Synthesis and Properties of Phosphorus Containing Advanced Epoxy Resins

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ABSTRACT: A series of advanced epoxy resins with various epoxy equivalent weights were synthesized from a reactive phosphorus-containing diol, 2-(6-oxido-6H-dibenz[c,e][1,2]oxaphosphorin-6-yl)-1,4-dihydroxy phenylene and diglycidyl ether of bisphenol A and then cured with 4,4′-diaminodiphenyl sulfone, phenol novolac, or dicyandiamide. The parameters of the polymerization reaction (such as reaction time, catalyst) are discussed in this article. Thermal properties of cured epoxy resins were studied using differential scanning calorimetry, dynamic mechanical analysis, and thermal gravimetric analysis. The flame retardancy of cured epoxy resins was tested by limiting oxygen index. The relations between thermal properties, flame retardancy, and epoxy equivalent weights were also studied. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 429–436, 2000

Key words: advancement; epoxy; flame retardancy; LOI

INTRODUCTION

Nearly all laminates suitable for printed wiring applications are based on thermosets. Compared with the commonly available thermoplastics, thermosets possess improved temperature performance and chemical stability because of the crosslinking that occurs upon curing to produce a three-dimensional rigid chemical structure. Epoxy resins possess a combination of desirable properties that have resulted in their widespread use for the fabrication of laminates. The most important desirable properties are high adhesive strength, low shrinkage, excellent chemical resistance, and thermal stability, ease of cure, and ready modification to optimize properties. Currently, >90% of thermosets used for printed wiring laminates are epoxy based. The resin in use is based mainly on the diglycidyl ether of bisphenol A (DGEBA) and the tetrabromo derivative of bisphenol A, which is used to provide flame retardancy. Present commercial laminates all contain tetrabromobisphenol A as a flame retardant which generates toxic and corrosive fumes upon combustion[1,2]; therefore, much effort has been focused on searching for a nonhalogen fire retardant. Recently, organophosphorus compounds have demonstrated good ability as a flame retardant for polymers and have also been found to generate less toxic gas and smoke than halogen-containing compounds.[3–22] In our previous article,[13] we developed a series of phosphorus-containing polyesters with a reactive phosphorus containing diol, 2-(6-oxido-6H-dibenz[c,e][1,2]-oxaphosphorin-6-yl)-1,4-dihydroxy phenylene (*I*) (Scheme 1), and established their thermal stability (T_d 5% > 460°C) and flame retardancy [limiting oxygen index (LOI > 37]. We also used this reactive phosphorus reagent (*I*) as a curing agent with the glycidyl ether of cresol formaldehyde novolac.[14] A V-0 grade in UL-94 vertical test[14] was achieved when the phosphorus content was > 1.1%. An advanced epoxy with epoxy equivalent weights (EEW) = 483 g/eq was also

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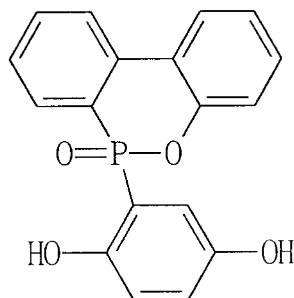


Scheme 1 The structure of 2-(6-oxido-6H-dibenz[c,e]-[1,2]oxaphosphorin-6-yl)-1,4-dihydroxy phenylene (*I*).

synthesized as reported in the same article[14] and a V-0 grade in UL-94 vertical test was also achieved when this advanced epoxy resin was cured with 4,4′-diaminodiphenyl methane. However, the effect of EEW on properties and reaction conditions for advancement (such as reaction time and catalyst) was not discussed. The purposes of this study were: 1. to synthesize a series of advanced epoxies with various EEW derived from (*I*) and DGEBA and discuss the effect of reaction time, type, and concentration of catalyst on the polymerization reaction. Furthermore, the effects of EEW (or phosphorus content) on thermal properties, flame retardancy, and moisture absorption were also studied; 2. to prepared FR-4 grade (flame retardancy, grade 4) laminate, that is, to prepare a varnish that contains advanced epoxy (EEW = 430 g/eq), dicyandiamide (DICY), and 2-methyl imidazole (2-MI) and then impregnate it into glass fiber cloth. Finally, the flame retardancy and thermal properties of the resulting laminate were tested.

EXPERIMENTAL

Materials

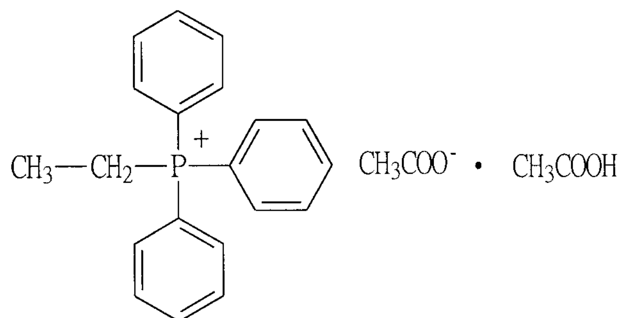
2-(6-oxido-6H-dibenz [c,e] [1,2] oxaphosphorin-6-yl)-1,4-dihydroxy phenylene was synthesized according to the previous procedure.[15] DGEBA with EEW 187 g/eq and phenol novolac (PN) with an OH equivalent weight of 105 g/eq were supplied kindly by CCP in the Republic of China. Ethyl triphenyl phosphonium acetate acetic acid complex (A-1) (Scheme 2) was purchased from Morton Chemical. 2-MI, triphenyl phosphine (Ph_3P), 4,4′-diaminodiphenyl sulfone (DDS) and DICY were purchased from Acros (Geel, Belgium). All solvents were commercial products and used without further purification.

Characterization

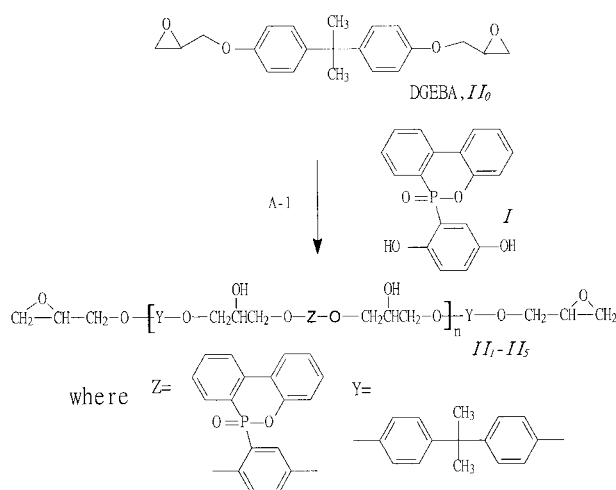
Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer TGA 7 at a heating rate of 20°C/min under nitrogen or air from 60 to 800°C. Dynamic mechanical analyses (DMA) were made with a Perkin-Elmer DMA 7e. The storage modulus G′ and tan δ were studied when the sample was subjected to temperature scan mode at a programmed heating rate of 5°C/min from ambient to 220°C at a frequency of 1 Hz and an amplitude of 4 μm. A sample 15 mm in length, 10 mm in width, and ≈1.5 mm in thickness was used. The test method was performed in the three point bending mode with a tension ratio at 110%. EEW of advanced epoxy resins were determined by the $HClO_4$/potentiometric titration method. Moisture absorption was tested as follows: Samples with 5-cm diameter and 0.3-cm thickness were dried under vacuum at 120°C until moisture had been expelled. After cooling to room temperature, the samples were weighed and then placed in water for 312 h and weighed at various times. The moisture absorption was calculated as percent weight gain = $(W/W_o - 1) \times 100$, where W = weight of sample after standing in water for various times, and W_o = weight of sample before placing in water. The LOI was determined with an Atlas Limiting Oxygen Index Chamber according to the standard procedure (ASTM D-2863-77).

Advancement of Epoxy

DGEBA (EEW 187, II_0) was reacted with various moles ratio of *I* at 160°C for 120 min in the presence of 0.1 wt % of A-1 catalyst (based on total weight). Thus, advanced epoxy resins with various EEW were obtained. A typical experimental procedure for II_3 (phosphorus content =2.14 wt %) is shown (see Scheme 3 and Table I).



Scheme 2 The structure of ethyl triphenyl phosphonium acetate acetic acid complex (A-1).



Scheme 3 Scheme of polymerization reaction.

To a four-neck round-bottom flask equipped with a heating mantle, stirrer, thermocouple, and temperature controller, DGEBA, 56 g was added. The epoxy resin was heated to 120°C and then vigorously stirred and dehydrated for 2 h. Under a nitrogen atmosphere, *I* 16.2g and 0.1 wt % A-1 catalyst were added at 120°C. The reaction temperature gradually rose to 150°C because of its exothermic character. After the exotherm subsided, the reaction mixture was then heated to 160°C and maintained at this temperature for 120 min.

The other advanced resins were synthesized in the same way as described above and the sample codes and EEW are shown in Table I.

Curing Procedure for Advanced Epoxy Resins

By Hot Plate Melting Method

The phosphorus containing advanced epoxy (II_1-II_5) and the DGEBA (II_0) were cured with DDS or PN. The reactants were mixed in a 1:1 equivalent ratio. The mixture was heated on a hot plate at ≈130–150°C with a continuous stirring until DDS or PN was completely dissolved in epoxy. Ph_3P (0.2 wt %) was added into the PN curing system (the DDS curing system did not require catalyst) and stirred by hand until a homogeneous solution was obtained. Then the mixtures were cured at 150°C for 1 h and postcured at 180°C for 4 h. After that, samples were allowed to cool slowly to room temperature to prevent cracking. The sample code for the II_0-II_5/DDS system was named III_0-III_5, and the II_0-II_5/PN system was named IV_0-IV_5.

By Solution (Immersed with Glass Fiber Cloth)

DICY, a popular curing agent for FR-4 laminate, with its high melting point (210°C), high reactivity, and low solubility in epoxy is very difficult to handle by the hot plate curing method. Because the surface of DICY particles will react with epoxy to form a gel encapsulating unreacted DICY in the center, a mixture of acetone and DMF as solvent was used to dissolve DICY, II_4 (its EEW is suitable for FR-4 laminate) and various amounts of 2-MI (0.3, 0.5, 0.7, and 0.9 phr, respectively, and the corresponding sample codes of cured epoxies are V_4-0.3, V_4-0.5, V_4-0.7, V_4-0.9, respectively) to form varnishes for the impregnation of glass fiber cloth. The viscosity of the varnish was adjusted to control the weight of resin remaining on the fiber glass cloth. The impregnated glass fiber was dried at 170°C for various times to control the gel time of prepreg which was ≈150 s (170°C) and then cured under pressure of 20 kg/cm^2 at a programmed temperature. The temperature program is shown in Figure 1.

Table I Sample Code and LOI of Advanced Epoxy and Cured Advanced Epoxy Resins

Epoxy	II_0	II_1	II_2	II_3	II_4	II_5
EEW	187	284	303	353	440	532
Phosphorus content (%)	0	1.41	1.70	2.14	2.70	2.89
Curing agent	DDS	DDS	DDS	DDS	DDS	DDS
Sample ID	III_0	III_1	III_2	III_3	III_4	III_5
LOI	22	28	30	31	31	32
Curing agent	PN	PN	PN	PN	PN	PN
Sample ID	IV_0	IV_1	IV_2	IV_3	IV_4	IV_5
LOI	21	26	30	31	32	32

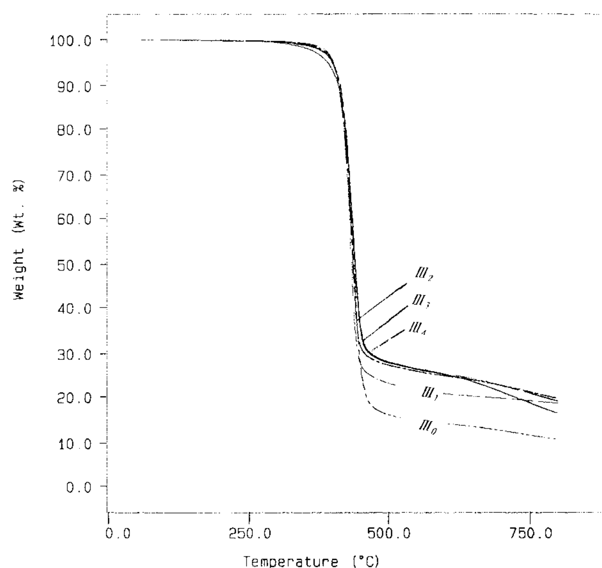


Figure 1 TGA curves of the *III* series epoxy resins under nitrogen.

RESULTS AND DISCUSSION

Effect of Reaction Time

Runs 1–5 shown in Table II display the effect of reaction time on EEW of polymerizing resins. The reaction is at ≈86% completion after the first 30 min. EEW increases with time and reaches a constant value after 120 min, assuming the reaction is near completion (conversion→95%) after 120 min.

Effect of Catalyst

Comparing the EEW of run 4 and run 7, we conclude that 2-MI is a better catalyst than A-1 for the polymerization reaction. 2-MI shows higher a reaction rate than A-1 even when the concentration of 2-MI is only 1/10th that of A-1. This may be attributed to the basicity of 2-MI which is higher than that of A-1; thus, it facilitates the polymerization reaction. However, 2-MI concentration exceeding 0.05 wt % (run 8) results in gel formation (with some gel particles insoluble in chloroform).

To increase the adhesion strength between layers, a broad molecular weight distribution is necessary. Thus, an advanced epoxy with high EEW (EEW ≒ 700) was synthesized and then blended with II_0 to broaden the molecular weight distribution. Thus, DGEBA/*I* =1.64/1 (runs 9–11) was used; however, all resulted in some gel particles even if the catalyst concentration was lowered. This strange phenomenon (which did not happen in DGEBA/BPA = 1.64/1 system) is still under investigation.

Thermal Properties of Cured Advanced Epoxy Resins

TGA Analysis

TGA traces of phosphorus-containing epoxy resins provided additional information regarding their thermal stability and thermal degradation behavior. TGA curves of *III* series resins under nitrogen and air are shown in Figures 1 and 2. The onset of degradation (T_d onset) temperatures for $III_1 \approx III_5$ are the same as DGEBA/DDS (III_0) under nitrogen, but slightly lower than III_0 under air. Compared with other phosphorus containing polymers,[6,7] the decomposition temperatures of $III_1 \approx III_5$ were extremely high even though this advanced epoxy has less crosslink density than III_0. Sato and Yokoyama[17-20] have reported that

Table II Reaction Condition and EEW of Advancement Resins

Run	1	2	3	4	5	6	7	8	9	10	11
DGEBA (g)	36	36	36	36	36	36	36	36	33.8	33.8	33.8
(*I*) (g)	14	14	14	14	14	14	14	14	16.2	16.2	16.2
DGEBA/I mol ratio	2.2 : 1	2.2 : 1	2.2 : 1	2.2 : 1	2.2 : 1	2.2 : 1	2.2 : 1	2.2 : 1	1.64 : 1	1.64 : 1	1.64 : 1
A-1 (wt %)	0.1	0.1	0.1	0.1	0.1				0.1	0.1	0.05
2-MI (wt %)						0.005	0.01	0.05			
EEW (g/eq)	414	430	443	454	457	417	484	(gel)[a]	(gel)[a]	(gel)[a]	(gel)[a]
Reaction time (min)	30	60	90	120	150	120	120	25	120	60	60

[a] With some gel particles insoluble in chloroform.

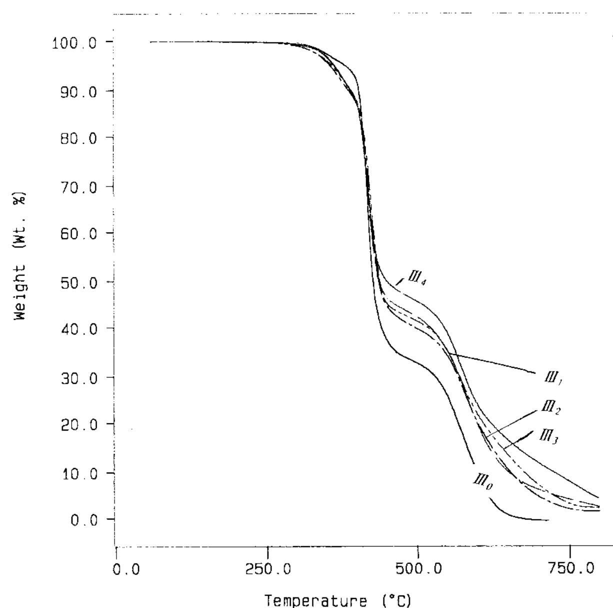


Figure 2 TGA curves of the *III* series epoxy resins under air.

polymers with a high aromatic content would possess both fire retardancy as well as thermal stability. The high T_d in the advanced epoxy may be attributed to the high aromatic content of the phosphorus containing diol (*I*). It may also be attributed to the cyclic O═P—O chain being more thermally stable than the open one,[6,7,10,11] that is, an introduction of doubly-stranded units into the backbone may enhance their thermal stability.[17–20] Chang and Chang[21] have reported on a series of flame-retardant phosphorus-containing copolyesters and found their decomposition temperature decreased with phosphorus content because of the thermal stability of these flame retardants not being as good as PET. However, this phenomenon was not observed in our system. Figures 1 and 2 show that the decomposition temperatures of III_1-III_5 are almost the same, which implies that the flame retardant in our system is thermally quite stable. TGA traces of the cured advanced epoxy resins showed higher char yields than III_0 under nitrogen and air. Less than 1% char yield was found in III_0 at 700°C under air; however, 10≈18% char yields were found in III_1-III_5. Van Krevelen[22] has proposed that the char residue on pyrolysis is linearly proportional to the oxygen index of halogen-free polymers. Increasing char formation limits the production of combustible gases, decreases the exothermicity of the pyrolysis reaction, and decreases the thermal conductivity of the burning materials, and consequently limits the flammability of the materials. The results shown in Figures 1 and 2 imply that the flame retardancy of the epoxy resins was elevated via the phosphorus group. Furthermore, the increase in char yield with phosphorus content also implies that the flame retardancy was increased with phosphorus content. This result is consistent with LOI measurements discussed below (Table I). Similar results were observed in *IV* series epoxy resins under nitrogen and air. Good thermal stabilities (T_d 5% ≒ 404°C in nitrogen and 378°C in air) were also observed when these advanced epoxy resins were cured with PN.

LOI Measurement

The LOI value can be used as another indicator for polymer flame retardancy. Thus, the cured advancement epoxy resins were examined further by measuring their LOI and the results are shown in Table I. Table I demonstrates that a higher LOI value is obtained with the increase in phosphorus content. LOI increases drastically from 22 to 28 (meets the flame-retardant criterion) when phosphorus content is increased from 0 to 1.41%. Thus, the incorporation of 1.4% phosphorus into cured epoxy chain has made these advanced epoxies of a flame-retardant grade. However, it reaches a plateau when the phosphorus contents exceed 2.1%. This phenomenon was also observed by Chang and Chang[21] who reported that 0.7% of phosphorus would make the copolyester meet the flame-retardant criterion reaching a plateau after P%→0.7%. Similar LOI values were observed for the ***IV*** series of epoxy resins (Table I).

DMA Analysis

Detailed information may be obtained from measurements of the dynamic mechanical behavior of samples as a function of temperature. Figure 3 shows the dynamic mechanical analyses curves of *III* series epoxy resins. All epoxy resins showed similar modulus by the dynamic mechanical analyses. Because their glass transition temperatures (T_gs) were difficult to obtain by differential scanning calorimetry, because of high crosslink density of cured epoxy resins, T_gs were also determined by DMA. T_g (taken as the peak of α relaxation, i.e., peak of tanδ) decreases with increasing EEW of advanced epoxy. III_0 has less tangent loss and higher T_g than III_1-III_5 which implies that III_0 is more rigid than III_1-III_5, which may be attributed to its higher crosslink density than

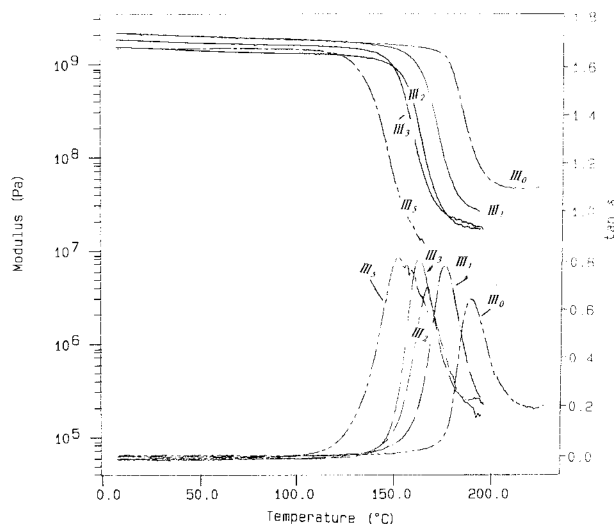
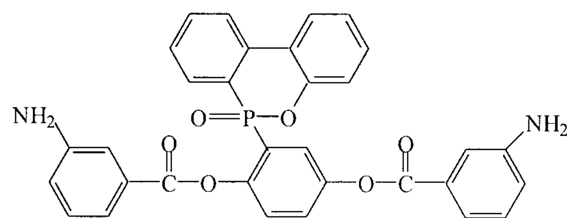


Figure 3 Dynamic mechanical analysis of the *III* series epoxy resins.

that of the advanced cured epoxy resins. For the *III* series, the best fitting equation between T_g and EEW is T_g (°C) = $3.4*10^{-4}$ EEW^2 − $3.5*10^{-1}$ EEW + 245. Similar DMA behaviors were observed (Fig. 4) when these advanced epoxy resins were cured with PN. For the *IV* series, the best fitting equation between T_g and EEW is T_g (°C) = $1*10^{-4}$ EEW^2 − $3.9*10^{-3}$ EEW + 155.

According to our previous article,[23] there is a β relaxation when phosphorus containing curing agent (shown in Scheme 4) is used to cure DGEBA.

The transition at 50–80°C has been assigned to the mobility of the side chain accompanied by some conformational rearrangements in the main chain.[24,25] DMA analyses shown in Figures 3 and 4 show that there is no β relaxation at ≈50–80°C for all cured advanced epoxy resins; thus, this phenomenon seems to conflict with our previous studies.[23] The reason why there is no β relaxation at ≈50–80°C when the bulky phosphorus group is on the epoxy chain, whereas a β relaxation exists when the bulky phosphorus group is on the curing agent is still unknown. Thus, additional work is required to characterize this reason.



Scheme 4

Figure 5 shows DMA curves of V_4-0.3, V_4-0.5, V_4-0.7, and V_4-0.9 (the meaning of the sample code is described in the Experimental section). Because they were glass fiber cloth reinforced epoxy resins, these systems have higher moduli than *III* and *IV* series resins. Their initial storage moduli were 30–110 Gpa, whereas *III* and *IV* series were ≈2 Gpa. The loss tangents of the *V* series were ≈0.15, also much less than those of the *III* and *IV* series. There is no correlation between concentration of catalyst on the T_g. When the quantity of 2-MI increases, the initial modu-

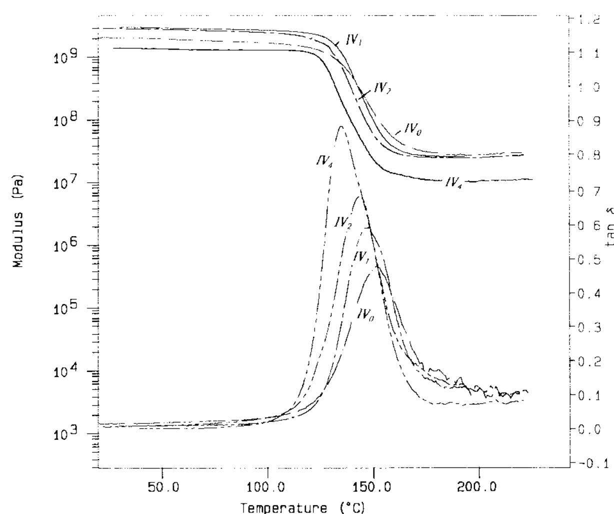


Figure 4 Dynamic mechanical analyses of the *IV* series epoxy resins.

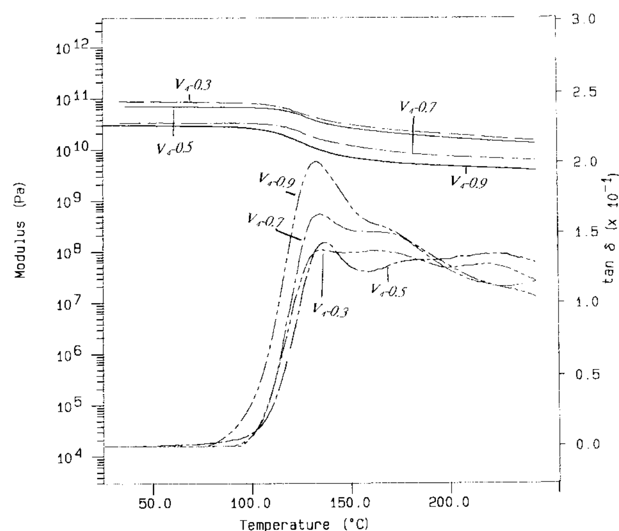


Figure 5 Dynamic mechanical analyses of the *V* series epoxy resins.

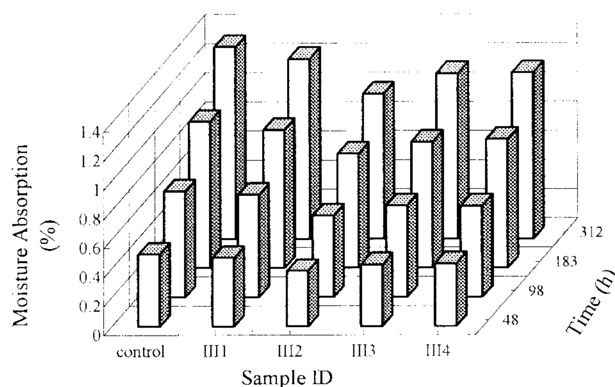


Figure 6 Moisture absorption of the *III* series epoxy resins.

lus decreases. T_gs of these laminates are ≈130°C, which is higher than the 120°C for regular FR-4 laminate made from tetrabromobisphenol A. LOI of the V_4 series is ≈34 which is higher than 28 (criterion for FR-4 laminate) and is also higher than the *III* and *IV* series. This may be attributed to the nitrogen content of DICY ($N\% = 67\%$) being higher than DDS ($N\% = 11.2\%$) and PN ($N\% = 0$). A nitrogen-phosphorus synergistic effect causes these laminates to exhibit higher flame retardancy.

Moisture Absorption

Figure 6 shows moisture absorption of the *III* series epoxies. An interesting phenomenon is observed: moisture absorption first decreases with the increase in EEW, then increases with increasing EEW. In general, advanced epoxy resin with a larger EEW has more OH groups (see repeating unit in Scheme 3) than DGEBA and, thus, should have higher moisture absorption. Furthermore, larger EEW has lower crosslink density than DGEBA, i.e., larger free volume than DGEBA, thus should also have higher moisture absorption. Thus, the observed phenomenon may be attributed to some reasons other than hydrogen bonding between OH and H_2O. The only structural difference between the *III* series epoxies is the quantity of "Z structure," i.e., bulky phosphorus containing group (see Scheme 3) which may have reduced the moisture absorption of the resins because of the hydrophobic properties of the "Z" group. Two competing effects existed in these advanced epoxy resin, i.e., "Z structure" effect was more important than EEW when EEW was smaller than 303 (III_2), whereas the EEW effect became more important than "Z structure" when EEW was larger than 303 (III_2). However, the actual reason is still under study.

CONCLUSION

A series of advanced epoxy resins were synthesized and their thermal properties and flame retardancy were examined. Among the epoxy resins investigated, III_2 had the least minimum moisture absorption. The T_gs of these cured advanced epoxy resins are higher than 130°C. For the *III* series, the best fitting equation between T_g and EEW is T_g (°C) = $3.4{*}10^{-4}$ EEW^2 − $3.5{*}10^{-1}$ EEW + 245. For the *IV* series, the best fitting equation between T_g and EEW is T_g (°C) = $1{*}10^{-4}$ EEW^2 − $3.9{*}10^{-3}$ EEW + 155. The 5% decomposition temperatures in nitrogen are approximately the same as DGEBA. LOI and char yields (at 700°C) of phosphorus containing advanced cured epoxy resins were higher than those of the III_0 or IV_0 implying the flame retardancy of the epoxy resins was elevated via the phosphorus group. When 1.41% of phosphorus was introduced into the epoxy resins, an LOI value of 28 was achieved. These properties should make these epoxies attractive for practical applications such as flame-retardant laminates. More detailed studies, such as dielectric constant, dissipation factor, blister resistance, and other electrical properties will be examined in the future.

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