A Simple Imide Compound as a Curing Agent for Epoxy Resin. I. Synthesis and Properties

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ABSTRACT: A simple imide compound, 4-amino-phthalimide (APH), was synthesized as a curing agent for epoxy resin. APH was prepared from the hydration of 4-nitro-phthalimide, which was prepared from the nitration of phthalimide. The chemical structure of APH was verified by IR and ^{1}H-NMR spectra. The thermal properties and dielectric constant (ε) of a phosphorus-containing novolac epoxy resin cured by APH were determined and compared with those of epoxy resins cured by either 4,4′-diamino diphenyl methane (DDM) or 4,4′-diamino diphenyl sulfone (DDS). The results indicate that the epoxy resin cured by APH showed better thermal stability and a lower ε than the polymer cured by either DDM or DDS. This was due to the introduction of the imide group of APH into the polymer structure. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 2052–2059, 2008

Key words: additives; dielectric properties; resins; synthesis; thermal properties

INTRODUCTION

Epoxy resins are known to have many excellent properties, including good chemical and solvent resistances, high mechanical strengths, and high distortion temperatures. Therefore, they have been applied not only in the traditional fields such as adhesives and coatings but also in advanced technological areas such as the electronics and aerospace industries.[1] So they may be widely applied as materials in advanced technological areas, it is essential to improve the flame retardancy and thermal properties and reduce the dielectric constant (ε) of epoxy resins.[2–5] The latter factor is important especially in electronics packaging, as low dielectric materials can minimize crosstalk and maximize signal propagation speed in these devices.[5,6]

In general, the flame-retardancy and thermal and dielectric properties of epoxy polymers can be improved through modification of the molecular structure. For example, epoxy resins show enhanced flame retardancy and thermal properties when their structures incorporate phosphorous-containing compounds such as 9,10-dihydro-9-oxa-10-phosphaphenanthrene.[7,8] As polyimides show good thermal stability and low ε, the introduction of imide groups into the epoxide structure to make epoxy–imide resins have been prepared and developed.[2–5,9,10]

Three methodologies are often used to make epoxy–imide resins: (1) the modification of the backbone of the epoxy with imide groups, (2) the use of a curing agent that contains imide groups, and (3) a combination of these two methods.[11] With regard to the second methodology, curing agents containing imide groups such as hydroxyl-terminated imide compounds, imide acid, and imide amine have been used.[3,4,12–15] In this study, a simple imide compound, 4-amino-phthalimide (APH), was synthesized as a curing agent for novolac epoxy resin. APH was prepared from the hydration of 4-nitro-phthalimide (NPH), which was prepared from the nitration of phthalimide. The thermal properties and ε of the epoxy resin cured by 4-amino-phthalimide (APHE) were determined and are discussed. These properties were compared with those of an epoxy resin cured by 4,4′-diamino diphenyl methane (DDME) and an epoxy resin cured by 4,4′-diamino diphenyl sulfone (DDSE).

EXPERIMENTAL

Materials

Phthalimide (Acros, Morris Plains, NJ, 99%) was purified by boiling water and ethanol. SnCl$_2$·H$_2$O (Showa, Tokyo, Japan), 4,4′-diamino diphenyl methane (DDM; Aldrich, St. Louis, MO; 97%), and 4,4′-diamino diphenyl sulfone (DDS; Acros, 97%) were used without further purification. A phosphorous-containing novolac epoxy resin (trade name NPCN-
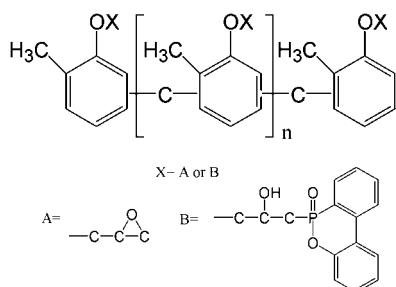
Figure 1 Chemical structure of NPCN-703H.

703H) with an epoxide equivalent weight of 398.2 was kindly supplied by Nan Ya Plastics (Taipei, Republic of China). NPCN-703H was prepared from cresol formaldehyde novolac epoxy resin reacted with 9,10-dihydro-9-oxa-10-phosphaphenanthrene. Figure 1 shows the chemical structure of NPCN-703H. N,N-Dimethylformamide (Tedia, high performance liquid chromatography grade, Tedia, Fairfield, OH grade) was purified by distillation under reduced pressure over P_2O_5.

Synthesis of APH

APH was prepared from the hydration of NPH, which was prepared from the nitration of phthalimide.[16,17] The reaction equations are shown next:
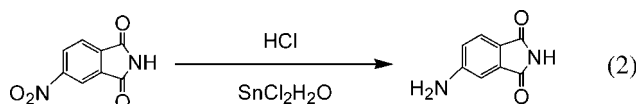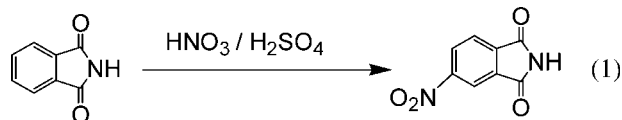
Phthalimide (40 g) was added and dissolved gradually in a four-necked, round-bottom flask containing 270 mL of $4M$ $HNO_3/13.5M$ H_2SO_4 at 15°C. The reaction mixture was heated to 35°C. The degree of reaction was monitored by thin-layer chromatography (TLC) with ethyl acetate/n-hexane in a volume ratio of 1 : 4 as an effluent. The reaction was complete in 1 h from the TLC analysis. The solution was then cooled in ice water, and the solvent was removed by filtration under reduced pressure. The filtered precipitate was purified by recrystallization from ethanol and then dried in a vacuum oven at 80°C for 12 h. The dried precipitate was NPH, and the yield was about 52%.

NPH (10 g) and $SnCl_2·H_2O$ (50 g) were added and dissolved gradually in a four-necked, round-bottom flask containing 270 mL of $9M$ HCl at room temperature. The reaction mixture was heated to 50°C and

maintained at that temperature for 2 h. From the TLC analysis of the reaction mixture, the reaction was complete. The solution was then cooled, and the solvent was removed by filtration under reduced pressure. The filtered precipitate was washed further with distilled water to remove excess HCl solution. The washed solid was purified by recrystallization from ethanol and then dried in a vacuum oven at 80°C for 12 h. The dried precipitate was APH, and the yield was about 69%.

Curing of the epoxy resins

NPCN-703H was cured separately with APH, DDS, and DDM. The reactant compositions were mixed in a 1/1 equivalent ratio. The mixture was dissolved in N,N-dimethylformamide solution. The solvent was then removed in a vacuum oven. The curing behavior of each dried epoxy/curing agent mixture was first studied by differential scanning calorimetry (DSC) measurements. Thereafter, the curing procedures for the preparation of cured polymers were determined, as listed in Table I.[7,18] Different dried mixtures had different curing periods, depending on which curing agent was incorporated. The curing equation of NPCN-703H with APH is shown next:
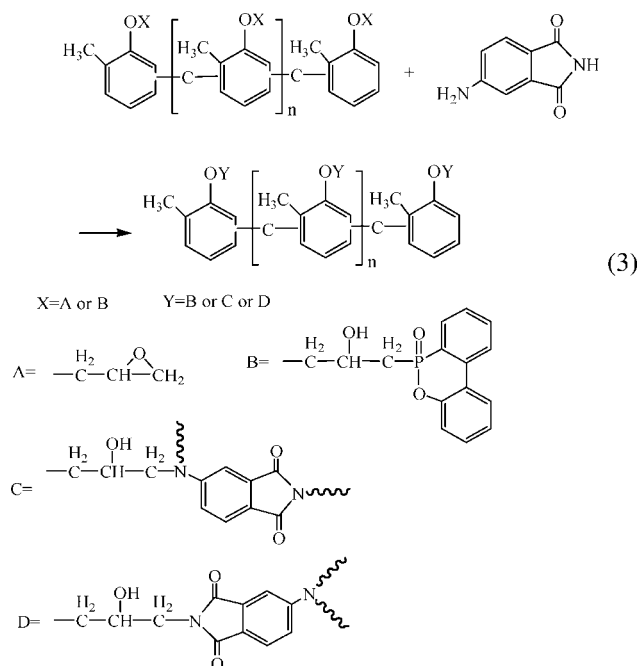

TABLE I
Curing Periods of the Resin Mixtures

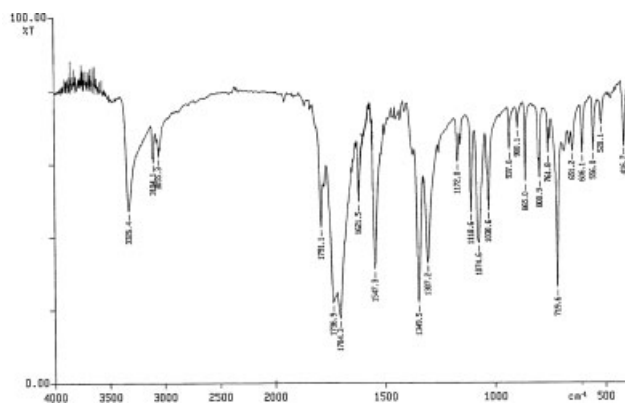| Resin mixture	Curing agent	Precuring curing		Postcuring
DDME	DDM	110°C, 2 h	140°C, 3 h	170°C, 3 h
DDSE	DDS	140°C, 2 h	170°C, 3 h	200°C, 3 h
APHE	APH	140°C, 2 h	170°C, 3 h	200°C, 3 h

Figure 2 IR spectrum of NPH.

Identification of NPH and APH

Either the dried NPH or APH was ground into a powder before the determination of its chemical structure or other procedures. In the identification of the chemical structure, transmission infrared spectra of powder samples were recorded with a Perkin-Elmer Paragon 500 Fourier transform infrared spectrometer (Waltham, MA). Moreover, some powder samples were also dissolved in D_2O, and ^{1}H-NMR spectra were obtained from a Jeol JNM-ECX 400 NMR spectrometer (Tokyo, Japan). Finally, the molar mass of the prepared compound was analyzed by a

Finnigan TSQ 700 mass spectrometer (Thermo Fisher Scientific, Waltham, MA).

Measurements and tests

The curing reactions of the epoxy/curing agent samples were studied by DSC on a DSC-50 (Shimadzu, Kyoto, Japan) at a heating rate of 10°C/min from 50 to 300°C. Experimentally, 5 g of epoxy/curing agent mixture (in a 1/1 equivalent ratio) was put in a sample holder under a nitrogen atmosphere. The gas flow rate was 20 mL/min. The thermal resistance of the sample was evaluated by thermogravimetric analysis (TGA) on a TGA 2950 (TA Instruments, New Castle, DE) at a heating rate of 20°C/min from 50 to 700°C. Experimentally, 3 g of cured resin sample was put into a sample holder under either a nitrogen or oxygen atmosphere. The gas flow rate was 50 mL/min. Also, dynamic mechanical analysis (DMA) of the samples ($40 \times 5 \times 1$ mm^3) was carried out with a DMA 2980 instrument (TA Instruments) under a nitrogen atmosphere at a heating rate of 5°C/min from 40 to 250°C at a vibration frequency of 1 MHz. The storage modulus and tan δ of each sample were obtained thereafter. Finally, the dielectric properties of the sample ($120 \times 12 \times 2$ mm^3) were examined in an HP4194A impedance analyzer (Agilent Technologies, Santa Clara, CA) under a nitrogen atmosphere, at a vibration frequency of 1
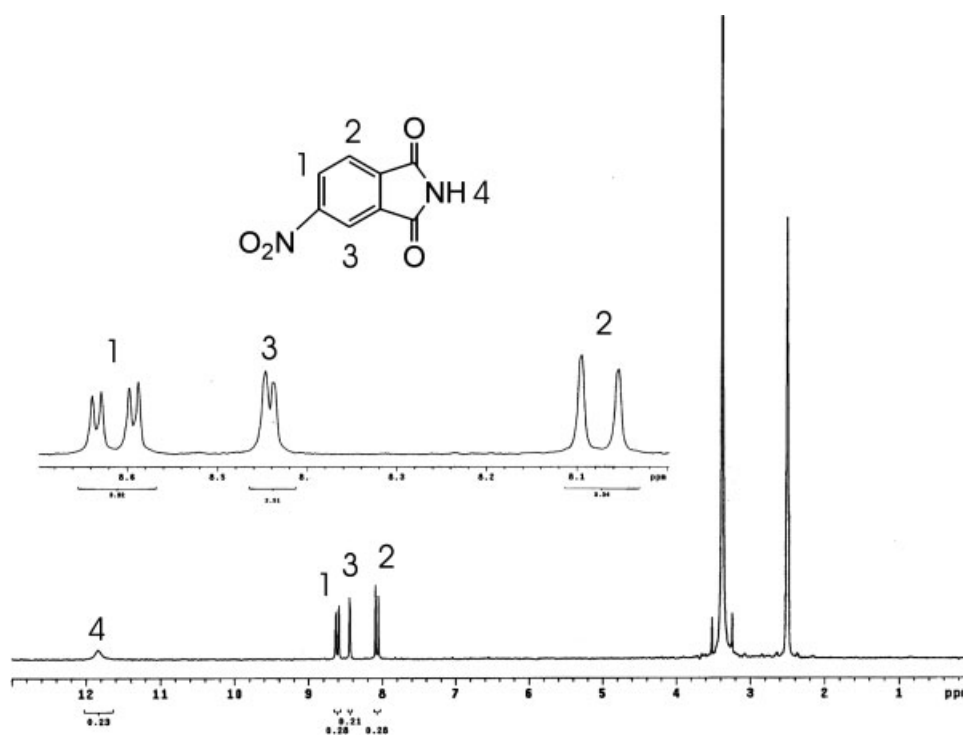

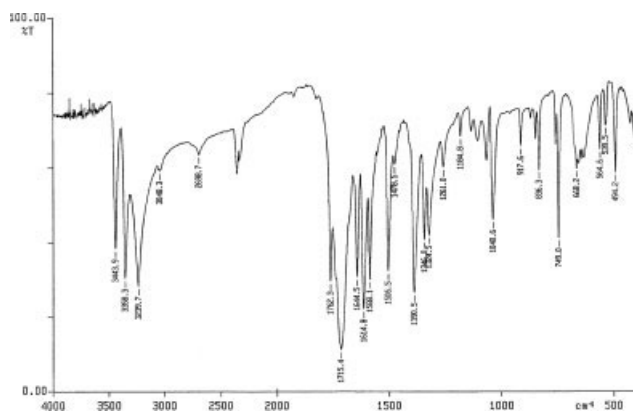**Figure 3** ^{1}H-NMR spectrum of NPH.

Figure 4 IR spectrum of APH.

MHz, and at room temperature. The capacitance and ε of the sample were then determined.

RESULTS AND DISCUSSION

Identification of NPH and APH

The structures of NPH and APH were verified from their IR and ^{1}H-NMR spectra, respectively, as shown in Figures 2–5.

Figure 2 shows that the IR spectrum of NPH displayed characteristic adsorption peaks at 3326 (—N—H stretching), 1736 and 1704 (—C=O stretching), 1547 and 1349 (—NO$_2$ stretching), and 719 cm^{-1} (C—N—C bending). The ^{1}H-NMR spectrum

shown in Figure 3 gave signals at δ = 11.8 (s, 1H), 8.6 (d, d, 2H), 8.4 (d, 1H), and 8.1 ppm (d, 1H).[5,19–21] In addition, the molar mass of the prepared compound determined from the mass spectrum was 192, which agreed with that of NPH.

Figure 4 shows that the IR spectrum of APH displayed characteristic adsorption peaks at 3443 and 3358 (—NH$_2$ stretching), 3259 (—NH stretching), 1715 (—C=O stretching), and 749 cm^{-1} (C—N—C bending). Clearly, the adsorption peak related to the NO$_2$ group at 1547 cm^{-1} in Figure 2 is not shown in Figure 4, and new adsorption peaks related to the NH$_2$ group at 3443 and 3358 cm^{-1} appeared. This indicated the formation of APH from the reduction of NPH. The ^{1}H-NMR spectrum shown in Figure 5 gave signals at δ = 10.7 (s, 1H), 7.4 (d, 1H), 6.9 (d, 1H), 6.8 (d, d, 2H), and 6.4 ppm (s, 2H). Compared to Figure 3, a new signal related to 5H occurred in the spectrum shown in Figure 5. Also, the molar mass of the prepared compound determined from the mass spectrum was 162, which agreed with that of APH.

Curing studies of the epoxy resins

Figure 6 shows the DSC diagrams of the epoxy resins cured by three different curing agents in nitrogen. Generally, an exothermal peak associated with curing for each sample was observed in each DSC diagram. The exothermic starting temperature of the polymers clearly increased in the order DDME <
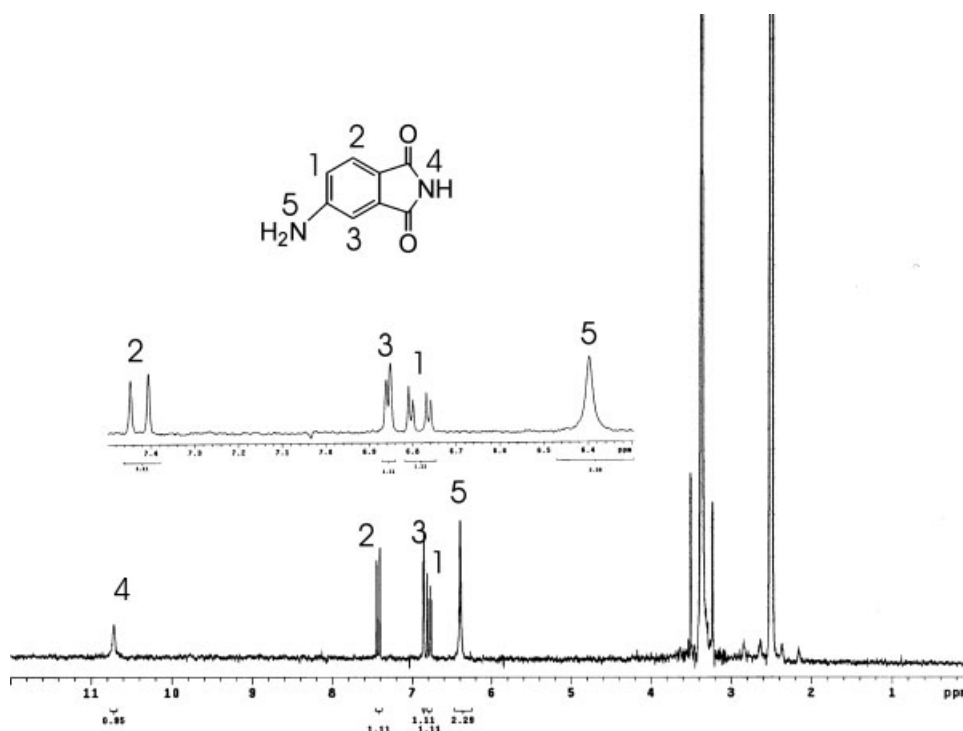

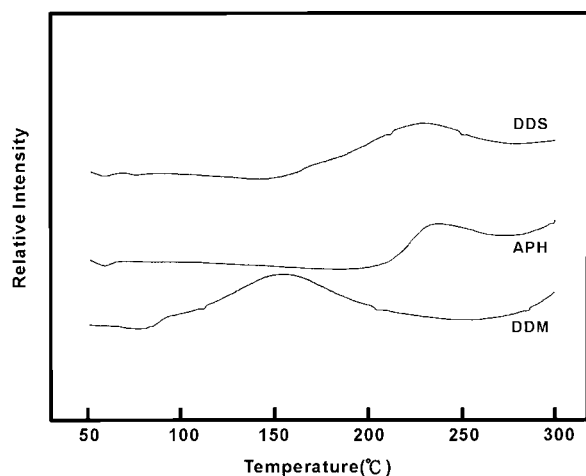**Figure 5** ^{1}H-NMR spectrum of APH.

Figure 6 DSC diagrams of the cured epoxy resins in nitrogen.

DDSE < APHE. A curing agent that caused a lower exothermic starting temperature under the same set of curing conditions was more reactive toward the epoxy resin. Thus, the chemical reactivities of these three different curing agents toward the epoxy resin were DDM > DDS > APH. This was attributed to different electronic effects of the three curing agents toward the polymer.[18] The methyl group in DDM caused a positive inductive effect but no mesomeric or resonance effects; this increased the electron density of the amine nitrogen and, subsequently, increased its nucleophilic attack on the oxirane ring of the polymer. In contrast, the electron-withdrawing sulfone group in DDS caused not only a negative inductive effect but also a mesomeric effect; this reduced the electron density of the amine nitrogen and its nucleophilic attack on the oxirane ring of the polymer. Therefore, DDM was more reactive than
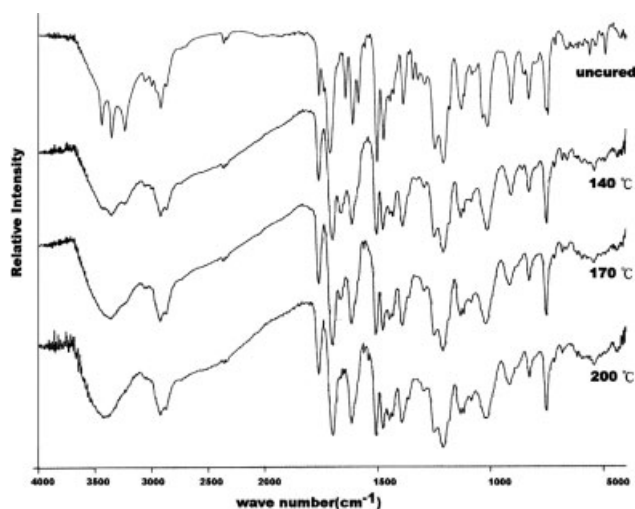
DDS. Similarly, APH contained two C=O electron-withdrawing groups, which also caused both a negative inductive effect and a mesomeric effect. Also, the functionality (fc) of APH was 3, which was lower than that of either DDM or DDS (fc = 4). Accordingly, DDS was more reactive toward the epoxy resin than APH.

From the DSC scanning results and Lin and Wang's work,[7] the curing procedures for the preparation of the cured polymers were determined and are listed in Table I. To ensure that the epoxy/APH mixture was completely cured under the curing conditions listed in Table I, the IR spectra of the epoxy/APH mixture after each curing period were recorded by a Fourier transform infrared spectrometer, as shown in Figure 7. For the uncured mixture at room temperature, adsorption peaks at 3200–3450 (—NH and —NH$_2$ stretching), 2400 (P—H), about 1600 (—NH and —NH$_2$ bending), and 915 cm^{-1} (oxirane ring) were observed.[7,22] After the mixture sample was cured at a higher temperature, the peak intensities related to —NH and —NH$_2$ and oxirane became smaller, and a new adsorption peak corresponding to —OH stretching at 3400 cm^{-1} appeared. This indicated that the epoxy resin reacted with the curing agent and became a cured polymer. At the end of curing or after the postcuring period, the adsorption peak related to —NH$_2$ disappeared completely, and only that related to —OH stretching remained.

Thermal properties of the cured epoxy resins

The thermal properties of the cured epoxy resins and the effects of the curing agents were determined by their TGA measurements. Figure 8 shows the TGA diagrams of the epoxy resins cured by the three different curing agents in air. The decomposition temperature (T_d) and char yield values of these
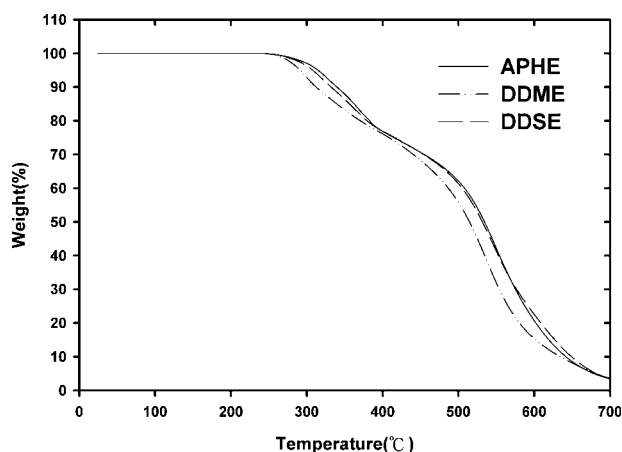

Figure 7 IR spectra of an epoxy/APH mixture after each curing period.

Figure 8 TGA diagrams of the cured epoxy resins in air.

TABLE II
T_d **and Char Yield Values of the Cured Resins**

| Resin sample | 5%T_d (°C) | | 10%T_d (°C) | | Char yield (%)[a] | | | |
| | | | | | 500°C | | 600°C | |
	N_2	Air	N_2	Air	N_2	Air	N_2	Air
DDME	309	291	328	313	54.2	55.8	47.0	15.3
DDSE	325	308	345	332	44.0	61.3	39.4	22.4
APHE	328	315	353	340	45.3	62.0	37.6	20.5

[a] Weight of the polymer remaining.

cured polymers are summarized in Table II. The temperatures for 5% weight loss (5%T_d's) of the polymers in air were about 291, 308, and 315°C for DDME, DDSE, and APHE, respectively. The temperatures for 10% weight loss (10%T_d's) of the polymers were about 313, 332, and 340°C for DDME, DDSE, and APHE, respectively. Among the three cured resins, the polymer cured by APH, that is, APHE, appeared to show a higher T_d than DDME or DDSE. The thermal properties of the cured resin were affected by the polymeric structure and crosslink density. In the case of APHE, the polymer contained the APH moiety, which had aromatic and cyclic C=C—C rings in the structure. An introduction of doubly stranded units into the backbone would exhibit better thermal stability than the open one.[7] In contrast, when the polymer contained either DDM or DDS moieties, which had flexible —C— or —S— linkages between two benzene rings, this interrupted the aromaticity, which decreased the thermal stability. However, the crosslink density in APHE was expected to be lower than that in either DDME or DDSE. This was because APHE was cured by APH, whose fc was lower than that of either DDM or DDS. A polymer with a lower crosslink density usually has poorer thermal properties. As APHE showed a better thermal stability than DDME and

DDSE, this revealed that the high rigidity of APH may have somewhat overcome the loss in crosslink density in the cured polymer.

Figure 9 shows the TGA diagrams of the epoxy resins cured by the three different curing agents in nitrogen. The 5%T_d values of the polymers were about 309, 325, and 328°C for DDME, DDSE, and APHE, respectively. The 10%T_d values of the polymers were about 328, 345, and 353°C, for DDME, DDSE, and APHE, respectively. Again, APHE showed a higher T_d than DDME or DDSE. In addition, T_d was clearly higher in nitrogen than in oxygen for the same cured polymer, as oxygen enhanced the degradation of the polymer molecules.

The TGA diagrams in Figures 8 and 9 indicate that the epoxy resins in air had two decomposition steps. From the argument of Wang and Lin,[18] the first step occurred as the polymer was oxidized and became carbonaceous residues; the second step was related to the oxidative degradation of the carbonaceous residue. The maximum decomposition temperature (T_{max}) of the polymers was estimated from the first derivative of each TGA curve versus temperature. The T_{max} values of these cured polymers are summarized in Table III. The two T_{max} values in each cured resin in air were 301 and 535°C for DDME, 359 and 545°C for DDSE, and 367 and 550°C for APHE. In contrast, only one decomposition step was observed in each cured resin in nitrogen. T_{max} was 346°C for DDME, 386°C for DDSE, and 396°C for APHE. It was clear that the T_{max} values of the cured polymers in air or in nitrogen varied as follows: DDME < DDSE < APHE.
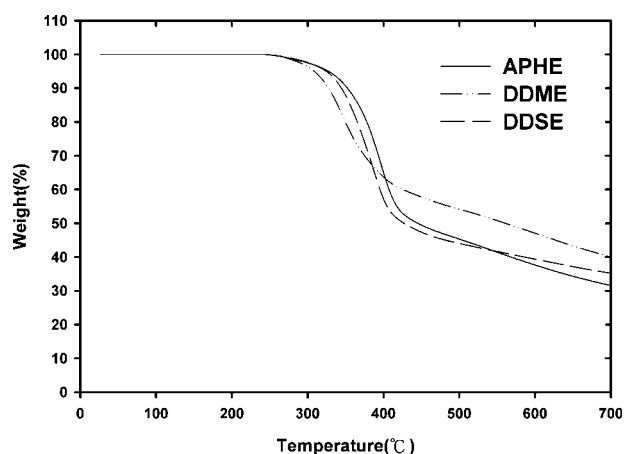

Figure 9 TGA diagrams of the cured epoxy resins in nitrogen.

TABLE III
T_{max} **Values of the Cured Resins**

| Resin sample | T_{max} (°C) | | | |
| | Step 1 | | Step 2 | |
	N_2	Air	N_2	Air
DDME	346	301	—	535
DDSE	386	359	—	545
APHE	396	367	—	550
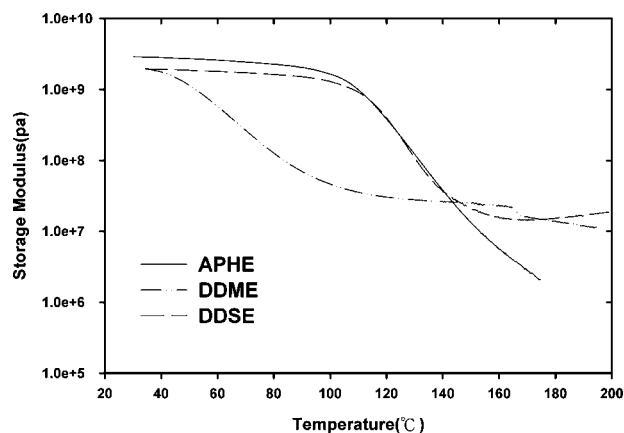
Figure 10 Relationship between the storage modulus of the cured epoxy resins and the temperature.

TABLE IV
T_g and ε Values of the Cured Resins

Resin sample	T_g (°C)	ε
DDME	72	4.97
DDSE	133	4.03
APHE	141	3.08

As indicated in Table II, the char yields in air at 500°C were 55.8, 61.3, and 62% for DDME, DDSE, and APHE, respectively. The high char yield of APHE suggested that the incorporation of imide groups into the epoxy structure also improved the flame retardancy of the polymer.[2] However, the char yields in air at 600°C were 15.3, 22.4, and 20.5% for DDME, DDSE, and APHE, respectively. The char yield of APHE at 600°C was lower than that of DDS. In fact, the char yield of APHE in nitrogen at 600°C was even lower than that of DDM. The low char yield of APHE at this high temperature may have been due to its lower crosslink density than DDME and DDSE.

The thermal behavior of the cured epoxy resins was further examined from measurements of their dynamic mechanical behavior at a heating rate of 5°C/min. Figures 10 and 11 shows the effect of curing agents on the storage modulus and tan δ values of the cured resins as a function of temperature. As shown in Figure 10, an increase of temperature was

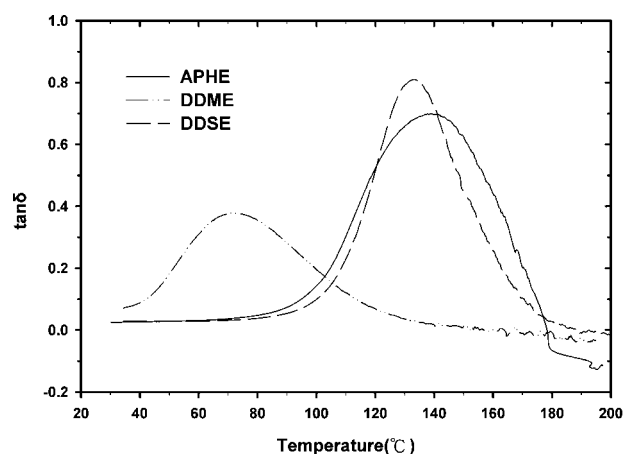expected to decrease the storage modulus. Figure 11 shows that tan δ initially increased with temperature, reached a maximum, and decreased afterward. The temperature at which a sharp drop in the storage modulus, shown in Figure 10, occurred or that of the maximal tan δ, shown in Figure 11, indicated the glass-transition temperature (T_g) of the cured polymer. The T_g values were about 141, 133, and 72°C for APHE, DDSE, and DDME, respectively. It was clear that the T_g of APHE was higher than that of the epoxy cured by either DDS or DDM. This was attributed to the incorporation of the rigid imide group in the cured resin structure. However, APHE retained a lower storage modulus at a temperature greater than 145°C. This was attributed to the lower crosslink density in this polymer.

ε of the cured epoxy resins

The ε values of the cured epoxy resins with the three different curing agents were examined in an impedance analyzer under a nitrogen atmosphere at a vibration frequency of 1 MHz and at room temperature; the results are listed in Table IV. The values were 4.97, 4.03, and 3.08 for APHE, DDSE, and DDME, respectively. As APH contained imide groups, which reduced the intermolecular electronic interactions, APHE showed a lower ε than either DDME or DDSE. Nonetheless, dielectric properties are temperature- and frequency-dependent physical properties. Thus, the dielectric properties of these cured polymers at different temperatures or frequencies remain to be further studied.

CONCLUSIONS

In this study, a simple imide compound, APH, was synthesized as a curing agent for novolac epoxy resin. The chemical structure of APH was verified by IR and ^{1}H-NMR spectra. The 5%T_d values of APHE in nitrogen and air were 328 and 315°C, respectively; these were higher than those of either DDME or DDSE. The T_{max} values of APHE in nitrogen and air were also higher than those of either DDME or DDSE. The T_g values of APHE, DDSE, and DDME on the basis of DMA were about 141, 133, and 72°C, respectively. This indicated that APHE showed higher thermal properties than either

Figure 11 Relationship between tan δ of the cured epoxy resins and the temperature.

DDSE or DDME. Moreover, the ε at 1 MHz of APHE was lower than those of the other two cured polymers.

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