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

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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 in multi-functional epoxy resin (EP) cured with two types of diamines 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 maximum weight reduction of the aged specimens was 5.1 wt% for 5000 h. Although CA on the surfaces of PCF was lost by aging, the storage modulus (E') increased at a lower temperature −140°C and decreased from 25°C to 200°C compared with untreated specimens (UA). The maximum water absorption rate for the wetted specimens was 5.6 wt%. The value of E' increased at lower temperatures but decreased above room temperatures. The influence by both aging and wetting on the mechanical dynamic properties was similar even though the mechanism for each is different. These results are compared with specimens cured by acid anhydrides.

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] in a multi-functional epoxy resin [3]. The multi- functional epoxy resins were given a high glass transition temperature and high modulus [4–6] by the functional fiber, such as pitch-based carbon short fibers. The effect of hardeners [7] for epoxy resin and coupling agents [8] for short fibers was also investigated. A difference in affinity between the epoxy resin and short fibers was observed with different hardeners. When short fibers were treated with coupling agents, the affinity with epoxy resin increased and the dynamic mechanical properties were

also improved [9, 10]. Water-resistance and heat-resistance of short fiber filled multi- functional epoxy resin were 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) [11], for materials filled with pitch-based carbon and graphite short fibers without surface treatment [12] and treated with coupling agents and cured with acid anhydride [13]. A similar study for materials filled with Aramid short fiber of length 1 mm was also reported [14]. In this paper, multi-functional epoxy resin cured with two types of diamine filled with pitch-based carbon short fibers at 22.2 wt% and 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°C to +300°C using the same methods as in previous reports [11−14]. The results were compared with materials filled with short fibers treated with coupling agents and cured with acid anhydrides [13] and matrices [11]. The utility of the materials was also evaluated.

2. EXPERIMENTAL

Three types of multi-functional epoxy resin (abbreviated, EP), five types of coupling agents (CA) and pitch-based carbon short fibers (PCF) were used. As these were the same types of materials as those used in the previous reports [13], the same abbreviations are used in this paper for the specimens, except for the hardeners employed in the study. The diamine hardeners (DA) used are listed in Table 1. The

Table 1.
Hardeners

Code	Chemical structure
E	p,p′-Diaminodiphenyl methane (DDM)
F	m-Phenylendiamine (MPDA)

Table 2.
Curing condition

Epoxy resin	Component of hardener (phr)		Curing condition
	E	F	
EP-C	49.5	28.5	Room temp./14 h + 90°C/2 h + 120°C/12 h + 180°C/2 h
EP-L	42.0	21.0	Room temp./14 h + 100°C/2 h + 180°C/4 h
EP-Y	52.0	26.0	Room temp./14 h + 100°C/2 h + 180°C/4 h

acid anhydride, used previously as hardener, was abbreviated as AA. The curing conditions of mixtures (EP, DA and PCF) are listed in Table 2.

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 reports [11–14]. 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 on the specimens by degassing and were kept at 21°C under atmospheric pressure for 5000 h. The change in weight of the specimens due to the treatment was calculated from the difference in weight before and after the treatment.

Similar to the previous reports [6, 7, 9–15], the dynamic mechanical pproerties were measured by a Rheovibron DDV-25FP (manufactured by Orientec Inc.). 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 AND DISCUSSION

3.1. Effects on aging

SEM photographs of the fractured surfaces of specimens showed a similar tendency for the specimens filled with CA-untreated (UT) [12] or CA-treated [13] cured with AA before and after aging.

Figure 1 shows the time dependence of decrease of weight of coupling agents (GS and TA) treated PCF filled specimens cured with E aged up to 5000 h. The weight of these specimens decreased linearly for up to 5000 h over the range of 3.4–5.1 wt%.

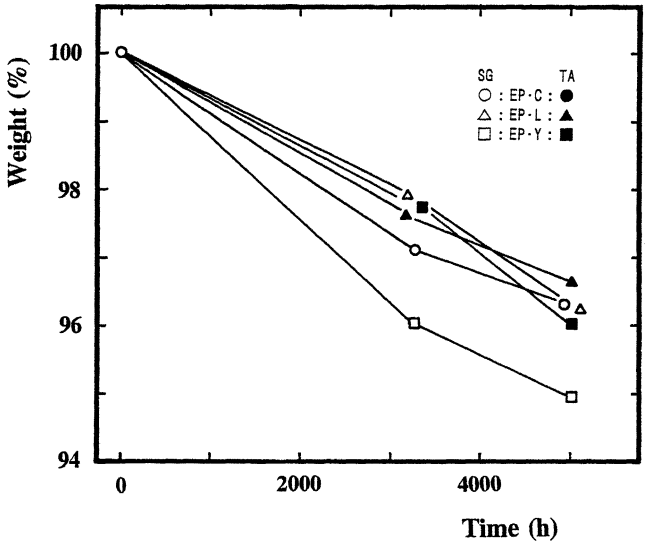

Figure 1. Time dependence of decrease of weight of CA-treated PCF filled specimens cured with E (DDM) aged up to 5000 h.

The values for untreated specimens cured with E, which were 2.7−3.9 wt% [12], were smaller than those for CA-treated specimens except EP · EC-SG.

Table 3 lists the decrease in weight of all the specimens that were aged for 5000 h. The decrease in weight (%) of specimens treated for 5000 h is in the range 2.4−5.8 wt%. The values for the specimens using EP · EL or EP · EY as matrix depend on the hardener, in this case, hardener E; they are larger than those for CA untreated specimens, but, with hardener F, the results are reversed. The values for the specimens cured with acid anhydrides are 1.9−3.6 wt%. They are smaller than specimens cured with diamine in this study (2.4−5.8 wt%). The values for the specimens treated with Si- and AL-based CAs were larger than those for the specimen treated with TA-based CA.

Figure 2 shows the temperature dependence of the storage modulus (E') and $\tan\delta$ for EP · EL-E-SG aged for 5000 h. The values of E' are similar compared with the UA specimens over the temperature range from low to 150°C, but they decreased in the higher temperature region. The α-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 curve near 150°C became flat. The large broad β-peak at about −20°C was also shifted towards the lower temperature side. For some of other specimens, the values of E' decreased much more than for this case in the high- temperature range, and the α-peak at 150°C for the $\tan\delta$ curve disappeared. Such behavior was also observed in the previously reported cured with diamine [11] UT specimens [12], the matrices and the AFP filled specimens [14].

Table 4 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 −7.0−+4.5°C and the values of $T_{ga}(5000)$ for half of the specimens were below and others were above those for the UA specimens. Such behavior is due to the fact that disorder of molecular arrangement and unreacted parts disappeared by aging [16], and reduction of surface interaction between EP and PCE, owing to differences in the expansion coefficient. The values of T_{ga} for tetra-functional EP specimens

Table 3.
Decrease of weight (%) of specimens after aging 130°C for 5000 h

Epoxy resin	Hardener	Coupling agent					
		UT[a]	SB	SG	SP	AL	TA
EP-C	E	3.9	—	3.7	3.9	—	—
	F	2.9	3.7	2.8	2.4	3.7	—
EP-L	E	2.7	3.7	3.8	4.1	4.0	3.4
	F	4.8	—	3.8	—	3.9	2.5
EP-Y	E	3.2	5.0	5.1	5.8	5.4	4.0
	F	4.8	4.1	4.3	—	4.4	—

[a] CA-untreated specimen.

were below and for tri-functional EP resins were above those for the UA specimens. The values for F hardener specimens were larger than those for the E hardener. In CA types, the values for TA treated specimens only were below those for the UA specimens. The values of dT_{ga} for matrix [11] and for UT specimens [12] were up to within the range 3.0–20.0°C and 2.5–29.0°C respectively, but those of specimens treated CA and cured with AA [13], were down to the range −20.0 to −3.5°C.

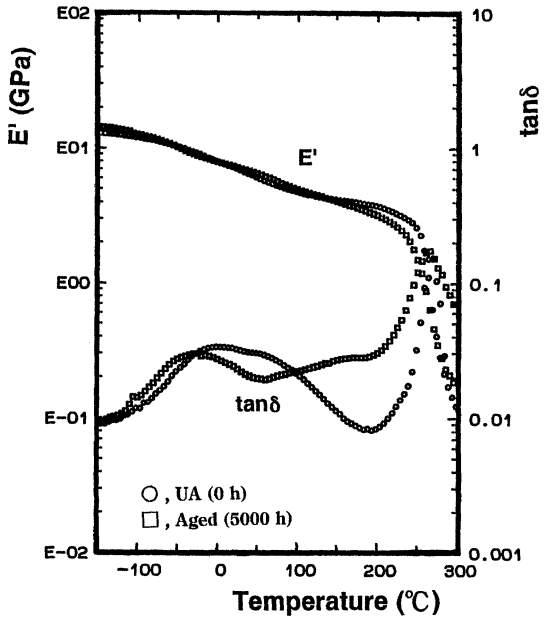

Figure 2. Temperature dependence of dynamic storage modulus (E') and tan δ of unaged and aged CA-treated PCF filled specimens, EP · EL-E-SG series.

Table 4.
Effect of aging for 5000 h on $dT_{ga}(dT_{ga}(5000) - T_g(0))$(°C) of CA-treated PCF-filled specimens

Epoxy resin	Hardener	Coupling agent					
		UT[a]	SB	SG	SP	AL	TA
EP-C	DDM	4.0	—	−6.0	−4.0	—	—
	MPDA	12.0	−2.5	−0.5	2.5	−7.0	—
EP-L	DDM	2.5	−5.0	−3.5	0.0	−5.5	−6.0
	MPDA	10.0	—	−0.5	—	2.0	−2.0
EP-Y	DDM	19.5	1.5	1.0	2.5	4.0	−0.5
	MPDA	29.5	4.5	2.0	—	1.5	—

[a] CA-untreated specimen.

The values of E' for aged specimens were 10−20 GPa at −140°C and 6−10 GPa at 25°C, and larger than those for specimens treated with CA and cured with AA hardeners (9−12 Gpa at −140°C; 5−7 GPa at 25°C). The relation of the modulus to UA specimens ($E'_a \cdot \mathrm{CA}(5000)/E'\mathrm{CA(O)}$) were 0.95−1.15 at low temperature and 0.90−1.10 at room temperature. These values were almost the same as for specimens cured with AA [13]. On the other hand, at high temperatures (200°C), the modulus was 0.50−0.80 for EP · C specimens and 0.65−0.90 for other EP specimens. These values were the same as for the AA cured specimens [13].

When the surface of PCF particles treated with SG or TA were examined by XPS, we confirmed that Si and Ti atoms were present on their surfaces [17]. The existence of a Si or Ti atom on the surface of PCF increases the affinity with the EP matrix [9, 10]. However, the effect of CA-treatment was no longer seen after aging and EP was peeled off whose remain did not stay. As 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 there was low affinity between then 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 specimens cured with AA [13] also gave the same result.

3.2. Influence of wetting

Table 5 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 2.8−5.6 wt%; the values for tri-functional EP were larger than those for the tetra-functional one and the influence of CA was small. These values were larger than those for matrices [11] of 2.5−5.1 wt%, for the UT specimens [12] of 2.3−5.2 wt% and the specimen treated with CA and cured with AA of 1.0−2.3 wt%. This result

Table 5.
Absorption of water (%) of specimens at 21°C for 5000 h

Epoxy resin	Hardener	Coupling agent					
		UT[a]	SB	SG	SP	AL	TA
EP-C	DDM	3.6	—	2.9	4.7	—	—
	MPDA	3.0	—	3.0	4.0	4.9	—
EP-L	DDM	2.3	3.3	3.3	3.5	3.5	3.0
	MPDA	2.6	—	2.8	—	3.0	2.9
EP-Y	DDM	3.1	4.4	4.5	5.6	3.7	4.7
	MPDA	5.2	5.3	5.5	—	3.7	—

[a] CA-untreated specimen.

implies that hydrogen bonding increased in the specimens as a result of the action of DA hardeners and CA.

Figure 3 shows the temperature dependence of E' and $\tan\delta$ for EP · EY-F-AL 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 (α''-peak) appeared on the low temperature side [12–14, 18]. For the matrix specimen alone, this shoulder (α'') became larger than the α-peak [11]. Further, a new small peak appeared in the 50–100°C range. The β-peak in low temperature inc reased on the low temperature side as well. In some of the $\tan\delta$ curves for other specimens, the α-peak became broader and the values of E' showed same as UA specimens.

Table 6 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 −82.0–+5.5°C. The influence of the type of EP was very evident and the decrease for tri- functional EP was larger than that for tetra-functional EP. Although the values of dT_{gw} for the UA specimens were larger than that for the CA treated specimens, this tendency was significant for specimens with α-peaks or shoulders. The values of dT_{gw} for all specimens was as follows: matrix 55.5–13.0°C [11], for UT-specimens; −42.0–+2.0°C [12] and for CA treated specimens cured with AA −21.5–3.5°C.

The values of E' for the wetted specimens were 11–20 GPa in the low temperature range and 6–10 GPa at the room temperature and larger than those for CA-treated

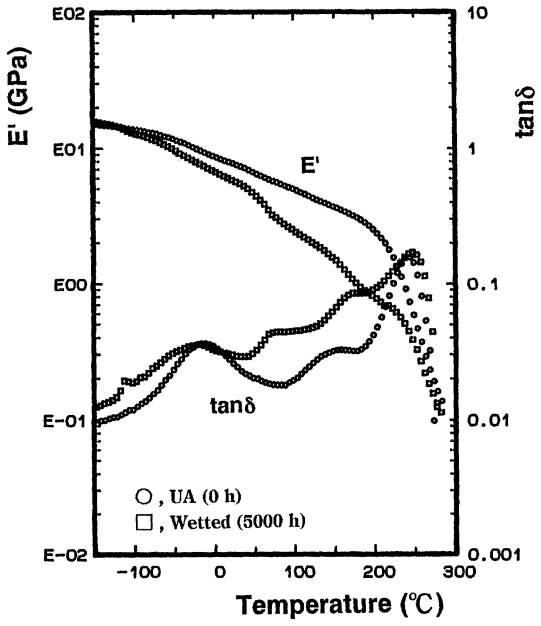

Figure 3. Temperature dependence of dynamic storage modulus (E') and $\tan\delta$ of unaged and wetted CA-treated PCF specimens, EP · Y-F-AL series.

Table 6.
Effect of wetting for 5000 h on $dT_{gw}(dT_{gw}(5000) - T_g(0))(^\circ C)$ of CA-treated PCF-filled specimens

Epoxy resin	Hardener	Coupling agent					
		UT[a]	SB	SG	SP	AL	TA
EP-C	DDM	−41.0	—	−43.0	0.5*	—	—
	MPDA	−6.0*	—	−42.0	0.5*	—	—
EP-L	DDM	2.0*	2.5*	−0.5*	5.5*	2.0*	2.0*
	MPDA	—	—	—	—	4.0*	—
EP-Y	DDM	−42.0	2.0*	−70.0	3.5*	—	−63.0
	MPDA	—	—	−82.0	—	−73.5	—

[a] CA-untreated specimen.
* Appeared only an $\alpha(\alpha')$-peak.

specimens cured with AA [13]; 10−12 GPa at low temperatureand 6−7 GPa at room temperature respectively.

On the other hand, in the high temperature range, the values of E' were below 3 GPa, which was almost the same as for the AA specimens. The ratios of E' for UA specimens (E'w · CA(5000)/E'CA(0)) were 0.75−1.20 in the low temperature range which were larger than those for the UA specimens and were 0.75−1.05 at room temperature which were about same as the UA specimens and were 0.30−0.60 at the high temperature which were smaller than UA specimens. The values for EP · EY specimens (tri-functional epoxy resin) mostly decreased at room temperature compared with other specimens but the difference due to the type of CA and hardeners for all the specimens was small.

The surfaces of all the specimens were machined in order to remove the influence of surface skin layers of the molded plates [15]. For this reason, it is believed that water entered cracks and voids in the matrix [19], and thence the interface between the fillers and EP and the matrix itself [11−14, 19] after wetting. As is already known, Si-based CA bonded glass is dissociated by water [8].

Hydrogen bonds were more easily formed in the specimens cured with DA hardeners than those cured with AA [17, 20], because DA specimens possess more hydroxyl groups than AA specimens. Further, the presence of CA accelerated the formation of hydrogen bonding in the specimens. Those hydrogen bonds were formed at the interface of the specimens where molecular EP was disordered and unreacted. Thus, water was left during the measurement of temperature rise (2°C/min) and α'' peaks or shoulders were seen instead of α-peaks. When the amount of remaining water was small, α-peaks on the low temperature side became broader [11−14]. The values of T_{gw} for those specimens which displayed only α'' peaks were mostly lower than those for UT specimens. From these results,

it is concluded that the specimens, such as tri-function EP · Yand treated with SG with epoxy end group, display a great influence of disordered and unreacted molecular.

4. CONCLUSIONS

Pitch-based carbon short fibers (PCF) as functional fillers were treated with five types of coupling agents (CA) and were filled in multi-functional epoxy resin (EP) cured with two types of diamines at 22.2 wt%. The influence of aging and wetting on the dynamic mechanical properties was investigated by the 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.

(1) As a result of aging for 5000 h, EP on the PCF surfaces was lost and the decrease of weight was 3.4−5.1 wt% which was larger than for the UT specimens and AA-cured specimens. The value of T_g for the specimens shifted in the range −7.0 to +4.0, compared with the UA specimens; the effect of CA-treatment and the difference due to the types of EP and hardeners were observed. The ratios of E' was above 1 and larger than that for the UA specimen at low temperatures and was smaller in the range from room temperature to high temperature.

(2) By wetting for 5000 h, the water absorption rates were 2.8−5.6 wt% which were larger values than those for the UT specimens and CA-treated specimen cured with AA hardener. The value of T_g shifted −82.0 to 5.5°C compared with the UA specimen. In the tan δ curve, an α''-peak or a shoulder was observed for the α (α')-peak in the low temperature region. These peaks implied that water remained in the specimens after treatment by the hardeners or CA-treatment. The ratio of E' of the wetted specimens and UA-specimens was above 1 in the low temperature range, but smaller in the range from room temperature to high temperature. The effect due to the functional radical numbers of EP was observed only at room temperature.

(3) The value of E' was larger compared with the UT specimen in the low temperature range even if DA-cured specimens were aged or wetted for a long time. The mechanisms of water absorption and thermal aging above room temperature are different but the values of E' decreased for all the specimens. From the material standpoint, a high elastic modulus is expected for materials cured with DA compared with materials cured with AA when CA-treated materials are heated or wetted.

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