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Influence of aging and wetting on dynamic mechanical properties of multi-functional epoxy resins filled with pitch-based carbon short fibers

Muneaki Yamaguchi [a], Yuko Tanaka [b] & Katsutoshi Tanaka [c]

[a] Osaka National Research Institute, AIST, 1-8-31, Midorigaoka, Ikeda 563, Osaka 563, Japan

[b] Osaka National Research Institute, AIST, 1-8-31, Midorigaoka, Ikeda 563, Osaka 563, Japan

[c] Osaka National Research Institute, AIST, 1-8-31, Midorigaoka, Ikeda 563, Osaka 563, Japan

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Influence of aging and wetting on dynamic mechanical properties of multi-functional epoxy resins filled with pitch-based carbon short fibers

MUNEAKI YAMAGUCHI, YUKO TANAKA and KATSUTOSHI TANAKA
Osaka National Research Institute, AIST, 1-8-31, Midorigaoka, Ikeda 563, Osaka 563, Japan

Abstract—Pitch-based carbon and graphite short fibers (PCF and PGF) as functional filler materials were filled in multi-functional epoxy resin (EP) using five types of hardeners with 22.2 wt%. Influence of aging and wetting on dynamic mechanical properties of these materials was measured by the use of the nonresonant forced vibration method. Aging of the specimens were carried out at 130°C for 5000 h and wetting was carried out at 21°C in distilled water for 5000 h. The longer the aging time, the less the weight of the specimens which reached a maximum was 5.3 wt% after 5000 h. The glass transition temperature (T_g) for all the specimens increased. The storage moduli (E') for the aged specimens did not change much at low and room temperatures compared with those for the unaged specimens (UA) but they increased at high temperatures. The maximum wetting rate of the specimens was 5.1 wt% and the values of T_g decreased for all the specimens. The values of E' increased in the range from a low temperature (−140°C) to a room temperature (25°C) but they decreased at a high temperature (200°C). This tendency was more significantly observed in specimens cured with diamine hardeners than specimens cured with acid anhydrous hardeners.

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

1. INTRODUCTION

We have been investigating the filling effect of functional short fibers [1–3] on dynamic mechanical properties. Pitch-based carbon short fibers [4, 5], PAN-based carbon short fibers [6] and aramid short fibers [7] that were filled in polyvinyl chloride (PVC) after roll mixture and press molding have been studied. The short fibers were aligned in the machine direction but all were broken at the roll mixing. In order to fill short fibers without breaking, multi-functional epoxy resin [8, 9] was adopted as the matrix and was cured after mixing with these short fibers. When the type of a hardener was changed, affinity was also changed between the epoxy resin and the pitch-based carbon short fibers [10] or aramid short fibers [11]. It was possible to increase the affinity for the pitch-based carbon short fibers by using a coupling agent [12, 13].

It was revealed that several factors contributed to the dynamic mechanical properties of the filled materials. It is desirable that functional composite materials possess aging and wetting resistance.

In order to investigate long-term durability effects for heat and water, multi-functional epoxy resin filled with functional short fibers was processed by aging for up to a maximum of 5000 h and by wetting for up to 5000 h to study the dynamic mechanical properties. The effects of aging and wetting on the dynamic mechanical properties of multi-functional epoxy resin (matrix) [14] and aramid short fiber filled specimens [15] have already been reported.

In this report, pitch-based carbon and graphite short fibers that are drawing attention as promising functional filler materials are explored. Three types of multi-functional epoxy resin filled with the short fibers at 22.2 wt% using five types of hardeners were aged at 130°C for 5000 h and wetted at 21°C for 5000 h and the dynamic mechanical properties were measured in the temperature range between −150°C and +300°C. The obtained results were compared with unfilled specimens (matrices) [14] and aramid short fiber filled specimens [15] and the usefulness of the tested materials was also examined.

2. EXPERIMENTAL

2.1. Materials

Pitch-based carbon and graphite short fibers (Kureha Chop® M-102S and M-201S, abbreviated as PCF and PGF, respectively, manufactured by Kureha Chemical Inc.) were used as fillers as shown in Table 1 and they were dried under vacuum at 105°C for 2 h.

Three types of multi-functional epoxy resin used as the matrix (to be called EP thereafter) are shown in Table 2 and di-functional epoxy resin of bisphenol A type was used as a reference.

Table 3 shows five types of hardeners used to cure the above mentioned multi-functional epoxy resin. For acid anhydride, 1 phr of N,N'-dimethylbenzylamine was added as an accelerator.

EP mixed with a hardener was filled with PCF and PGF to 22.2 wt%; the product was degassed under vacuum, and cured under the condition listed in Table 4 to make mold sheets with a thickness of 5–6 mm and a plane area of 70 × 80 mm^2 (EP·C-A-PCF represents EP·C mixed with hardener A filled with PCF).

Table 1.
Pitch-based carbon short fibers

Material	Code	Length (μm)	Diameter (mm)	Aspect ratio	Density (g/ml)
Carbon	PCF	200	11.7	17.1	1.61
Graphite	PGF	130	13.5	9.6	1.56

Table 2.
Multi-functional epoxy resins

Code	Chemical structure
Multi-functional epoxy resin	
EP·C	Tetraglycidyl-1,3-bis(aminomethyl)cyclohexane (Tetrad C)[a]
EP·L	Tetraglycidyl-diamino-diphenylmethane (Epikote 604)[b]
EP·Y	Triglycidyl-p-aminophenol (Epikote YX-4)[b]
Di-functional epoxy resin	
EP·S	Bisphenol-A type epoxy resin (Epikote 828)[b]

[a]Offered by Mitsubishi Gas Chemical Inc.
[b]Offered by Yuka Shell Epoxy Inc.

Table 3.
Hardeners

Code	Chemical structure
A	1,2-Cyclohexane dicarboxyric anhydride (HHPA)
B	Hexahydro-4-methylphthalic anhydride (MHPA)
C	Methylnadic anhydride (MNA)
E	p,p′-Diaminodiphenylmethane (DDM)
F	m-Phenylenediamine (MPDA)

Table 4.
Curing condition

Epoxy resin	Curing condition
EP·C	RT/14 h + 90°C/2 h + 120°C/2 h + 180°C/2 h
EP·L[a]	RT/14 h + 100°C/2 h + 180°C/4 h
EP·Y[a]	RT/14 h + 100°C/2 h + 180°C/4 h
EP·S[a]	RT/14 h + 100°C/2 h + 180°C/4 h

[a]Added *N*,*N*′-dimethylbenzylamine (DMBA) as accelerator using acid anhydride by 1.0 phr.

The entire surfaces of the specimens used for measuring the dynamic mechanical properties were polished in order to remove the influence of the surface skin layer and ultimately producing short sheets with a thickness of 3 mm, a width of 4 mm and a length of 70–80 mm [16]. Residual strains in the specimens were removed by annealing at 80°C for 48 h.

The specimens for evaluating the aging effects were kept at 130°C for a maximum duration of 5000 h using a gear oven. The specimens for evaluating the wetting effects were kept at 21°C for 5000 h after removing attached air by soaking the specimens in distilled water and de-compressing. The weight change of the specimens was computed from the difference in weight before and after the processing.

2.2. Measurements

The dynamic mechanical properties were measured using a Rheovibron DDV-25FP (manufactured by Orientec Inc.) with a nonresonant forced vibration method, as reported in the previous papers [10–15].

The distance between the clamps was set at 52 mm, the clamping torque of the specimens to the clamps 1.2 N m, and measurement was carried out in an increment of 5°C in the temperature range of −150 to +300°C with a frequency of 110 Hz, the amplitude was ±10 μm and the temperature increase rate was 2°C/min and the interval of measured temperature was 5°C.

The surfaces and the dispersion state of PCF and PGF in the specimens before and after aging were observed using a scanning electron microscope (the SEM, JEM-5200, manufactured by JEOL Ltd.)

3. RESULTS AND DISCUSSIONS

3.1. Surfaces of carbon short fibers and dispersion state

Figure 1 shows SEM photographs of fractured surfaces of the filled specimens. The short fibers in PCF-filled EP·C-A-PCF (Fig. 1a) and in PGF-filled EP·L-E-PGF (Fig. 1b) both of which were unaged (UA, 0 h specimens) were randomly distributed and did not change after aging for 5000 h (Figs 1c and 1d). This tendency was also observed in other specimens.

Figure 2 shows SEM photographs of the surfaces of short fibers in the specimens before and after aging. It is seen that a large amount of EP powders are dispersed on the surfaces of the UA specimens but the amount decreased after aging. This was also observed in the reference EP·S based specimens as well as in the specimen filled with aramid short fibers (AFP) [15].

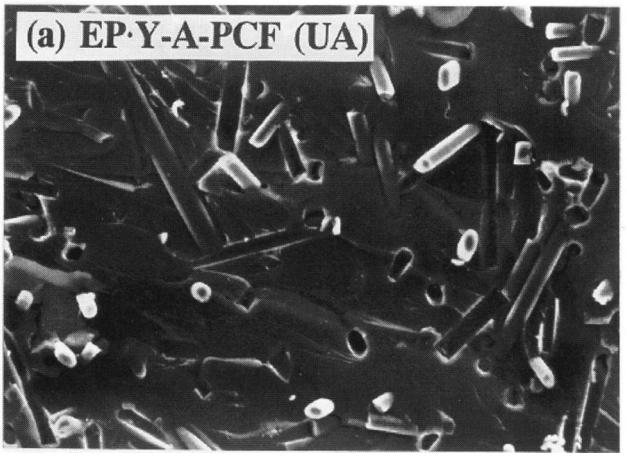


Figure 1. SEM photographs of fractured surface of PCF- and PGF-filled specimens unaged and aged for 5000 h.

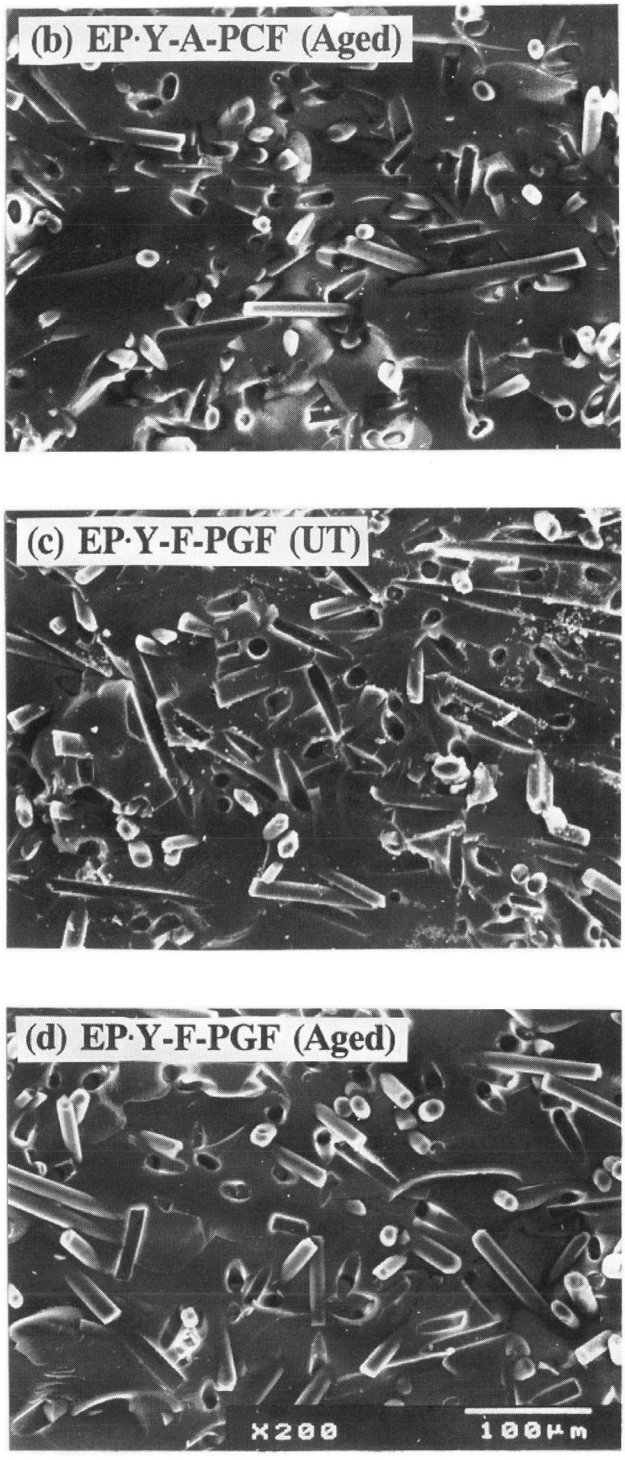


Figure 1. (Continued).

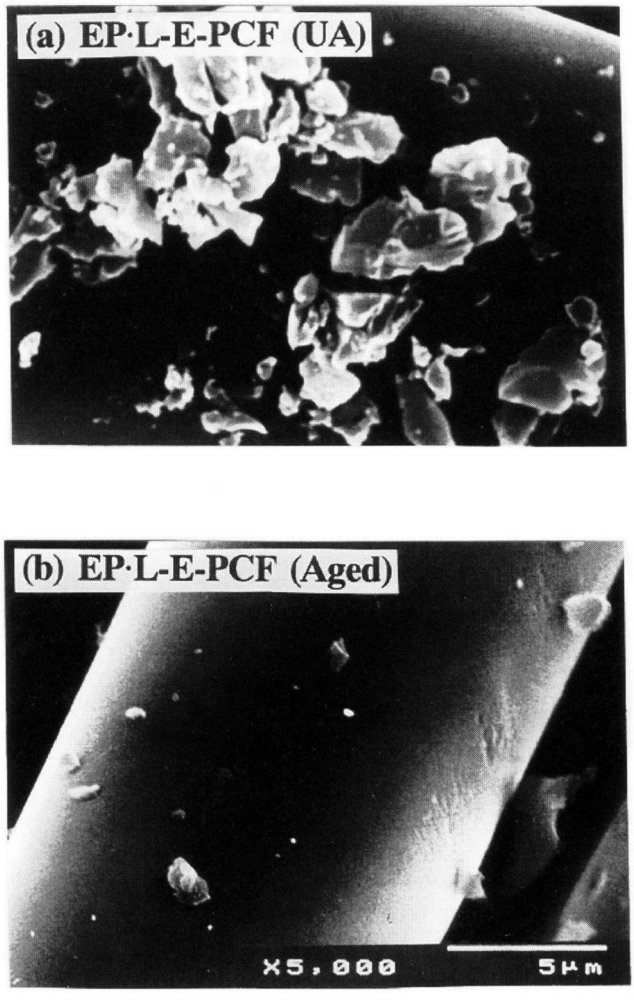


Figure 2. SEM photographs of surface of PCF and PGF fibers unaged and aged for 5000 h.

3.2. Influence of aging

3.2.1. Weight change of specimens due to aging. Figure 3 shows the weight change of PCF-filled specimens cured with A and E hardeners due to aging. The weight reduction rates of the specimens up to 3000 h are relatively small but the rates increased thereafter until 5000 h. The weight reduction of multi-functional EP specimens is larger than that of the reference EP·S and the weight reduction for the specimens cured with A is smaller than that for the specimens cured with E. These results coincide with the results for aged unfilled specimens (matrices) [14] and AFP-filled specimens [15].

Tables 5 and 6 show the weight reduction rates for all the specimens aged for 5000 h. The weight reduction rates for the PCF and PGF filled EP are 1.3–5.3 wt% and

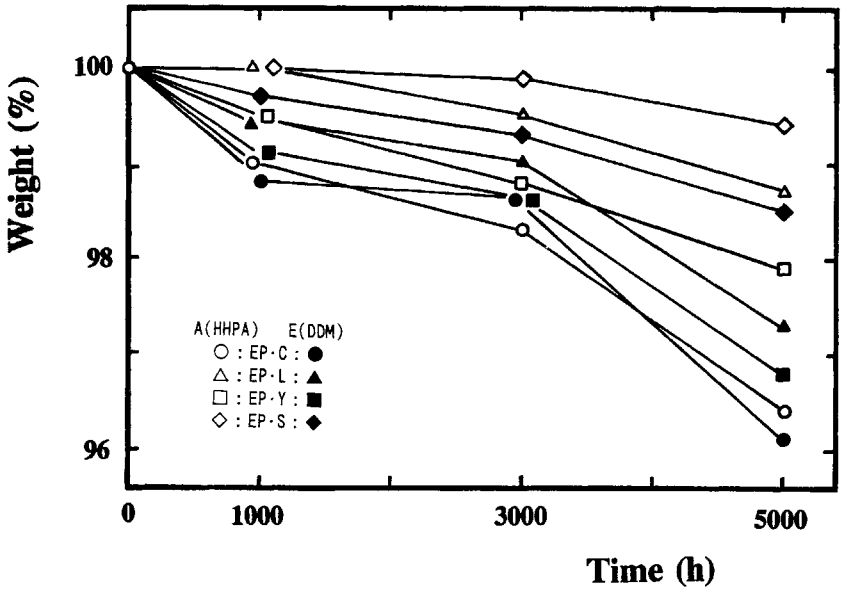


Figure 3. Time dependence of decrease of weight of PCF-filled specimens cured with A (HHPA) and E (DDM) aged up to 5000 h.

Table 5.
Decrease of weight (%) of PCF-filled specimens after aging for 5000 h at 130°C

Resin	Hardener				
	Acid anhydride			Diamine	
	HHPA	MHPA	MNA	DDM	MPDA
EP·C	2.5	1.3	2.3	3.6	3.9
EP·L	1.3	1.7	1.4	2.3	2.9
EP·Y	1.4	—	1.8	3.1	5.3
EP·S	0.5	—	0.8	2.5	2.0

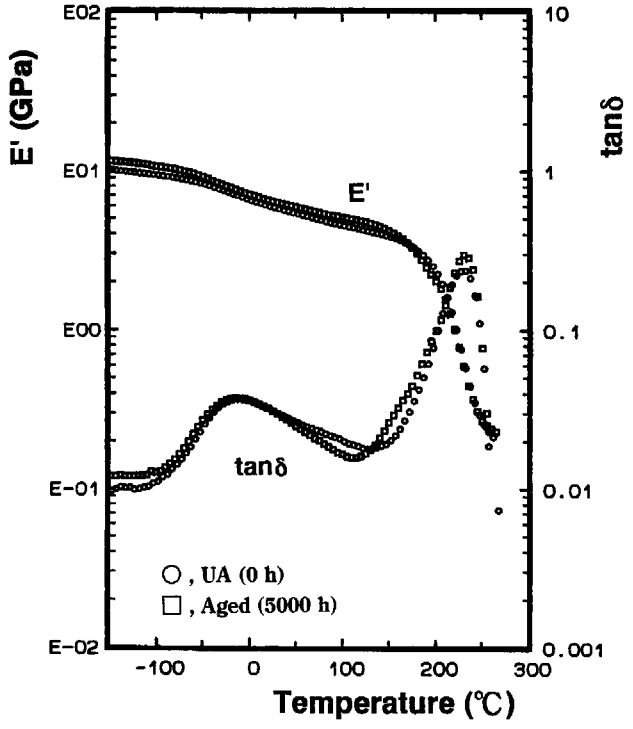
Table 6.
Decrease of weight (%) of PGF-filled specimens after aging for 5000 h at 130°C

Resin	Hardener				
	Acid anhydride			Diamine	
	HHPA	MHPA	MNA	DDM	MPDA
EP·C	1.5	1.1	1.3	1.9	2.5
EP·L	0.8	1.0	1.3	1.9	2.8
EP·Y	1.1	—	1.8	2.6	5.0
EP·S	0.4	—	0.6	2.1	1.7

0.8–5.0 wt%, respectively. As shown in Fig. 3, the reduction rate for the specimens cured with diamines is larger than that for the specimens cured with acid anhydrides and among the diamine cured specimens, the rate for the specimen cured with F is larger than the specimen cured with E. Some of these values are larger than those for aged AFP-filled specimens [15] because the interface area with EP increased as the filling amount of PCF or PGF was larger than that of AFP. Although the values for the reference EP·S specimens were small, a similar result was obtained.

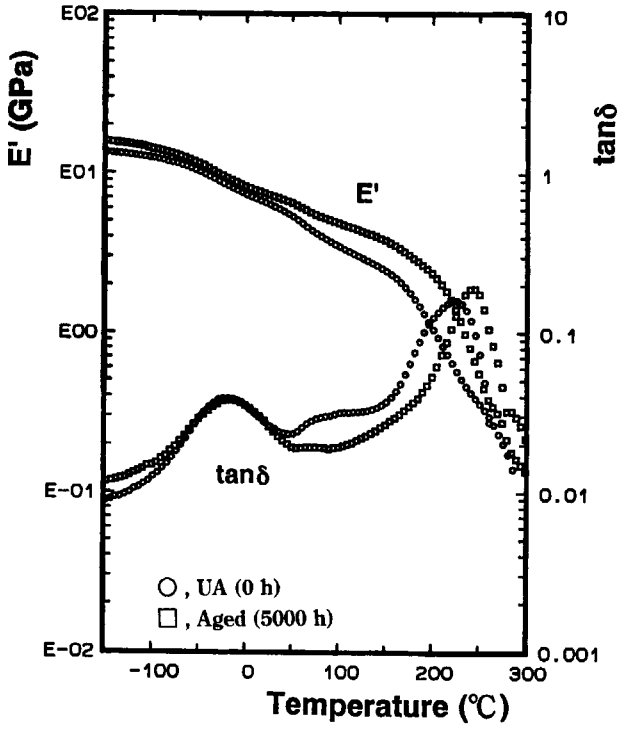
3.2.2. Temperature dependence of dynamic mechanical properties. Figure 4 shows the temperature dependence of the storage modulus (E') and $\tan\delta$ of the specimens aged for 5000 h. The values of E' for EP·C-A-PCF cured with acid anhydride are larger than those for the UA specimens in the temperature range between low temperatures and 150°C but become smaller in the higher temperature range. The α-peak that indicates the glass transition temperature (T_g) of the $\tan\delta$ curve is sharp. The values of E' for EP·Y-E-PCF cured with diamine increased over the entire temperature range and the increase at 200°C is significant.

In the $\tan\delta$ curve, the broad α-peak is shifted to the high temperature side by aging becoming sharper and the small peak around 100°C disappeared. However, the change of the broad and large β-peak at about −20°C is small. A similar result was



(a)

Figure 4. Temperature dependence of dynamic storage modulus (E') and $\tan\delta$ of unaged and aged PCF-filled specimen: (a) EP·C-A-PCF series; (b) EP·Y-E-PCF series.



(b)

Figure 4. (Continued).

Table 7.
Effect of aging for 5000 h on dT_{ga} ($T_{ga}(5000) - T_g(0)$) (°C) of PCF- and PGF-filled specimens

Hardener	Epoxy resin							
	EP·C		EP·L		EP·Y		EP·S	
	PCF	PGF	PCF	PGF	PCF	PGF	PCF	PGF
HHPA	+3.5	+7.5	+3.0	+6.0	+2.0	+3.5	+0.5	+2.0
MHPA	+1.5	+1.5	+1.0	+1.0	—	—	—	—
MNA	+4.0	+6.5	+2.5	+1.0	+8.5	+6.5	+1.0	+4.0
DDM	+4.0	+5.0	+2.5	+2.0	+19.5	+14.0	+4.0	+1.0
MPDA	+12.0	+6.5	+10.0	+2.0	+29.0	+14.5	+15.5	+8.0

observed for other specimens. This is because orientation disturbance and unreacted parts of molecules disappeared due to aging [14, 17, 18].

Table 7 shows the difference of T_g ($dT_{ga}(5000)$), i.e. difference between $T_{ga}(5000)$ and $T_g(0)$. The values of $T_{ga}(5000)$ increased compared with $T_g(0)$ and the values for the PCF-filled specimens increased more than the PGF-filled specimen. The values for the AFP-filled specimens also increased more than those for the UA specimens [15]. The values of $T_{ga}(5000)$ for the tri-functional EP·Y specimens are larger than those

for the tetra-functional EP·C and EP·L specimens. In particular, the value for the EP·Y-F-PCF specimens was as large as 29.0°C because the small α''-peak on the low temperature side in the UA specimen disappeared due to aging. The values for the reference EP·S specimen all increased more than the UA specimens but were smaller than the values for the multi-functional EP specimens. The values for the specimens cured with diamines are larger than those for the specimens cured with acid anhydrides. A similar tendency was observed for aged matrices [14] and AFP-filled specimens [15].

3.2.3. Storage modulus. Figure 5 shows the ratios of E' for all the filled specimens to E' for the UA specimens ($E'_a(5000)/E'(0)$). The values of $E'_a(5000)$ for the multi-functional EP specimens are larger than those for the reference EP·S specimens and the values for the specimens cured with diamines are larger than those for the specimens cured with acid anhydrides.

The values for the PCF-filled specimens are smaller than those for the PGF filled specimens. In the PCF-filled specimens (Fig. 5a), the values of $E'_a(5000)/E'(0)$ are 0.8–1.3 at a low temperature (−140°C) and 0.9–1.5 at room temperature (25°C). At low temperatures, the values for the specimens cured with A and E are larger than 1 while the values for specimens cured with C and F are smaller than 1.

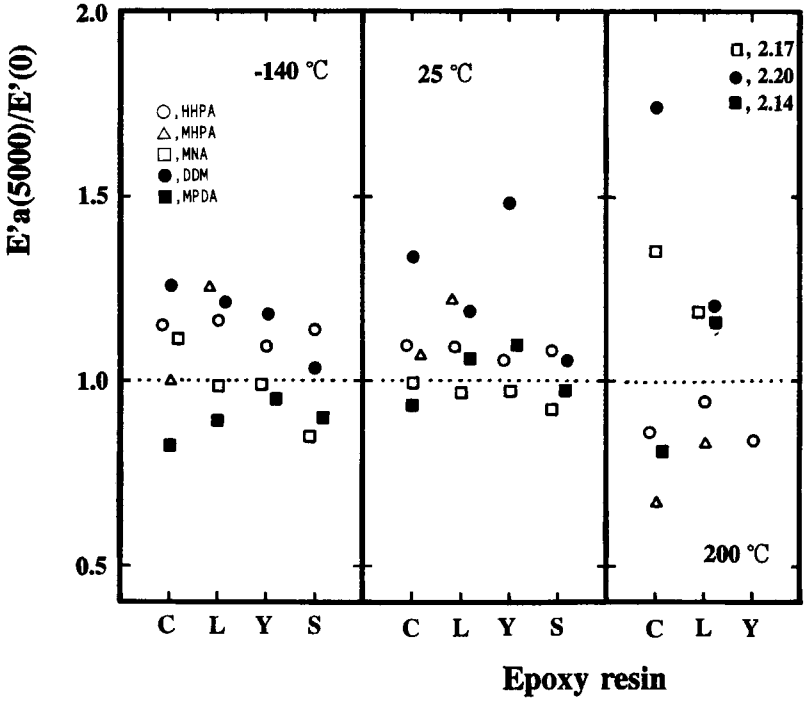
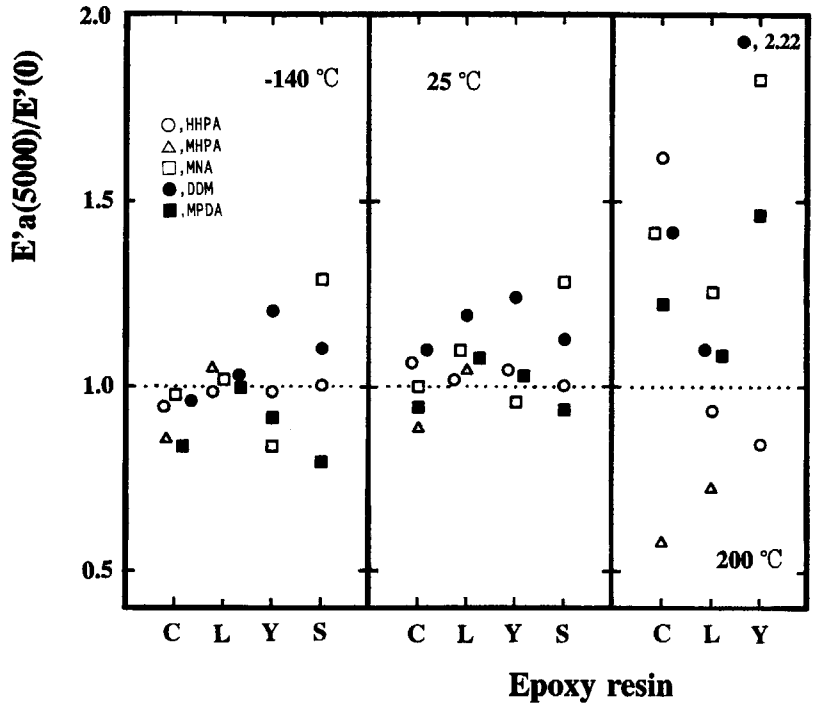


Figure 5. Ratios of dynamic storage modulus (E') of PCF- and PGF-filled specimens aged for 5000 h and unaged (UA, 0 h) specimens ($E'_a(5000)/E'(0)$): (a) PCF-filled specimens; (b) PGF-filled specimens.



(b)

Figure 5. (Continued).

A similar tendency is found in the PGF-filled specimens (Fig. 5b) and the values for almost all the specimens cured with diamines are larger than 1 at room temperatures. At high temperatures, although the values for the specimens cured with acid anhydride A and B are less than 1, the values for the specimens cured with diamine E and F as well as the specimens cured with acid anhydride C are large. In particular, in the EP·Y specimens, the temperature around 200°C is a transition region that changes from the glass to rubber range and because the value of $E'_a(5000)$ increased by aging, all the values except for the specimen cured with A became larger than 2.0. This tendency was also observed in unaged specimens (matrices) [14] and AFP-filled specimens [15].

3.3. Influence of water absorption

3.3.1. Weight change by water absorption. Tables 8 and 9 show the water absorption rates of all the specimens after wetting for 5000 h. The water absorption rates of PCF- and PGF-filled EP are 1.3–5.1 wt% and 1.2–4.4 wt%, respectively, and the values for the specimens cured with diamine are larger than those for the specimens cured with acid anhydrides.

The values for most of the specimens are larger compared with those for wetted matrices [14] and AFP-filled specimens [15]. Water absorption of composite materials begins by water filling in cracks and voids of the matrix followed by diffusion into the matrix and water entrance to the interface between the filler material and the

Table 8.
Absorption of water (%) of PCF-filled specimens after wetting for 5000 h at 21°C

Resin	Hardener				
	Acid anhydride			Diamine	
	HHPA	MHPA	MNA	DDM	MPDA
EP·C	3.6	3.7	2.3	3.9	2.9
EP·L	1.3	2.2	1.4	2.7	4.8
EP·Y	3.1	—	3.4	3.6	5.1
EP·S	0.6	—	1.3	2.5	3.1

Table 9.
Absorption of water (%) of PGF-filled specimens after wetting for 5000 h at 21°C

Resin	Hardener				
	Acid anhydride			Diamine	
	HHPA	MHPA	MNA	DDM	MPDA
EP·C	2.5	2.4	1.6	2.9	2.2
EP·L	1.2	1.7	1.4	2.5	3.4
EP·Y	2.9	—	2.8	3.2	4.4
EP·S	0.4	—	0.9	2.3	2.5

matrix [19]. In this experiment, all the surfaces of the specimens were planed in order to remove the effect of the skin layer formed at the time of molding. For this reason, water enters the interface between EP and PCF or PGF at the same time as water enters cracks and voids of the matrix and the diffusion into the matrix progresses.

The volume fractions ϕ_f of PCF and PGF are 0.18 which is larger than the 0.021 of AFP [15] so that the amount of water absorption increases as the interface between the matrix and the short fibers increases. In the specimens cured with diamines, the water absorption amount is increased because of many hydrogen bondings formed as there are many amino radicals in the hardener [20].

3.3.2. Temperature dependence of dynamic mechanical properties. Figure 6 shows the temperature dependence of E' and $\tan\delta$ for the specimens wetted for 5000 h. The value of E' for the specimen cured with acid anhydride (EP·C-A-PCF, Fig. 6a) increased at low temperatures compared with the UA specimen and decreased at high temperatures above the room temperature.

The α-peak temperature ($T_{gw}(5000)$) of $\tan\delta$ decreased as the temperature decreased but increased in the temperature range of 50–100°C and the β-peak at low temperatures also increased. The temperature dependence of E' and $\tan\delta$ for other specimens cured with acid anhydrides showed similar behavior. The value of E' ($E'_w(5000)$) for the diamine cured EP·Y-E-PCF (Fig. 6b) increased at low temperatures but decreased

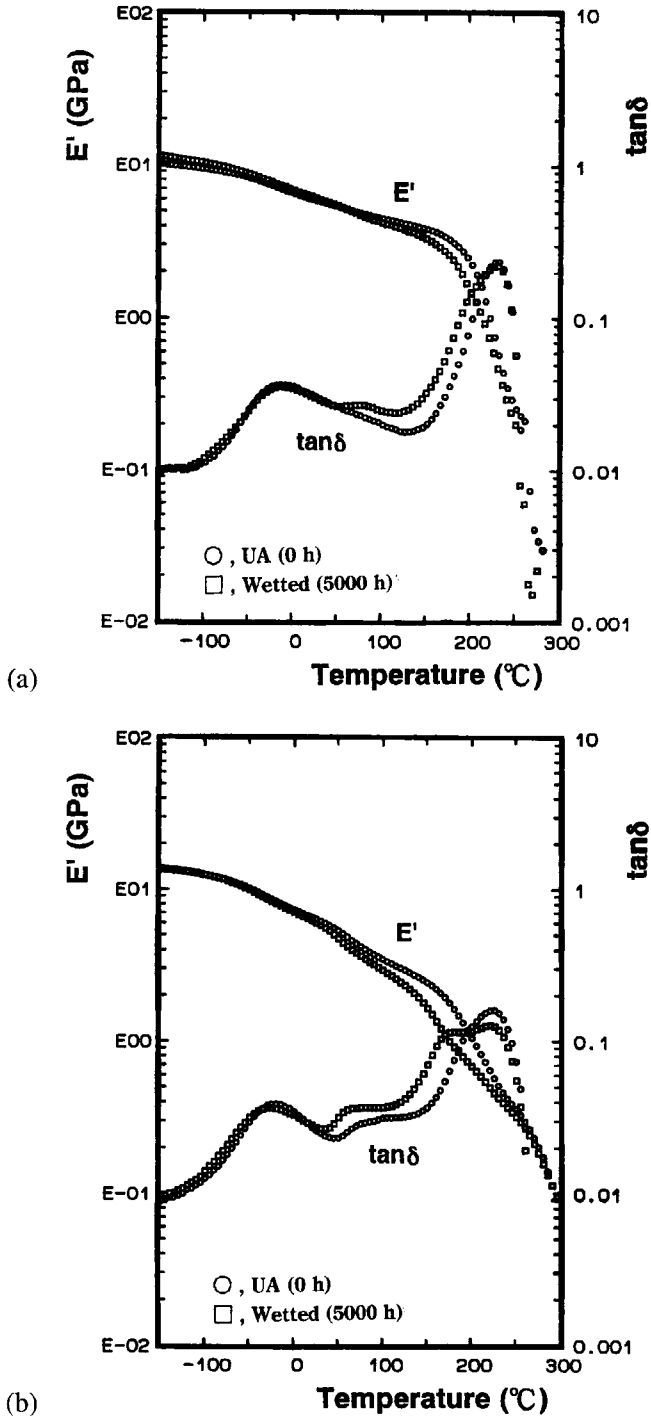
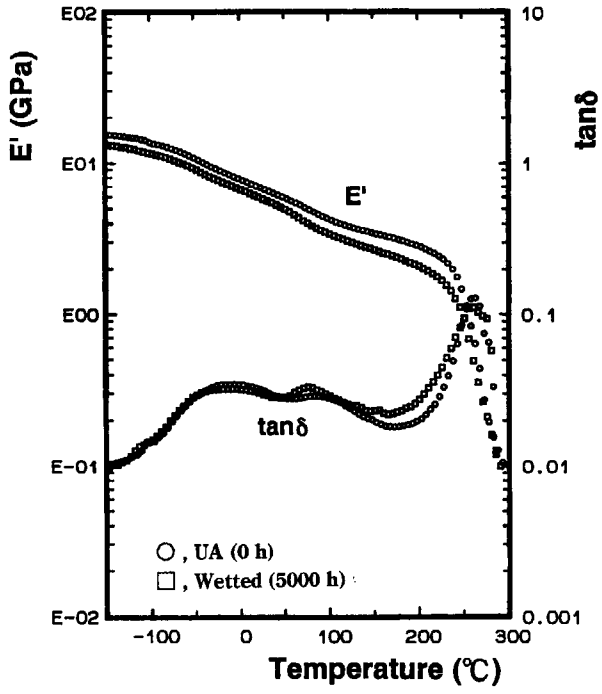


Figure 6. Temperature dependence of dynamic storage modulus (E') and $\tan\delta$ of unaged and wetted PCF- and PGF-filled specimens: (a) EP·C-A-PCF series; (b) EP·Y-E-PCF series; (c) EP·L-E-PGF series.



(c)

Figure 6. (Continued).

in the temperature range above room temperature and the rate of decrease in the high temperature range is significant.

The α-peak on the tan δ curve shows a large α''-peak on the low temperature side [14, 15, 21] and the values for 50–100°C increased and shifted toward the low temperature side but the change in the β-peak at low temperature was small.

The value of $E'_w(5000)$ for the PGF-filled specimen EP·L-E-PGF (Fig. 6c) was lower than that for the UA specimens over the whole temperature range. The α-peak temperature of tan δ was lower than the UA specimens but the temperature difference was small. The behavior that the values for 50–100°C and the β-peak increased and shifted to the low temperature side was also found in EP·Y-E-PCF (Fig. 6b) and the specimens cured with F also showed a similar tendency. Similar behavior due to the hardener was observed in the matrices [14] and the AFP-filled specimens [15].

Table 10 shows the difference ($dT_{gw}(5000)$), difference between T_g's ($T_{gw}(5000)$ and $T_g(0)$) of the wetted specimens for 5000 h and UA specimens. The values of $dT_{gw}(5000)$ for PCF- and PGF-filled specimens are 1.0–42.0°C, and 1.5–56.0°C, respectively. In particular, the decrease of $T_{gw}(5000)$ for the specimens cured with diamines where an α''-peak or a shoulder appeared by wetting is significant. No α''-peak or shoulder appeared on the tan δ curves in any of the specimens cured with acid anhydrides though a shoulder was visible in some specimens cured with diamines. This is because either water evaporated or there was insufficient water in the mechanism of an α''-peak or a shoulder while measuring the dynamic mechanical

Table 10.
Effect of wetting for 5000 h on dT_{gw} ($T_{gw}(5000) - T_g(0)$) (°C) of PCF- and PGF-filled specimens

Hardener	Epoxy resin							
	EP·C		EP·L		EP·Y		EP·S	
	PCF	PGF	PCF	PGF	PCF	PGF	PCF	PGF
HHPA	−2.5*	−1.5*	−1.5*	−2.0*	−9.0**	−5.0*	−3.0*	−2.0*
MHPA	−1.0*	−6.0*	−3.5*	−2.5*	—	—	—	—
MNA	−1.5*	−6.5*	−6.0*	−4.5*	−3.5**	−2.5*	−1.0*	−0.5*
DDM	−41.0	−7.0*	−2.0*	−2.0*	−42.0	−53.5	−40.0	−3.5*
MPDA	−6.0*	−38.5	—	—	—	−56.0	−21.0	−26.0

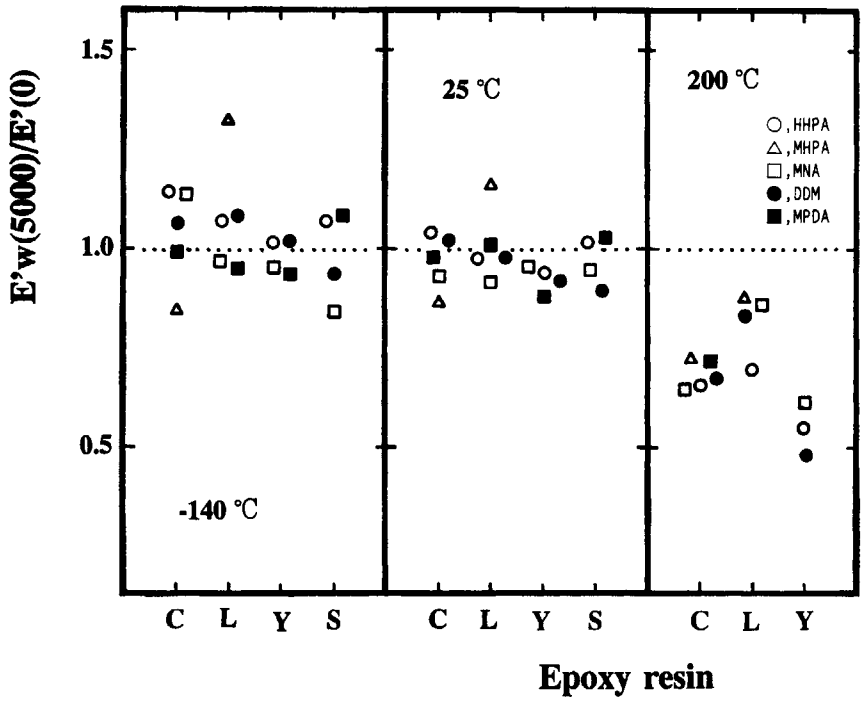
*Appeared only an $\alpha(\alpha')$-peak.
**The peak was broadened to low temperature side.

properties at the rising temperature of 2°C/min. A similar phenomenon was also observed in the AFP-filled specimens [15].

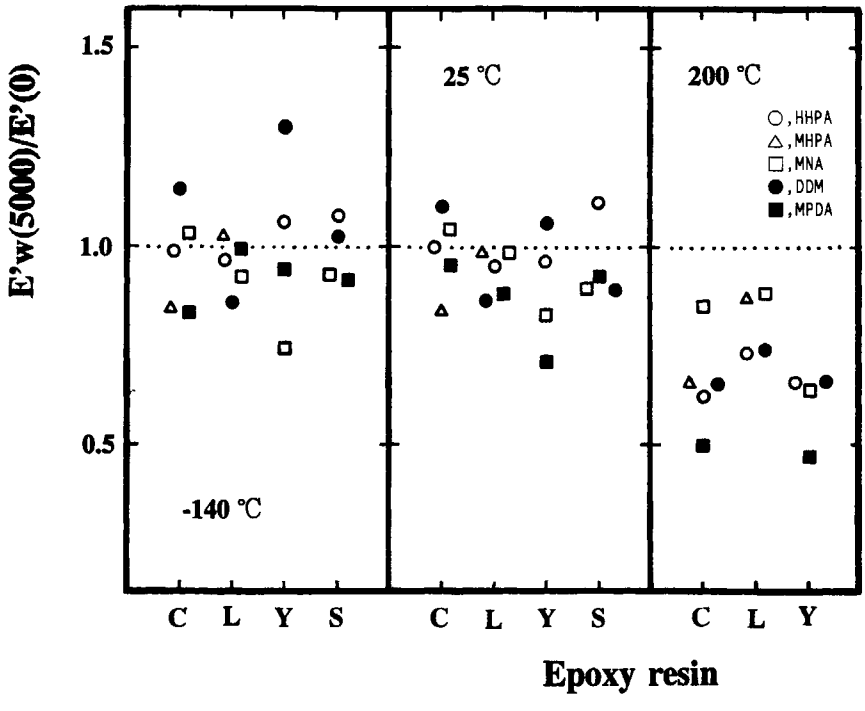
3.3.3. Storage modulus. Figure 7 shows the ratios of E' of all the specimens to E' of the UA specimens ($E'_w(5000)/E'(0)$). The values of $E'_w(5000)$ for the diamine cured specimens are larger than those for the acid anhydride cured specimens at a low temperature (−140°C) but the difference became smaller from the room temperature (25°C) to a high temperature (200°C). The difference between the PCF-filled specimens and the PGF-filled specimens is also small. The value of $E'_a(5000)/E'(0)$ at low and room temperatures lies between 0.7 and 1.3 and the interval becomes narrower at room temperatures. The values at high temperatures are found between 0.4 and 0.9 and the difference with the values for the matrix (0.35–1.0) [14] and the AFP-filled specimens (0.5–1.0) [15] is small.

3.4. Comparison of storage modulus between PCF- and PGF-filled specimens

Figure 8 shows the ratios (E'_{PCF}/E'_{MAT} and E'_{PGF}/E'_{MAT}) of E' (E'_a and E'_w) for the aged specimens and the wetted specimens for 5000 h to E' for the matrix (unfilled specimens [14]) at 25°C. The values for the aging specimens are as large as 1.0. This is because EP was completely cured by aging [17] and the values of E'_{PCF}/E'_{MAT} are larger than those of E'_{PGF}/E'_{MAT} in many specimens. The values for most of the aged multi-functional EP specimens including the reference EP·S specimen are larger than 1.3. The values for the AFP-filled specimen [15] are less than 1.3 as ϕ_f for the AFP-filled specimen is small. The values for the PGF-filled specimens are larger than those for the PCF-filled specimens. On the other hand, the values for the wetted specimens are as large as 1.0 and many are larger than 1.5. This is because hydrogen bonding was formed [20] as remaining water was abundant at 25°C and this behavior is very significant in the specimens cured with diamine F. The values of $E'_w(5000)$ for some PCF-filled specimens are larger than those for the PGF-filled specimens especially among the F cured specimens that show an α''-peak or a shoulder.



(a)



(b)

Figure 7. Ratios of of dynamic storage modulus (E') of PCF- and PGF-filled specimens wetted for 5000 h and unaged (UA, 0 h) specimens ($E'_w(5000)/E'(0)$): (a) PCF-filled specimens; (b) PGF-filled specimens.

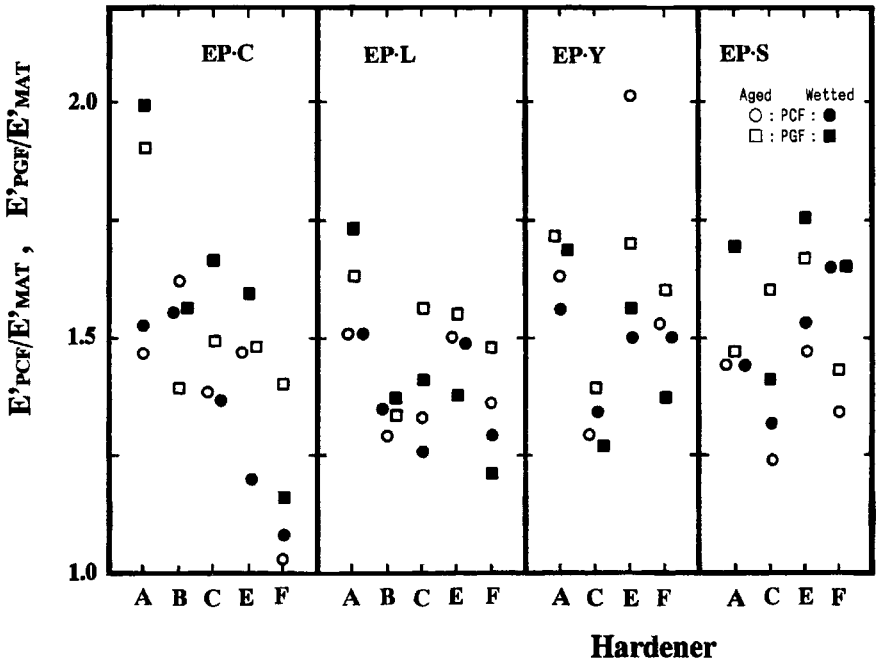


Figure 8. Ratios of dynamic storage modulus (E') of aged and wetted for 5000 h for PCF- and PGF-filled specimens and matrices (unfilled) (E'_{PCF}/E'_{MAT} and E'_{PGF}/E'_{MAT}) at 25°C.

4. CONCLUSIONS

Three types of multi-functional epoxy resin (EP) cured with five types of hardeners were filled with pitch-based carbon short fibers (PCF) and graphite short fibers (PGF) distributed randomly at 22.2 wt% and were aged at 130°C for 5000 h or wetted at 21°C for 5000 h. The following results were obtained by investigating the dynamic mechanical properties of these specimens.

4.1. Influence of aging

The weight decrease rates of PCF- and PGF-filled specimen were 1.3–5.3 wt% and 0.8–5.0 wt%, respectively, and the rates for the specimens cured with diamines were larger than those for the specimens cured with acid anhydrides in any case. The values of T_g ($T_{ga}(5000)$) for the specimens increased by 1.0–29.5°C (for PCF) and by 1.0–14.5°C (for PGF) compared with $T_g(0)$ of the unaged (UA) specimens but a difference was recognized depending on the type of EP.

The storage modulus ($E'_a(5000)$) was small at a low temperature (−140°C) but increased at a high temperature (200°C) compared with the values for the UA specimens ($E'(0)$). The ratios ($E'_a(5000)/E'(0)$) showed some variance depending on the types of EP and hardeners.

4.2. *Influence of wetting*

The water absorption rates of the specimens were 1.3–5.1 wt% and 1.2–4.4 wt%, respectively, and the values for the specimens cured with diamines were larger than those for the specimens cured with acid anhydrides and these values varied depending on the types of EP.

The values of T_g ($T_{gw}(5000)$) for the filled specimens decreased by 1.0–42.0°C and 1.5–56.0°C, respectively, compared with those for the UA specimens. The decrease for the specimens cured with acid anhydrides was small but the decrease for the specimens cured with diamines in which a peak (α''-peak) of the $\tan\delta$ curve or a shoulder appeared on the low temperature side was large. Although water was removed while measuring the temperature rise for dynamic mechanical properties, the influence of remaining water was large in the specimens cured with diamines.

The values of $E'_w(5000)$ increased from the low temperature to the room temperature compared with $E'(0)$ but some difference was seen depending on the types of EP and hardeners. The values of $E'_w(5000)$ were all less than $E'(0)$.

From the above, excellent heat resistance can be expected for PCF- and PGF-filled EP [9, 10] and the reduction in elastic moduli is small similar to the matrix [14] and aramid (AFP) filled specimens [15]. The reduction in the storage modulus of wetted specimens was small below the room temperature but significant influence of wetting was observed at high temperatures. The effect of the hardener and the type of EP was also significant. Except for wetted specimens at high temperatures, the influence of aging and wetting on the elastic moduli is small from the standpoint of materials.

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