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Influence of aging and wetting on dynamic mechanical properties of multi-functional epoxy resins

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Abstract—Multi-functional epoxy resins with high heat resistance (high glass transition temperature, T_g) were cured with acid anhydrides and diamines. The influence of aging (thermal processing) and wetting (water absorption processing) on the dynamic mechanical properties of these materials was investigated. The aging was carried out by keeping the specimens in air at 130°C for a maximum of 5000 h and wetting was carried out in water at 21°C for 5000 h. The temperature dependence of multi-functional epoxy resins on the dynamic mechanical properties was measured.

The longer the aging time, the larger the weight reduction of the aged multi-functional epoxy resin, which reached a maximum of 3.9% after 5000 h. For the effect of hardeners, the specimens cured with diamines showed larger values. The value of T_g for all the specimens increased. Compared with the unaged materials, the dynamic storage modulus (E') of aged specimens was large at low temperatures (−140°C) for the samples cured with acid anhydrides and at high temperature (200°C) for the samples cured with diamines. The maximum water absorption rate of the wetted specimens was 5.1 wt% and those cured with diamines showed larger values while T_g decreased for all the specimens. Compared with the unaged material, some of the wetted specimens showed an increased E' at low temperatures (−140°C) and room temperatures (25°C) but all decreased at higher temperatures (200°C).

Keywords: multi-functional epoxy resin; aging; wetting; dynamic mechanical properties.

1. INTRODUCTION

Epoxy resin is a polymer material that has superior characteristics such as heat resistance and chemical resistance in addition to high strength [1]. Epoxy resins have many different chemical structures and there are also many types of hardener used in such resins as well [1]. For this reason, the mechanical properties such as dynamic storage modulus, glass transition temperature (T_g) and flexural strength vary greatly depending on the combination of epoxy resins and hardeners [2–4]. Three types of multi-functional epoxy resins were cured with multiple general purpose hardeners of acid anhydrides and diamines and were filled with functional short fibers made of Aramid or pitch-based carbon fibers [5–7] in order to develop heat-resistant composite materials. The affinity between the matrix and filled materials varied greatly among these materials [4, 8]. For carbon short fibers, the short fibers were treated

with plural coupling agents and were filled in the matrix in order to increase the affinity between the short fibers and the matrices. The dynamic mechanical properties and flexural strength of these filled materials increased even further as the affinity increased [9, 10].

In order to explore the usefulness of these materials, durability against sustained high temperature and water was investigated. In this paper, matrix (unfilled) materials were aged in air up to 5000 h at 130°C for heat-resistance and were wetted in distilled water for 5000 h at 21°C for water-resistance and the influence of each treatment on the dynamic mechanical properties of the materials was studied and compared with the result of unaged (0 h) materials [4].

2. EXPERIMENTAL

2.1. Materials

Table 1 shows three types of multi-functional epoxy resins (EP) and their abbreviations. EP·C and EP·L are tetra-functional and EP·Y is tri-functional. For comparison purposes, bisphenol-A type epoxy resin (EP·S) was used as a reference specimen. These EP materials were cured with three types of acid anhydrides and two types of diamines shown in Table 2. The curing condition is shown in Table 3 which is identical to the previous report [4] (for example, EP·C-A is EP·C cured with HHPA (abbreviated as A)).

Table 1.
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 2.
Hardeners

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

Table 3.
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 DMBA as accelerator using acid anhydride by 1.0 phr.

The molding boards obtained were 70 × 80 mm^2 in plane area and their thickness was 7–8 mm. They were thinned to a thickness of 3 mm and were cut to a width of 4 mm. The entire surfaces of the specimens were polished so that the surface skin layer of the specimens did not influence the elastic moduli [11] and were annealed at 80°C for 48 h for the measurement of dynamic mechanical properties.

The test specimens were thermally processed using a gear oven at 130°C which is lower than the glass transition temperature (T_g) of the reference specimen, EP·S. The aging time was 1000 h, 3000 h and 5000 h as well as 500 h for some specimens.

In the water absorption processing, the specimens were immersed in distilled water, vacuum pumped to remove air attached to the specimens and were then kept at 21°C under atmospheric pressure for 5000 h. These specimens were taken from water to be used for the measurement of the dynamic mechanical properties after the surfaces were wiped over with filter paper.

2.2. Measurements

2.2.1. Weight change of specimens. The weight change rates of the aged (thermally processed) specimens and the wetted (water absorption processed) specimens were obtained from the difference of weight before and after the processing. The specimens before the aging are called unaged (UA (0 h)) specimens [4].

2.2.2. Measurement of dynamic mechanical properties. The dynamic mechanical properties were measured using a Rheovibron DDV-25FP (manufactured by Orientec Inc.) of forced elastic type. The distance between the clamps was 52 mm, the clamping torque of the specimens to the clamp was 1.2 N m, the frequency was 110 Hz, the amplitude was 20 μm, the temperature range was −150°C to 300°C, the temperature increase rate was 2°C min^{-1} and the interval of measured temperature was 5°C.

3. RESULTS AND DISCUSSIONS

3.1. Influence of thermal processing

3.1.1. Weight change at thermal processing. Figure 1 shows the weight change of multi-functional epoxy resin (EP) specimens cured with acid anhydrides A(HHPA)

and diamine E(DDM) as hardeners. For the type of EP, the weight reduction of EP·C and EP·Y specimens was as small as 1–2 wt% over 500–3000 h. However, the weight reduction of multi-functional EP after it was aged for 5000 h increased to 1.4–3.9 wt%. The weight reduction of all the A-cured specimens, including the reference EP·S, was smaller than that of the E-cured specimens.

Table 4 shows the weight reduction of all the specimens after aging for 5000 h. The weight reduction of multi-functional EP was larger than that of the reference EP·S specimens regardless of the type of hardeners. The weight reduction of multi-functional EP cured with acid anhydrides was less than 2.8 wt% which was smaller than the 3.0–3.9 wt% of the diamine cured specimens. For the specimens cured with acid anhydride, the weight reduction cured with the C(MNA) hardener was small and for the specimens cured with diamine, the difference between the E(DDM) and the F(MPDA) series specimens was small. The weight reduction of the reference EP·S series was as small as 0.1–1.8 wt% and that of the specimens cured with diamine was small as well.

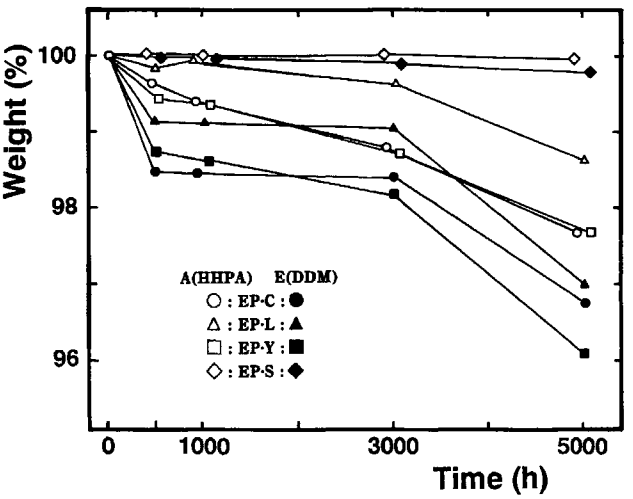

Figure 1. Time dependence of decrease of weight for aged specimens cured with A(HHPA) and E(DDM).

Table 4.
Decrease of weight (%) of epoxy resins after aging for 5000 h at 130°C

	Hardener				
	Acid anhydride			Diamine	
Epoxy resin	HHPA	MHPA	MNA	DDM	MPDA
EP·C	2.3	2.8	1.6	3.2	3.9
EP·L	1.4	1.3	1.6	3.0	3.5
EP·Y	2.3	–	1.1	3.9	3.5
EP·S	0.4	–	0.1	1.6	1.8

3.1.2. Temperature dependence of dynamic mechanical properties. Figure 2 shows the temperature dependence of E' (denoted as $E'_a(5000)$) and $\tan\delta$ of EP·L-C cured with C(MNA), which is acid anhydride, after aging for 5000 h. The value of $E'_a(5000)$ for EP·L-C increased in both the low temperature and high temperature ranges compared with $E'(E'(0))$ of the UA (0 h) specimen. The temperature dependence of $\tan\delta$ decreased in the temperature range higher than 75°C by the 5000 h aging and the α-peak became sharp.

A shoulder was observed at the α-peak shown by the $\tan\delta$ curve of aged EP·C-A as shown in Fig. 3, to the lower temperature side (175–225°C). This shoulder grew as the aging lasted longer for 500 and 1000 h and reached a maximum after 3000 h before getting smaller. This phenomenon is believed to be due to disturbance of molecular arrangement by curing of unreacted parts of the epoxy resin. However, the change of temperature (glass transition temperature, T_g) when the α-peak reached its maximum was just less than 3.0°C and the value of $\tan\delta$ was within the range of 0.310–0.315, reduced from 0.340 of the UA specimens. The specimens cured with B(MHPA) exhibited behavior similar to that of samples cured with A(HHPA).

Figure 4 shows the temperature dependence of $E'_a(5000)$ and $\tan\delta$ of EP·C-E cured with diamine E(DDM). The dependence of EP·C-E decreased at lower temperatures but increased in the higher temperature range. Other diamine cured specimens showed

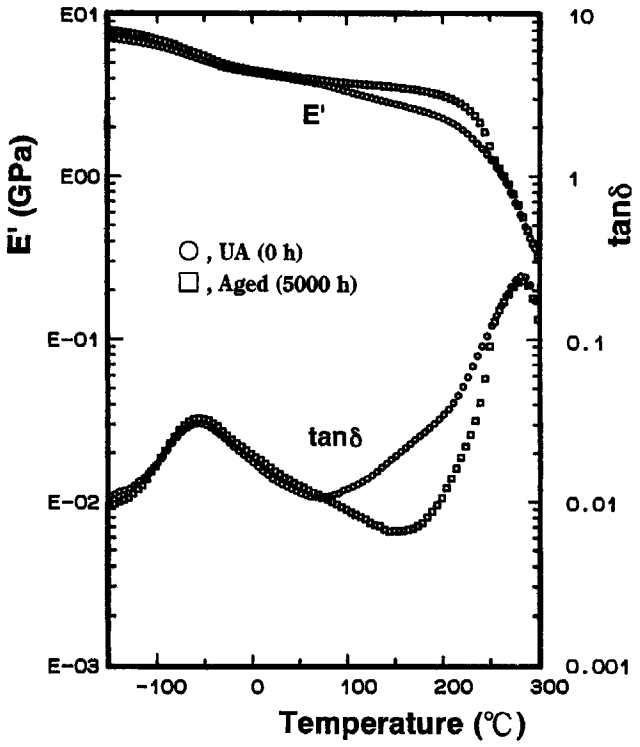

Figure 2. Temperature dependence of dynamic storage modulus (E') and $\tan\delta$ of multi-functional epoxy resin of EP·L-C(MNA) series.

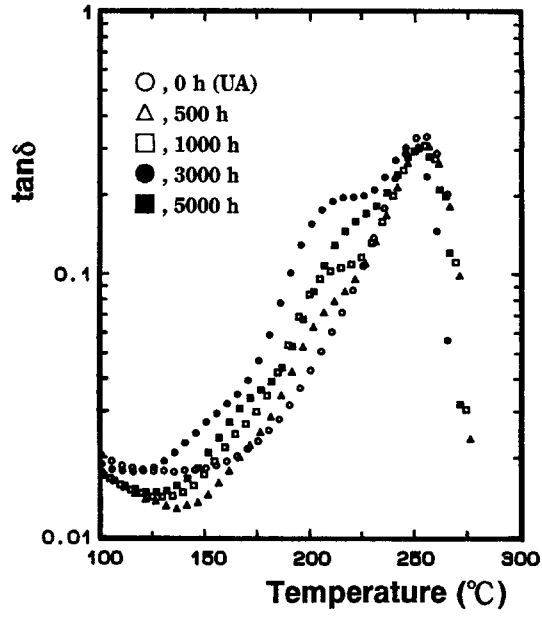

Figure 3. Temperature dependence of tan δ of aged EP-C-A(HHPA) specimens.

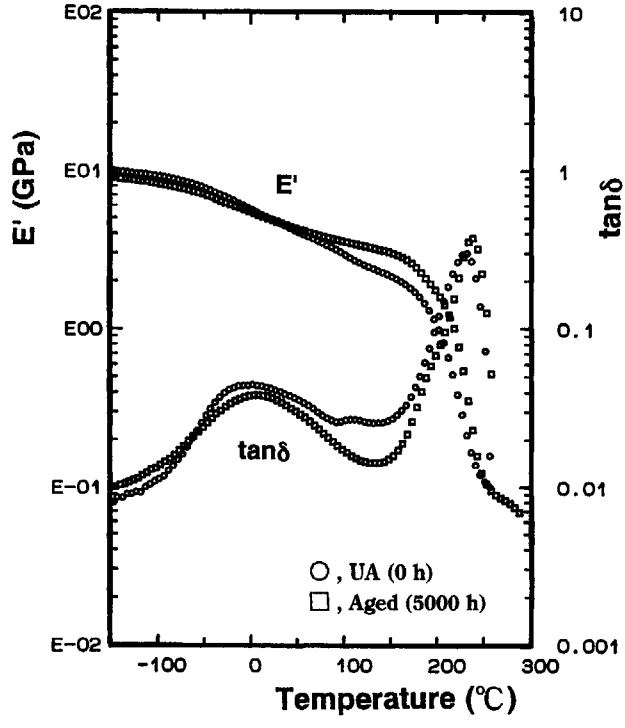

Figure 4. Temperature dependence of dynamic storage modulus (E') and tan δ of multi-functional epoxy resin of EP-Y-F(MPDA) series.

similar behavior but the increase of $E'_a(5000)$ of F(MPDA)-cured specimens in the high temperature range was larger than that of E-cured specimens.

In the tan δ curve of EP·C-E, the small peak of the UA specimens around 100°C disappeared upon aging and the α-peak became sharper shifting to the high temperature side. The broad β-peak around 0°C shifted to the high temperature side. Other diamine cured specimens showed similar behavior as EP·C-E and in particular the α-peak was significantly shifted to the high temperature side. According to thermal analysis of EP·L cured with p,p'-diaminodiphenylsulfone (DDS), thermal decomposition starts at above 250°C [13]. It was observed in this study that the small peak of the tan δ curve around 100°C disappeared, and the α-peak T_g became sharp and shifted to higher temperature; it can thus be concluded that the unreacted part was reacted by aging, thereby eliminating molecular arrangement disturbance [12].

3.1.3. Glass transition temperature. Table 5 shows the temperature where the α-peak of the UA (0 h) specimen [4] reaches the maximum, T_g of the specimen aged for 5000 h ($T_{ga}(5000)$), and their differences ($dT_{ga}(5000)$). The value of T_g for aged multi-functional EP rose faster than that of the UA specimens and the value of $dT_{ga}(5000)$ was in the range of 1.5–22.0°C.

For the type of multi-functional EP, the values of $dT_{ga}(5000)$ for all the EP·C and EP·L specimens except for the F(MPDA)-cured specimens were small while the values for the EP·Y specimens were more than 12.0°C. For the type of hardeners, the values of the EP·Y specimens cured with acid anhydrides were as large as 12.0–22.0 but the values for other specimens were small. In general, the values of $dT_{ga}(5000)$ for tetra-functional EP, i.e. EP·C and EP·L, were small and the values for tri-functional EP·Y specimens were large. The values of $dT_{ga}(5000)$ for the reference EP·S were larger than 0 and the values for EP·S-C(MNA) were as large as 23.5°C but the values for other cured specimens were small, including those cured by diamines.

3.1.4. Dynamic storage modulus. Figure 5 shows the aging time dependence of the dynamic storage modulus (E'_a) of aged EPs cured with A(HHPA) and E(DDM). The value of E'_a decreased for the first 1000 h for many specimens but the decreasing rate became smaller thereafter until 3000 h and the value more or less fluctuated if aged for 5000 h at −140°C in the low temperature range. At room temperature of 25°C,

Table 5.
Effect of aging for 5000 h on T_g of epoxy resins

	Epoxy resin											
	EP·C			EP·L			EP·Y			EP·S		
Hardener	UA	Aging	dT_g(°C)	UA	Aging	dT_g(°C)	UA	Aging	dT_g(°C)	UA	Aging	dT_g(°C)
HHPA	243.5	245.0	+1.5	252.5	257.0	+4.5	202.0	214.0	+12.0	150.0	156.5	+6.5
MHPA	240.0	245.5	+5.5	244.5	246.5	+2.0	–	–	–	–	–	–
MNA	256.0	–	–	280.0	282.0	+2.0	218.5	240.5	+22.0	176.5	200.0	+23.5
DDM	231.0	236.5	+5.5	262.5	265.5	+3.0	221.5	238.0	+17.5	182.5	186.0	+3.5
MPDA	242.5	254.5	+12.0	273.0	277.0	+4.0	224.5	244.5	+20.0	188.0	193.0	+5.0

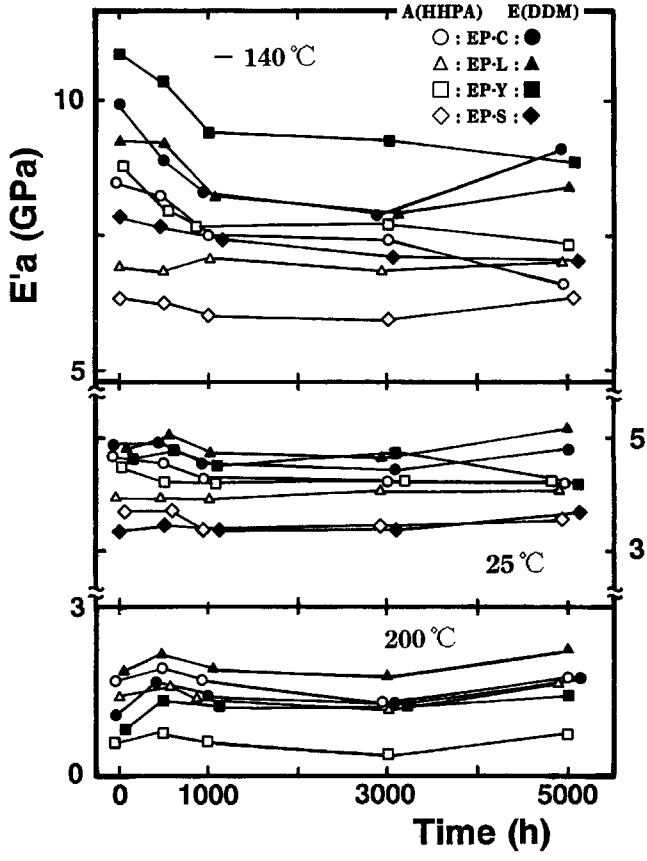

Figure 5. Time dependence of dynamic storage modulus of aged specimen (E'_a) cured with A(HHPA) and E(DDM).

the decreasing rate fluctuated depending on the type of EP but its range of variation was smaller than that at −140°C and at high temperature of 200°C, E' for many specimens increased.

Figure 6 shows the values of $E'_a(5000)$ at various temperatures for specimens, including specimens cured with other hardeners. For multi-functional EP, EP·Y > EP·C > EP·L at low temperature (−140°C) but at room temperature (25°C), the value for EP·C was larger and at high temperature (200°C), the value for EP·L was larger. The value for the reference EP·S was smaller than those for EPs over all the temperature ranges.

The value of $E'_a(5000)$ for the specimens cured with diamines was larger than that for the specimens cured with acid anhydrides and the value for F(MPDA)-cured specimens was the largest. For specimens cured with acid anhydrides, it was found that C(MNA) > A(HHPA) and B(MHPA).

Figure 7 shows the ratios of $E'_a(5000)$ to $E'(0)$ for each specimen. The value of $E'_a(5000)/E'(0)$ for multi-functional EP at low temperature (−140°C) was in the range of 0.7–1.4. For the type of hardeners, the value for the specimens cured with

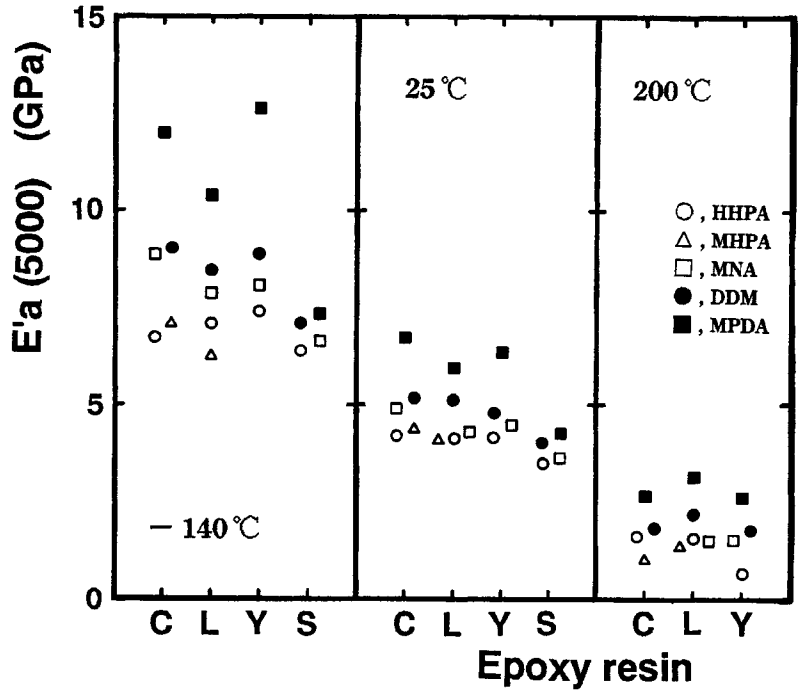

Figure 6. Dynamic storage moduli of aged multi-functional epoxy resins ($E'_a(5000)$).

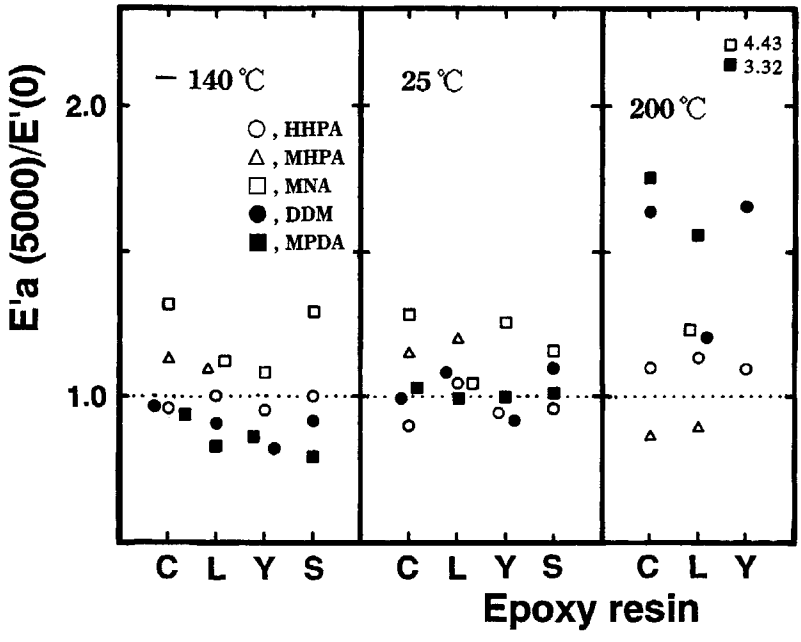

Figure 7. Ratios of dynamic storage modulus of specimens aged for 5000 h and UA (0 h) specimens ($E'_a(5000)/E'(0)$).

A(HHPA) was about 1 and the values for other specimens cured with acid anhydrides were larger than 1. For the specimens cured with diamines, although the value of E'_a was large but its ratio was less than 1. The value of $E'_a(5000)/E'(0)$ at room temperature (25°C) was as small as 0.9–1.3. For the specimens cured with acid anhydrides, the difference with the value at high temperature was small but the value for the specimens cured with diamines was around 1. At high temperature (200°C), the value of $E'_a(5000)/E'(0)$ for the specimens cured with acid anhydrides was greater than 1 for the A(HHPA)-cured specimens but was less than 1 for the B(MHPA)-cured specimens. On the other hand, all the values for the specimens cured with diamines increased and reached 1.75 for EP·C-F(MPDA). Both EP·Y-C(MNA) and F(MPDA) were in the transition range at 200°C and as a result of the increase of $E'_a(5000)$ by aging, the value of $E'_a(5000)/E'(0)$ became larger. The values of the reference EP·S specimens were about the same as those for multi-functional EP at both low and room temperatures.

3.2. *Influence of water absorption*

3.2.1. Water absorption rate. Table 6 shows the change of weight for each specimen, wetted by water absorption for 5000 h. Water absorption for unfilled polymer materials begins at cracks and voids on the specimen surfaces followed by diffusion into the polymer materials [14]. As the entire surfaces of the specimens were polished in this study in order to remove the influence of the skin layer of the surface, the water absorption rate was larger than that for the materials whose surface was covered by a skin layer, so the influence of water absorption was enhanced. The weight increase (water absorption rate) of multi-functional EP by wetting for 5000 h was in the range of 1.2–5.1 wt%. The value for the specimens cured with acid anhydrides was less than 3.0 wt% and the value for the specimens cured with B(MHPA) was as small as 1.2 wt%. On the other hand, the water absorption rate for the specimens cured with diamines was as large as 2.5–5.1 wt% and the value for EP·Y-F(MPDA) was the maximum. In general, the value for tetra-functional EP was smaller than that for tri-functional EP. The water absorption rate for the reference EP·S specimens was in the range of 0.4–0.6 wt% for the specimens cured with acid anhydrides and in the range of 1.6–2.0 wt% for the specimens cured with diamines, all of which were smaller than those for multi-functional EP.

Table 6.
Absorption of water (%) of epoxy resins after wetting for 5000 h at 21°C

	Hardener				
	Acid anhydride			Diamine	
Epoxy resin	HHPA	MHPA	MNA	DDM	MPDA
EP·C	1.7	1.2	1.9	3.1	2.7
EP·L	1.4	1.2	1.6	2.9	3.6
EP·Y	3.0	–	2.8	2.5	5.1
EP·S	0.4	–	0.6	1.6	2.0

3.2.2. Temperature dependence of dynamic mechanical properties. Figure 8 shows the temperature dependence of E' (E' for wetted specimens is denoted as $E'_w(5000)$) and $\tan\delta$ for EP·L-C cured with acid anhydride C(MNA) wetted for 5000 h.

The values of $E'_w(5000)$ for EP·L-C increased in the low temperature range and decreased in the high temperature range compared with E' ($E'(0)$) for the matrix (UA). The α-peak was shifted toward the low temperature side in the $\tan\delta$ curve of EP·L-C and the values around 100°C and the β-peak also increased. Similar behavior was observed for other specimens cured with acid anhydrides.

Figure 9(a), (b) show the temperature dependence of $E'_w(5000)$ and $\tan\delta$ of the specimens cured with diamine wetted for 5000 h. The $\tan\delta$ curve of the diamine cured specimens showed rather complex behavior compared with the specimens cured with acid anhydrides. The values of $E'_w(5000)$ and $E'(0)$ of EP·C-E (Fig. 9(a)) [4] decreased over the whole temperature range while those of EP·Y-F (Fig. 9(b)) increased in the high temperature range. The α-peak in the low temperature range in the $\tan\delta$ curve of EP·C-E appeared as a shoulder and the peak near 100°C was shifted toward the lower temperature while the β-peak was shifted toward the lower temperature. This is similar to the phenomenon in which EP·S cured with 1,3-diaminopropane is degraded once it is soaked in boiling water and the α-peak split into α' and α''-peaks [15]. The behavior of α' and α''-peaks in the $\tan\delta$ curve of EP·Y-F was similar to that of EP·C-E but the α'-peak became a shoulder (the α'-peak value was 0.10)

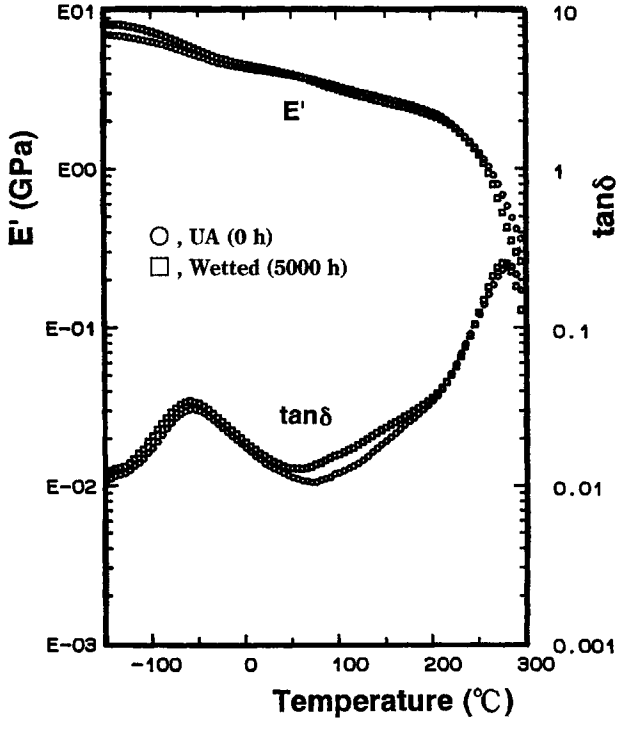

Figure 8. Temperature dependence of dynamic storage modulus (E') and $\tan\delta$ of multi-functional epoxy resin of EP·L-C(MNA) series.

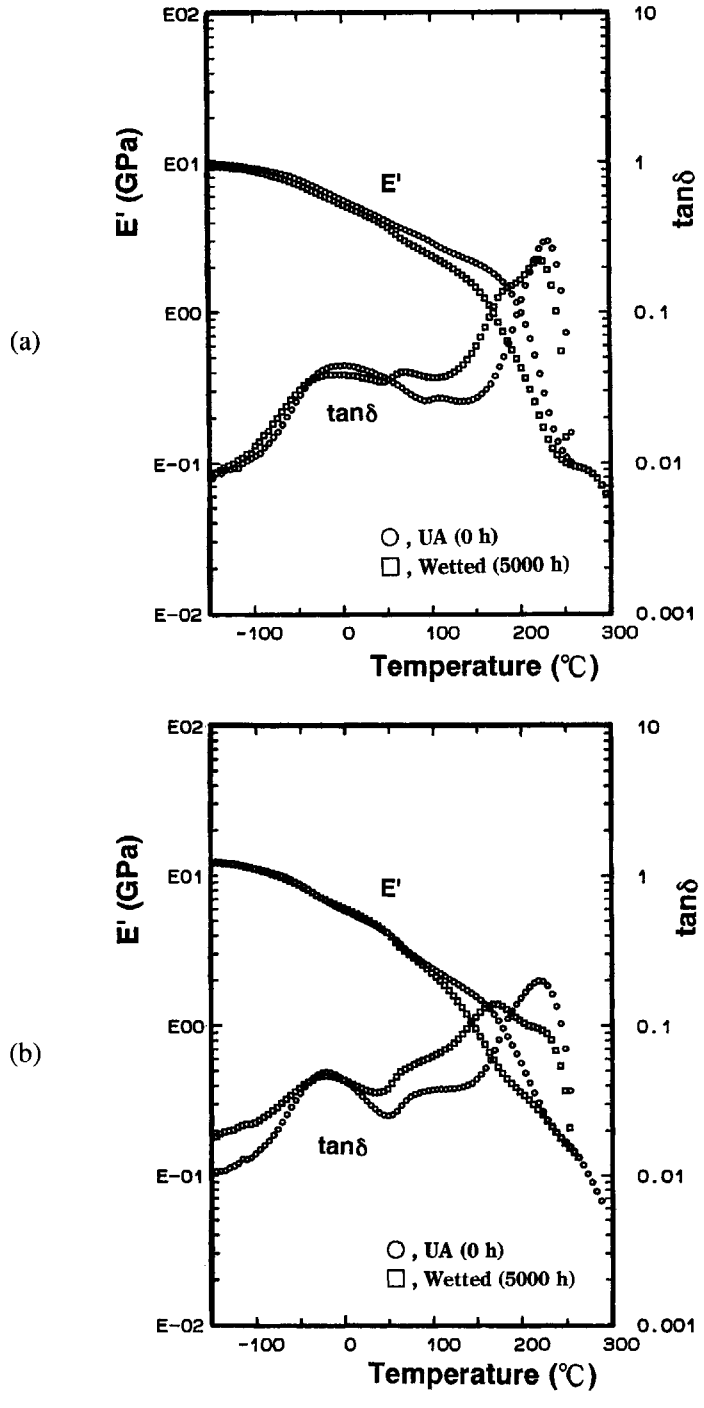

Figure 9. Temperature dependence of dynamic storage modulus (E') and tan δ of multi-functional epoxy resins cured with diamines. (a) EP·C-E(DDM) series; (b) EP·Y-F(MPDA) series.

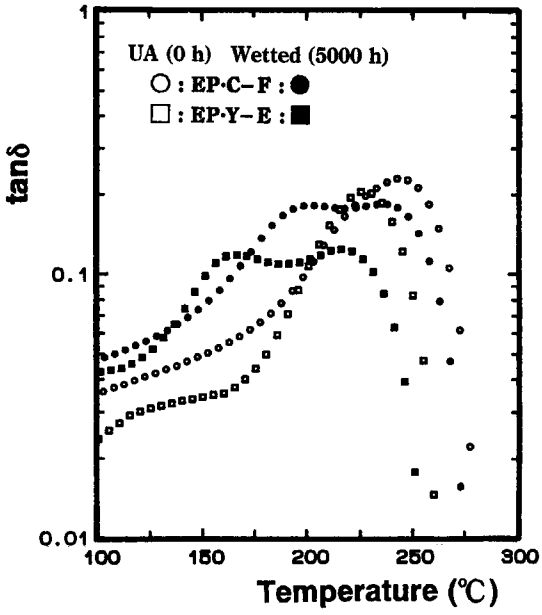

Figure 10. Temperature dependence of tan δ of wetted specimens.

and the value of the lower temperature was smaller than 0.14, which was the value of the α''-peak.

For the α-peak of the specimens cured with diamines, the α''-peaks of EP·C-F and EP·Y-E on the lower temperature side were larger, as shown in Fig. 10, and the α'-peak values on the high temperature side were 0.180 and 0.115 *versus* 0.179 and 0.120, which showed a smaller difference. Not only the values of the E-cured specimens but also the values of F-cured specimens decreased for the reference EP·S. In the specimens cured with diamines, many hydrogen bondings are formed in EP with an added hardener of amino groups [16]. When these specimens are wetted, water molecules tend to enter between the hydrogen bonding and, as a result, the α-peak is believed to split into α' and α''-peaks.

3.2.3. Glass transition temperature. Table 7 shows T_g of specimens wetted for 5000 h ($T_{gw}(5000)$). The value of $T_{gw}(5000)$ for multi-functional EP decreased more than that of the UA (0 h) specimens [4]. If a specimen has the α''-peak, its temperature is denoted as $T_{gw}(5000)$ but no α''-peak was observed in the specimens cured with acid anhydrides. However, the α''-peak was observed in many specimens cured with F(MPDA) among diamine-cured specimens and the value of $T_{gw}(5000)$ varied from -55.5 to -37.5. In the specimens cured with E(DDM), where no α''-peak was observed, the α''-peak may have disappeared during the process of raising temperature at 2 °C min^{-1}. In general, the influence of water absorption on $dT_{gw}(5000)$ is larger for the type of hardeners than for the number of functional groups of EP. The value of $dT_{gw}(5000)$ of the reference EP·S-F where the α''-peak was observed was as large as -29.5 °C.

Table 7.
Effect of wetting for 5000 h on T_g of epoxy resins

	Epoxy resin											
	EP·C			EP·L			EP·Y			EP·S		
Hardener	UA	Aging	dT_g(°C)	UA	Aging	dT_g(°C)	UA	Aging	dT_g(°C)	UA	Aging	dT_g(°C)
HHPA	243.5	238.5*	−5.0	252.5	243.0*	−9.5	202.0	199.0*	−3.0	150.0	143.0*	−7.0
MHPA	240.0	–	–	244.5	242.0*	−2.5	–	–	–	–	–	–
MNA	256.0	248.0*	−8.0	280.0	276.5*	−3.5	218.5	–	–	176.5	168.5*	−8.0
DDM	231.0	186.5	−55.5	262.5	249.5*	−13.0	221.5	168.5	−53.0	182.5	165.5*	−17.0
MPDA	242.5	205.0	−37.5	273.0	–	–	224.5	170.5	−54.0	188.0	158.5	−29.5

*Appeared only as an $\alpha(\alpha')$-peak.

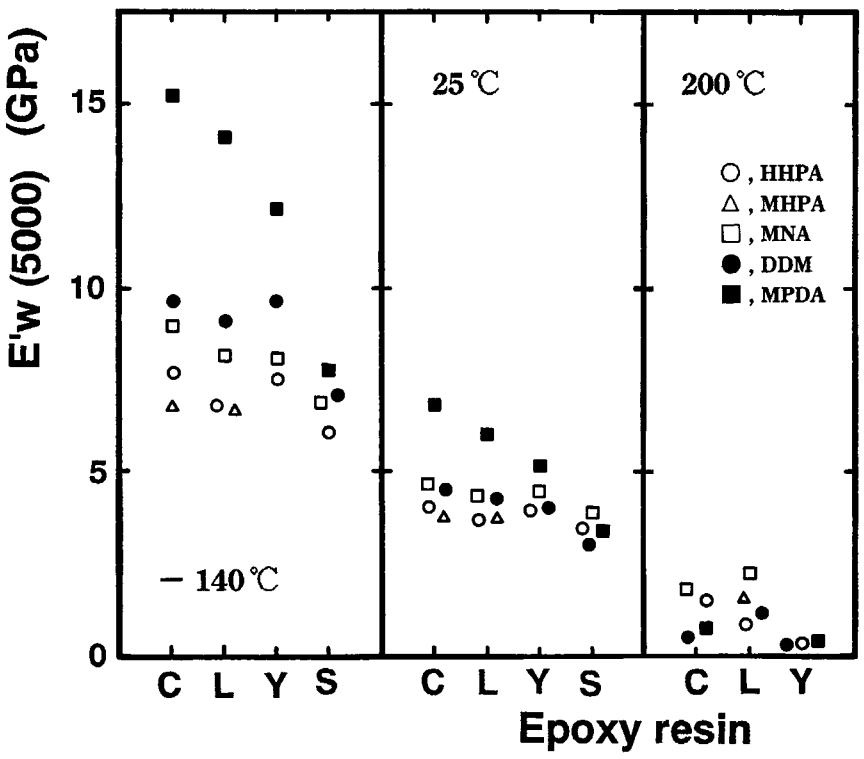

Figure 11. Dynamic storage moduli of wetted multi-functional epoxy resins ($E'_w(5000)$).

3.2.4. Dynamic storage modulus. Figure 11 shows the dynamic storage moduli ($E'_w(5000)$) of all the specimens wetted for 5000 h at −140, 25 and 200°C. In multi-functional EP, E' for the specimens cured with diamine was larger than that for the specimens cured with acid anhydrides, even in UA (0 h) specimens [4]. $E'_w(5000)$ for the wetted specimens cured with diamines at low temperature (−140°C) was large and the value for the specimens cured with F(MPDA) was large in particular. At room temperature (25°C), the value for the F-cured specimens was also large but

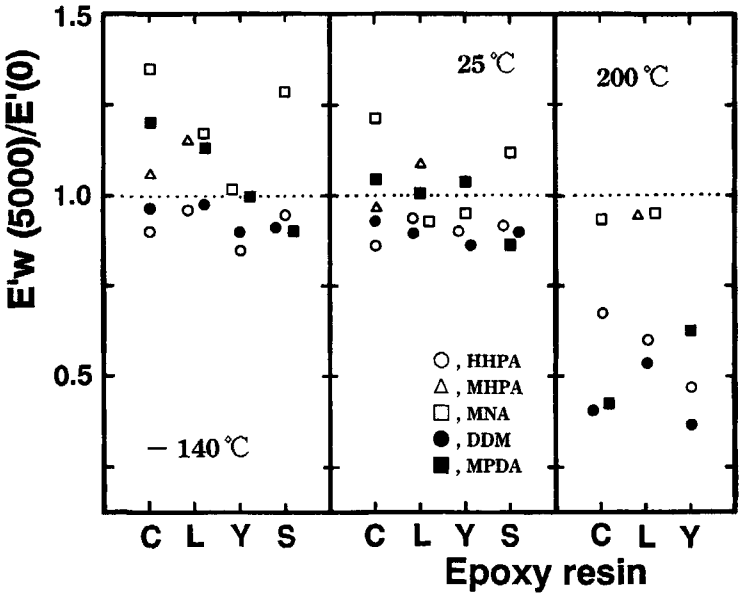

Figure 12. Ratios of dynamic storage modulus of specimens wetted for 5000 h and UA (0 h) specimens ($E'_w(5000)/E'(0)$).

the value for the specimens cured with E(DDM) was about the same as that for the specimens cured with acid anhydrides. At high temperature (200°C), the value for the specimens cured with diamines was influenced heavily by water absorption and was smaller than that for the specimens cured with acid anhydrides.

Figure 12 shows the ratios of E's ($E'_w(5000)/E'(0)$) of the specimen wetted for 5000 h and UA (0 h) specimens [4]. The value of $E'_w(5000)/E'(0)$ at low temperature (−140°C) was in the range of 0.9–1.4. For hardeners, the difference between acid anhydride and diamine was small but the values for the specimens cured with B(MHPA), C(MNA) and F(MPDA) were all larger than 1. At room temperature (25°C), $E'_w(5000)/E'(0)$ was in the range of 0.8–1.2. Only the F-cured specimens exhibited the value greater than 1 and the values for A- and E-cured specimens were less than 1, similar to those at low temperature. At high temperature (200°C), the values for all the specimens were between 0.3–1.0 and those for the specimens cured with diamine were as small as 0.5, which implies that the influence of water absorption was large. The influence of multi-functional groups of EP was small. The difference of the values of $E'_w(5000)/E'(0)$ for the reference EP·S specimens at low and room temperatures with those for multi-functional EP was small except for the F-cured specimens.

4. CONCLUSIONS

Three types of multi-functional epoxy resins (EP) cured with acid anhydrides and diamines, from which skin layers of the whole surfaces were removed, were aged

(processed thermally) for 5000 h and wetted (by water absorption) for 5000 h. By measuring the dynamic mechanical properties of these specimens, the following results were revealed:

1. Influence of aging (thermal processing). The weight decrease of multi-functional EP was in the range of 1.1–3.9 wt% but the value for the specimens cured with diamine was larger than that for the specimens cured with acid anhydride. The $\tan\delta$ curve varied depending on the type of hardeners but the α''-peak which was present in the diamine-cured specimens disappeared. The glass transition temperature (T_g) for all the specimens increased but the value for diamine-cured specimens were larger than that for the specimens cured with acid anhydride. The storage moduli of the aged specimen (E'_a) increased in the specimens cured with acid anhydrides at low temperature (−140°C) and decreased in the specimens cured with diamines. At high temperature (200°C), E'_a increased in many specimens and the value for the specimens cured with diamines was significantly larger.
2. Influence of wetting (water absorption). The water absorption rate of the specimens was 1.2–5.1 wt% and the value for the specimens cured with diamines was larger than that for the specimens cured with acid anhydrides. There was no α''-peak in the $\tan\delta$ curve of the specimens cured with acid anhydride but a large α''-peak appeared in the specimens cured with diamines on the lower temperature side and the α''-peak became larger than the α'-peak. The value of T_g decreased in all the specimens and this was very significant in the specimens cured with diamines. The influence of wetting on the dynamic storage modulus (E'_w) was small in the temperature range below room temperature but the decrease of E'_w was very significant at high temperature.
3. From the above, it is concluded that the influence of aging for 5000 h on the dynamic storage elastic modulus (E') of multi-functional EP is small. However, the influence of wetting on E' was large in the high temperature range and the difference with unaged specimens was large in the temperature range of over 50°C for the specimens cured with diamines and in the temperature range of over 100°C for the specimens cured with acid anhydrides.

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