
	MHPA	-3.5	—	-9.5	-7.0	-9.0	-6.5
	MNA	-6.0	—	-21.5	—	-21.0	—
EP·Y	HHPA	-9.0	-6.0	-5.5	-7.0	-7.0	-3.5
	MNA	-3.5	—	—	-5.0	-8.0	-4.5

<sup>a</sup> CA-untreated specimen.

**3.3.3. Storage modulus.** The ratios of  $E'$  for all the wetted specimens to  $E'$  for the UA specimens ( $E'_{w,CA}(5000)/E'_{CA}(0)$ ) were in the range of 1.0–1.2 at low temperatures and were 0.9–1.1 at room temperatures, which were similar to the values for the aged specimens of  $E'_{a,CA}(5000)/E'_{CA}(0)$ . However, the values in the high temperature range were 0.2–0.8, which were smaller than those for the aged specimens and in particular, the values for the A-cured specimens were as small as 0.2–0.7. The influence of the type of CA was also small in this case.

**3.3.4. Comparison with matrix storage modulus.** The ratios of  $E'$  for the wetted specimens for 5000 h to  $E'$  for the matrices at 25°C ( $E'_{w,CA}(5000)/E'_{w,MAT}(5000)$ ) were in the range of 1.2–1.8, which were similar to those for  $E'_{a,CA}(5000)/E'_{a,MAT}(5000)$  of tetra-functional EP. The values for tetra-functional EP were larger than those for tri-functional EP and those for A- and B-cured specimens were larger than those for C-cured specimens. The treating effect for Si-based CA was larger than that for other CA.

## 4. DISCUSSIONS

### 4.1. Aged specimens

As Si and Ti atoms are present on the surfaces of PCF particles treated with SG and TA, respectively [4], the affinity with EP for the UA specimen is large [8]. However, the effect of CA-treatment was no longer seen after aging as shown in Fig. 2 and, when EP was peeled off, no fragments remained. As a result, the affinity between PCF and EP interfaces decreased and the value of  $T_g$  which represented the interface affinity was reduced.

On the other hand, the value of  $E'$  for the CA-treated specimens was larger than that for the UT specimen because EP fastened PCF due to the difference in thermal expansion coefficients, even though EP and PCF were separated in the low temperature range. However, the influence of detachment due to the difference in thermal expansion coefficients was present in the high temperature range and the value was lower than that for the UA specimen. The maximum difference of  $E'_{a,CA}(5000)/E'_{CA}(0)$  was 15%, but no such difference was observed among CA for any of the specimens.

### 4.2. Wetting specimens

The surfaces of all the specimens were machined in order to remove the influence of surface skin layers of the molded plates [14]. For this reason, it is believed that water entered cracks and voids in the matrix [15], the interface between the fillers and EP and the matrix itself [11, 13, 15] after wetting.

For the UT specimens cured with acid anhydrides that were not CA-treated, the influence of water on  $E'$  was small because the absorbed water evaporated during the measurement of temperature rise [11]. However, hydrogen bonding was formed at the interface of the specimens where molecular EP was disordered and not reacted [10, 13] as molecular CA was added. Thus, water was left during the measurement of temperature rise and  $\alpha''$ -peaks or shoulders were seen instead of  $\alpha$ -peaks. When the amount of remaining water was small,  $\alpha$ -peaks on the low temperature side became broader. From these results, it is concluded that the influence of CA-treatment that introduced molecules CA with high water-attaching was larger than that of homogeneous CA molecular structures.

## 5. CONCLUSIONS

EP cured with acid anhydrides filled with pitch-based and CA-treated PCF was aged/wetted for 5000 h. The following were found by studying the dynamic mechanical properties for these specimens.

1. As a result of aging for 5000 h, the effect of CA-treatment on the PCF surfaces was lost and the decrease of weight was 2.2–3.6 wt% which was larger than for the UT specimens. The value of  $T_g$  for the specimens dropped by up to 20.0°C compared with the UA specimens and the effect of CA-treatment was observed. The value of  $E'$  was larger than that for the UA specimen at low temperatures and was smaller in the range from room temperature to high temperature but the difference due to the types of EP at high temperature was observed.
2. By wetting for 5000 h, the water absorption rates were 1.0–2.3 wt% which were smaller than those for the UT specimens and the value of  $T_g$  dropped up to 21.5°C compared with the UA specimen. In the  $\tan \delta$  curve, an  $\alpha''$ -peak or a shoulder was observed for  $\alpha$  ( $\alpha'$ )-peak on the low temperature region. A difference due to the functional radical numbers of EP was observed at high temperatures and the influence of CA-treatment was observed but the effect of the type of CA was small.
3. The value of  $E'$  was about the same or larger compared with that of the UT specimen at room temperatures even if CA-treated specimens were aged or wetted for a long time. The mechanisms of water absorption and thermal aging at high temperature range are different but the values of  $E'$  decreased for all the specimens while the influence of CA or EP was small. From the material standpoint, a high elastic modulus is expected at lower than room temperatures when CA-treated materials are heated or wetted.

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