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Preparation of Heat-Moisture Resistant Epoxy Resin Based on Phosphazene

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ABSTRACT: An amine-terminated curing agent for epoxy resin based on hexachlorocyclotriphosphazene was synthesized. Its chemical structure was characterized by ^{1}H-NMR, FT-IR, and elemental analysis. The curing temperature was determined by differential scanning calorimeter. The thermal stability, hydrophobicity, flame retardancy, and insulation property of the epoxy resin cured by the as-prepared curing agent were superior to those of the epoxy resin cured by 4,4′-diaminodiphenylsulfone. The epoxy resin cured by the new curing agent obtained the best heat-moisture resistance when the ratio of amino protons and epoxy group was 1.2 : 1. The temperature reached 318 and 376°C when the weight loss was 5 and 10% meanwhile the residue at 800°C was above 64%. The material achieved UL94 V-0 rating and the water absorption was only 0.57%. The electric insulation property was also improved especially when it was compared in wet conditions at water absorption saturation. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 248–255, 2013

KEYWORDS: flame retardance; resins; thermal properties; differential scanning calorimetry; properties and characterization

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INTRODUCTION

Epoxy resin materials play a vital role in many fields such as laminating, adhesive, surface coating due to their ease of processing, low cost, good adhesive properties, chemical resistance, low dielectric constant, and good mechanical strength.[1–4] However, the conventional epoxy resins are not able to satisfy some advanced applications which require greater properties. Therefore, it is important to design novel epoxy systems to meet the needs of wider application. One of the challenges encountered by many researchers is in the electronic packaging. As the lead-free jointing technology becomes popular in encapsulation, the epoxy resin materials must endure high temperature.[5] Conversely, wet environments compromise the mechanical strength, dimensional stability, and insulation property due to water absorption of the matrix.[6] Hence, epoxy resin materials must have higher heat resistance as well as moisture resistance.

Recent researches concerning the improvement of heat and moisture resistance focus on the incorporation of cycloaliphatic and aromatic groups into epoxy system.[7] Naphthalene is a common structure to increase the glass transition temperature and thermal stability. Naphthalene-based epoxy resins have been reported several times.[8–10] However, it is not easy to improve both the heat resistance and moisture resistance greatly. Although the incorporation of rigid structure like naphthalene makes it hydrophobic and thermal-stable, the free volume of the material increases and the water absorption is not easy to control.[11] Other approaches tend to introduce special elements or structures into epoxy system such as silicon, boron, nitrogen, and phosphorus because these elements have great thermal stability and hydrophobic property.[12,13] Researchers want to increase the proportion of the thermal resistant and hydrophobic structure in epoxy system so that the material will be heat-moisture resistant.

In this work, a novel amine-terminated curing agent for epoxy resin based on phosphazene was synthesized and the cured epoxy material was tested for its properties. Phosphazene is an inorganic–organic hybrid molecule. The phosphazene materials

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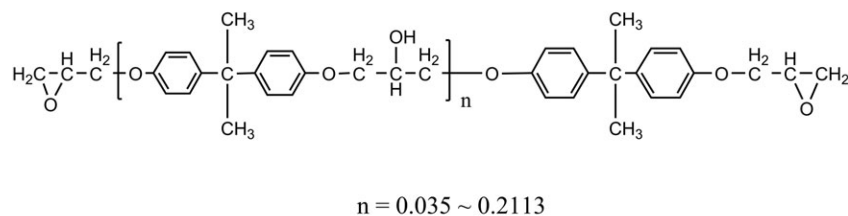

n = 0.035 ~ 0.2113

Figure 1. Chemical structure of E618.

possess good heat-moisture resistance and great flame retardancy mainly due to the high content of nitrogen and phosphorus in the main chain.[14–16] This indicates the incorporation of phosphazene into polymer matrix will greatly increase the content of heat-moisture resistant structure in polymer system thus the great properties of phosphazene can be transferred to the matrix. What is more, the chlorine atoms in the structure have moderate reactivity and it is convenient to link different functional group or molecular chain to the main chain through substitution reaction.[17] This means the phosphazene molecule is easy to be designed to create different properties to meet various demands. For example, heat-resistant and hydrophobic structures can be linked to phosphazene through some reactions to make them useful in electronic applications.

Specifically speaking, in this work, an amine-terminated curing agent for epoxy resin was synthesized through the introduction of bi-naphthalene structure and amine groups into phosphazene structure. The chemical structure was characterized by FT-IR, ^{1}H-NMR and elemental analyses (EA). The curing temperature was determined by differential scanning calorimeter (DSC). The relationship between the material properties and the proportion of synthesized curing agent was studied. The thermal stability, water absorption, flame retardancy, and insulation property of the materials with different curing agent were tested.

EXPERIMENTAL

Materials

Hexachlorocyclotriphosphazene (HCCP) was purchased from Aldrich and purified through sublimation before use. Tetrahydrofuran (THF) was obtained from Shanghai Chemical Reagents Corp. (Shanghai, China) and distilled from CaH_2 under dry N_2 purge before use. 4,4′-diaminodiphenylsulfone (DDS), sodium, ethanol, acetone and triethylamine (TEA) were purchased from Shanghai Chemical Reagents Corp. (Shanghai, China) and used without further purification. Epoxy resin 618 (E618) was purchased from Shanghai Haiqu Chemical Industrial Corp. (Shanghai, China). The structure of E618 is shown in Figure 1 and its average epoxy equivalent weight is 196 g equiv.$^{-1}$.

Instruments

The characterization of FT-IR was conducted on a Perkin-Elmer Paragon 1000 Fourier transform spectrometer at room temperature. The ^{1}H-NMR measurement was performed on a Perkin-Elmer advance 500AC 200P NMR spectrometer and dimethyl sulfoxide (DMSO) was used as solvent. The EA test was performed using a Perkin-Elmer 2400-II instrument. The thermal stability was tested on a TA Q5000 thermogravimetric analyzer (TGA) under nitrogen atmosphere. The curing temperature was determined on a Perkin-Elmer Pyris 1 DSC instrument at different heating rate from 0 to 300°C at the N_2 atmosphere. An EST 121 Digital Super Resistance Micro-current instrument (Beijing EST Science & Technology, China) was used to test the electrical properties of the cured epoxy resins according to the National Standard of China GB/T 1410-1989. The sample was 10 × 10 × 0.3 cm^3. Vertical burning tests were measured on CZF-3 instrument (Nanjing Jiangning Instrument Factory, China) based on ASTM D3801/UL-94V standard. The sample size was 125 × 13 × 3 mm^3. The contact angles (CA) of the samples were measured at 25°C using a sessile drop method (OCA 20 contact angle system, Dataphysics, 112 Instruments GmbH, Germany). Water droplets (about 3 μL) were dropped onto the samples.

Synthesis of the Curing Agent Based on Phosphazene (NPA)

Step 1: 1.725 g (0.075 mol) of sodium was cut to shreds and added slowly into a 250-mL flask containing 10 g (0.035 mol) of bi-naphthalene and 100 mL of THF. The reaction lasted 3 h at room temperature under nitrogen protection.

Step 2: 12.18 g of HCCP was dissolved in 100 mL of THF in a 500 mL three-neck-flask and the resulting solution of Step 1 was added dropwise into it over the period of 30 min. The reaction was maintained in the reflux condition for 3 h and then refrigerated to room temperature. The product was washed by water, THF and ethanol, and then dried at 100°C in vacuum oven for 24 h. The white solid obtained was the partly substituted HCCP.

Step 3: 34.8 g (0.14 mol) of DDS was dissolved in 200 mL of THF. The partly substituted HCCP and 15.18 g (0.15 mol) of TEA was added to the solution. The reaction was maintained in the reflux condition for 5 h. The product was washed by THF, acetone and ethanol, and then dried at 60°C in vacuum oven for 24 h. The resulting product was beige solid.

Determination of the Curing Temperature of NPA with E618

The curing reaction of epoxy with NPA in this study is similar to that with the common amine-based curing agents, such as DDS, 4,4′-diaminodiphenyl methane (DDM), and diethylenetriamine (DETA).[18,19] DSC was used to determine the curing temperature of NPA with E618. The samples of the mixture of E618 and NPA were tested on DSC instrument from 50 to 250°C at the different heating rate of 5, 10, 15, and 20°C min^{-1}, respectively. The characteristic temperatures for initial curing, exothermic peak and terminal curing were read from the exothermic curves. Three beelines can be obtained according to the linearity between heating rate and characteristic temperatures.[20] The three beelines were protracted to the heating rate 0°C min^{-1} and the corresponding temperatures were the critical lowest

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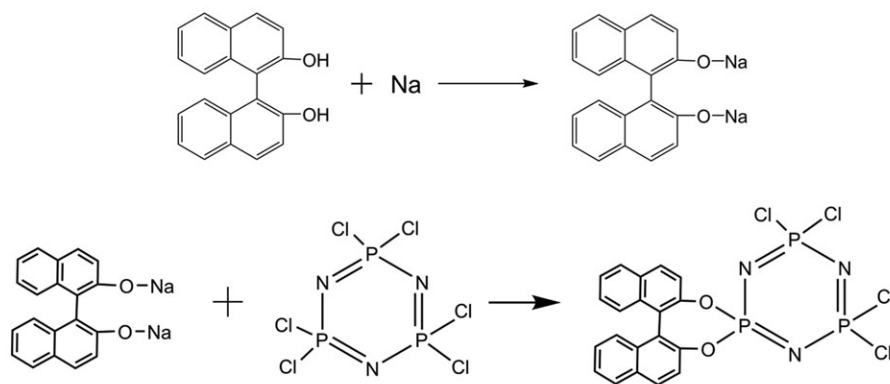

Figure 2. First and second steps of the synthesis of NPA.

curing temperatures. Thus the temperatures for precuring, constant-curing, and postcuring were determined.

Measurement of Water Absorption of the Cured Epoxy Resin

The water absorption of the epoxy resin was tested according to the National Standard of China GB/T 1034–2008. The sample was 10 × 10 × 3 mm^3. The sample was cleaned by ethanol and dried at the 50°C in vacuum oven for 24 h before the test. The weighing of the sample was at room temperature and the initial weight was recorded as M_0. The sample was then kept in the water for 12 h. Before it was weighed again, it was wiped by filter paper quickly in 1 min. The weight after 12 h was recorded as M_1. The weighing was repeated every 12 h until the weight did not change any more and the weight for each time was recorded as M_2, M_3,…M_n. The water absorption (C) can be calculated according to the formula below:

$$c = \frac{M_n - M_1}{M_1} \times 100\% \qquad (1)$$

RESULTS AND DISCUSSION

Characterization of NPA

The first and second steps are shown in Figure 2. Similar to the synthesis of sodium phenate,[21] disodium bi-naphtholate is synthesized by the reaction between sodium and bi-naphthalene, which is easier to take the substitution reaction in next step. The yield of the second step is 80%. The melting point of the product of the second step is 282°C.

The third step of the synthesis is shown in Figure 3. It aims to give amine groups to the structure thus it can be used as a curing agent for epoxy resin. The yield of this step is 70%. The melting point of NPA is 201°C.

The FT-IR spectra of HCCP, bi-naphthalene and the products for each step are shown in Figure 4. In spectrum a, the absorption peak at 3450 cm^{-1} (a) corresponds to –OH in bi-naphthalene. After the reaction of the second step, the peak corresponding to –OH disappears in spectrum c which proves occurrence of the substitution reaction and the peak at 980 cm^{-1} (b) appears indicating the formation of P–O–Ar. The peaks at 1510 cm^{-1} (c) and 1610 cm^{-1} (d) correspond to benzene ring. In spectrum d, the peaks at 3400 cm^{-1} (e) and 3200 cm^{-1} (f) correspond to $-NH_2$ and –NH–. The peak at 1150 cm^{-1} (g) corresponds to O=S=O. The characteristic peak of P–N band at 873 cm^{-1} (h) in spectrum c shows a little blue shift to 932 cm^{-1} (i) in spectrum d, demonstrating the formation of new P–NH– (Ph) band. It can be seen from the FT-IR spectra that bi-naphthalene and DDS have successfully reacted with HCCP.

The ^{1}H-NMR spectrum of NPA is shown in Figure 5. The peak at δ = 3.1 ppm (a) corresponds to secondary amine protons and the peak at δ = 6.0 ppm (b) corresponds to primary amine protons. The peaks at δ = 6.5–8.0 ppm (c-l) correspond to the

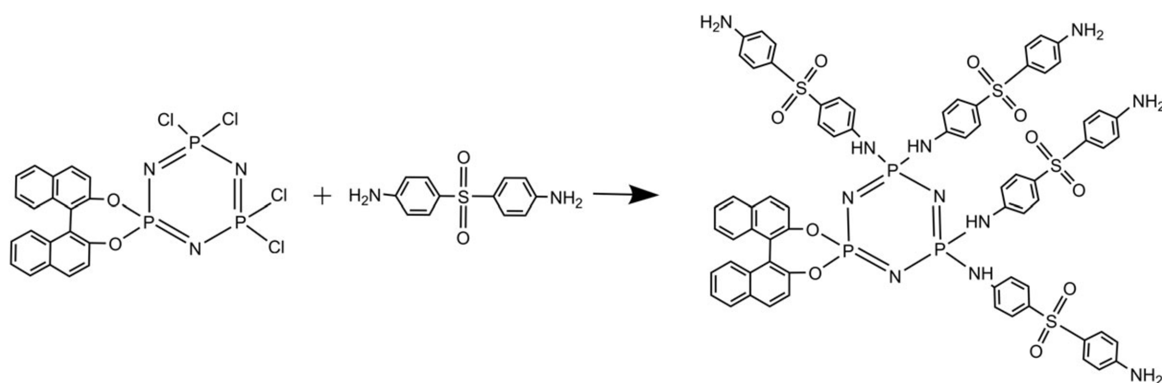

Figure 3. Third step of the synthesis of NPA.

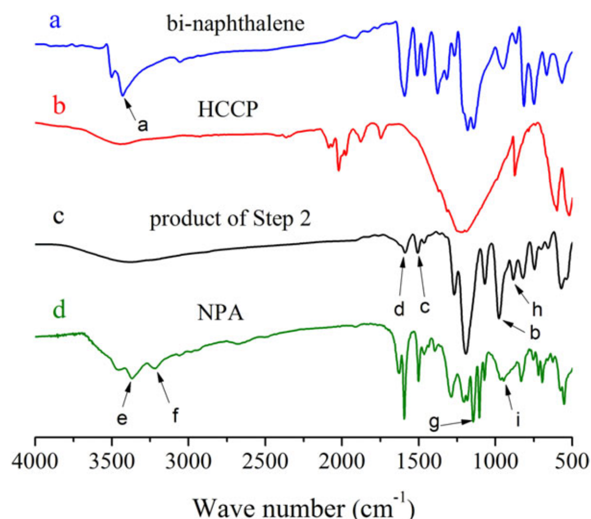

Figure 4. FTIR spectrum of bi-naphthalene, HCCP, the product of Step 2, and NPA: peak a (3450 cm^{-1}): (Ph)–OH, peak b (980 cm^{-1}): P–O–Ar, peak c (1510 cm^{-1}) and d (1610 cm^{-1}): benzene ring, peak e (3400 cm^{-1}): $–NH_2$, peak f (3200 cm^{-1}): –NH–, peak g (1150 cm^{-1}): O=S=O, peak h (873 cm^{-1}): P-N, peak i (932 cm^{-1}): P-NH-(Ph). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

benzene protons, thereinto, the sharp signals at about 6.5 and 7.5 ppm correspond to diphenylsulfone protons, and other weak peaks between 7.0 and 8.0 ppm are expected to bi-naphtalene protons. The peak at $\delta = 2.5$ ppm corresponds to the protons of the solvent DMSO and the peak at $\delta = 3.3$ ppm corresponds to the protons of absorptive H_2O. The ^{1}H-NMR spectrum confirms the synthesized curing agent contains both bi-naphthalene and DDS units.

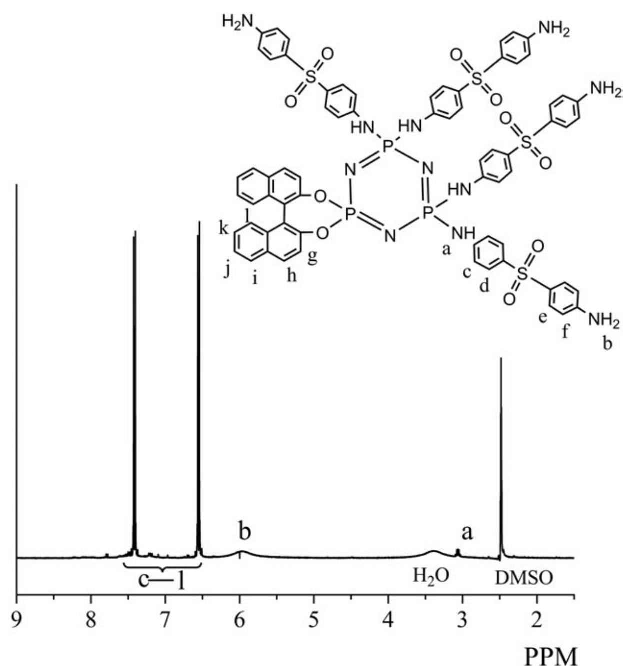

Figure 5. ^{1}H-NMR spectrum of NPA.

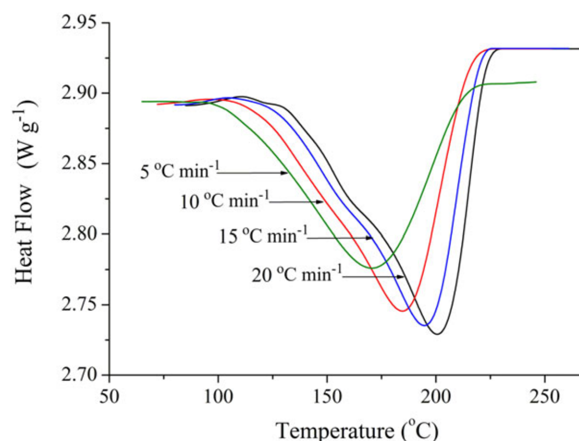

Figure 6. DSC curves of the curing reactions between NPA and E618 at different heating rate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

To further proof that all the DDS is linked to the cyclotriphosphazene, the EA test for the as prepared NPA gives the following results. Calc. for $C_{68}H_{56}O_{10}N_{11}P_3S_4$ (NPA): C, 58.0; H, 4.0; O, 11.4; N, 10.9; P, 6.6; S, 9.1%. Found: C, 55.3; H, 3.6; O, 11.9; N, 12.1; P, 6.8; S, 9.5%. In conclusion, FT-IR, ^{1}H-NMR and EA analyses indicate that we have obtained the expected curing agent.

Determination of the Curing Temperature of NPA with E618

Curing temperature has a great influence on the property of the epoxy resin material. It is reported that the lower temperature will cause the incomplete-curing and the higher temperature may cause fierce reaction leading to the accumulation of heat in the material.[22] Therefore, it is very important to determine the right curing temperature for each epoxy system including different resin and curing agent. DSC method is used to determine the curing temperature because curing reaction is accompanied by heat release and it has a scientific relationship with the heating rate.[23]

The DSC curves of the curing reactions between NPA and E618 at different heating rate are shown in Figure 6. As the curves showed, the peaks become sharper and narrower as the heating rate increased. The characteristic temperatures including initial curing temperature (T_i), peak temperature (T_p), and terminal temperature (T_t) move higher when the heating rate is increased. The characteristic temperatures of each sample are listed in Table I.

Three beelines are drawn according to the linearity between heating rate and characteristic temperatures (Figure 7). The beelines are protracted to the point where the heating rate is 0°C min^{-1} and the corresponding temperatures are the lowest curing reaction temperatures. The expressions of the temperatures are listed and the values of coefficient are also shown in Figure 7.

In summary, the temperatures for precuring, constant-curing, and postcuring are determined as 86, 163, and 216°C.

Table I. Characteristic Temperatures of Curing Reactions Between NPA and E618 at Different Heating Rate

Heating rate (°C min^{-1})	Characteristic temperature		
	T_i (°C)	T_p (°C)	T_t (°C)
5	94.6	170.1	219.2
10	98.7	184.1	223.7
15	104.2	194.8	226.4
20	117.0	199.0	229.9

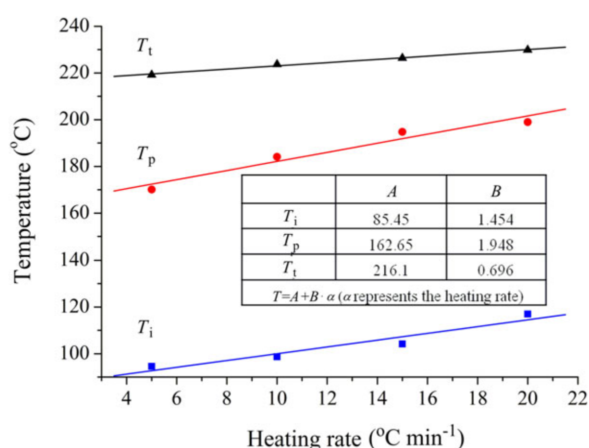

Figure 7. Linearity between heating rate and characteristic temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Influence of NPA's Proportion on the Property of Epoxy Material

Thermal Stability. The proportion of curing agent is a key factor which influences the thermal stability of the epoxy resin greatly as the crosslink density has a close relationship with the proportion of curing agent.[24] In this experiment, epoxy resin (E618) was cured by NPA with the functional ratio of 1 : 1, 1.1 : 1, 1.2 : 1 and 1.3 : 1 (amino protons : epoxy group) in the same procedure. The thermal stability of the cured resin was studied by TGA.

The TGA curves are shown in Figure 8. As the proportion of NPA increased, the initial degradation temperature increases. This can be explained by the improvement of crosslink density of the resin. The residue at 800°C also shows a climb when the proportion of NPA is increased. This mainly results from the increase in the content of heat-resistant groups, phosphazene and bi-naphthalene structures, besides the improvement of crosslink density. The ability to form residue is very important because it improves flame retardancy.[25]

Moisture Resistance. Water may be absorbed in epoxy resin in three main ways: dissolving in the resin matrix, attaching on the hydrophilic groups and existing in the micro-pores in the material.[26] When the resin matrix is chosen, the moisture resistance of the material will depend on the kind and the proportion of the curing agent. In this part, epoxy resin (E618) was

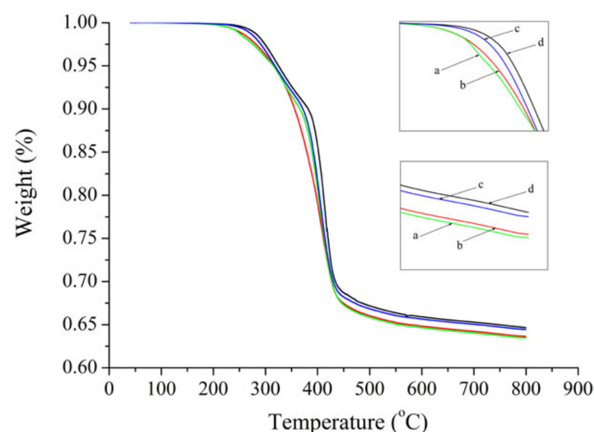

Figure 8. TGA curves of the cured resins obtained from E618 cured by NPA with the functional ratio (amino protons : epoxy group) of 1 : 1 (a), 1.1 : 1 (b), 1.2 : 1 (c), and 1.3 : 1 (d). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cured by NPA with the functional ratio of 1 : 1, 1.1 : 1, 1.2 : 1, and 1.3 : 1 (amino protons : epoxy group) in the same procedure. The moisture resistance was tested through water absorption experiment.

The water absorption result is shown in Figure 9. When the functional ratio is 1 : 1 (amino protons : epoxy group), the water absorption is 0.66%. The water absorption reaches the lowest point of 0.57% when the ratio is 1.1 : 1 and 1.2 : 1 which can be explained by the increased content of hydrophobic structures brought by NPA. When the ratio is 1.3 : 1, the water absorption increases to 0.76% due to the increase in the content of hydroxyl group (generated in curing reaction) and amino group (remaining after curing reaction). Additionally, the decrease of crosslinking density might also cause this phenomenon. It can be concluded that the moisture resistant property largely depends on the ratio of hydrophobic and hydrophilic structures. The curing agent based on phosphazene and bi-

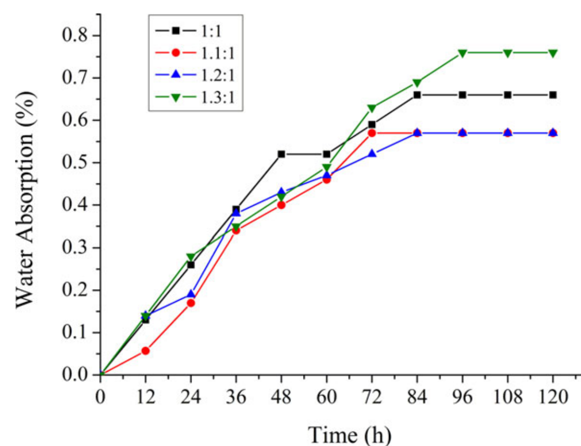

Figure 9. Water absorption curves of the cured resins obtained from E618 cured by NPA with the functional ratio (amino protons : epoxy group) of 1 : 1, 1.1 : 1, 1.2 : 1, and 1.3 : 1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

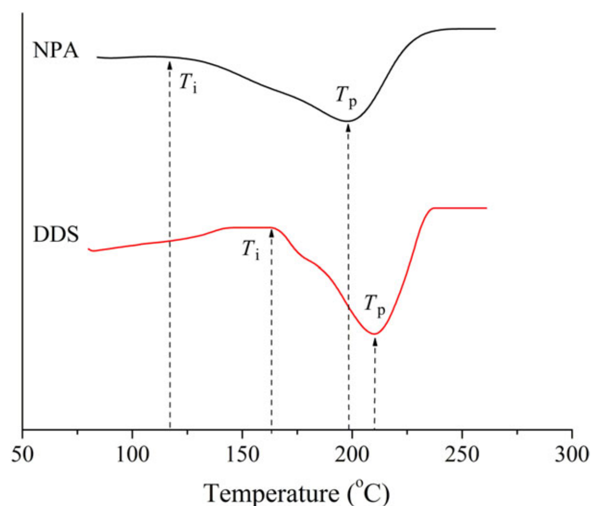

Figure 10. DSC curves of the curing reactions with curing agents of NPA and DDS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

naphthalene has a high content of hydrophobic structures or atoms such as naphthalene, nitrogen and phosphorus which improve the moisture resistance.

Comparison Between NPA-Cured and DDS-Cured Epoxy Resin

The synthesized curing agent NPA, a traditional curing agent DDS and their mixture were used to prepare the epoxy resin material and the properties of the materials were investigated.

Curing Temperature. The curing reactions were studied by DSC and the curing temperatures of NPA and DDS were compared. The DSC curves are shown in Figure 10 and the characteristic temperatures are marked in the figure. The T_i of NPA is 117°C and its T_p is 199°C. The temperatures are much lower than those of DDS which show as 163 and 210°C. This indicates NPA has a relatively higher reactivity and the curing temperature can be much lower. It can also be observed that the peak range of NPA is wider than that of DDS which implies the curing reaction with NPA will decrease the heat accumulation to reduce the internal stress of the epoxy material.

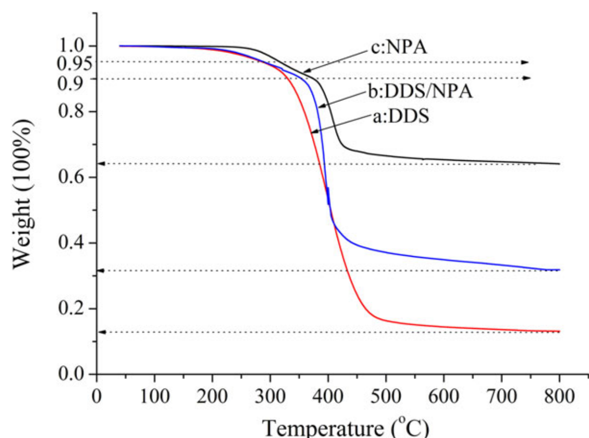

Figure 11. TGA curves of the cured resins obtained from E618 cured by DDS, NPA and their mixture (1 : 1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. TGA Results for the Cured Resin Obtained From E618 Cured by DDS, NPA, and Their Mixture (1 : 1)

	TGA results		
Curing agent	Weight loss 5 % (°C)	Weight loss 10% (°C)	Residue at 800°C (%)
DDS	287	328	13
DDS/NPA	288	355	32
NPA	318	376	64

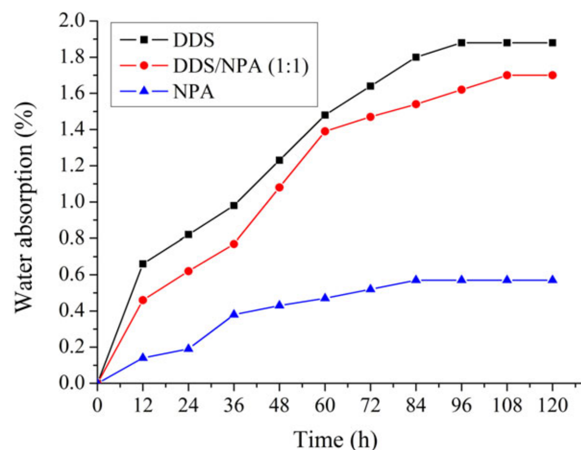

Figure 12. Water absorption curves of the cured resins obtained from E618 cured by DDS, NPA and their mixture (1 : 1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Heat Resistance. Samples cured by DDS, NPA and their mixture (1 : 1) were tested and the TGA curves are shown in Figure 11. The temperatures of 5% weight loss and 10% weight loss are listed in Table II, which also displays the value of residue at 800°C. Epoxy resin cured by DDS has a high

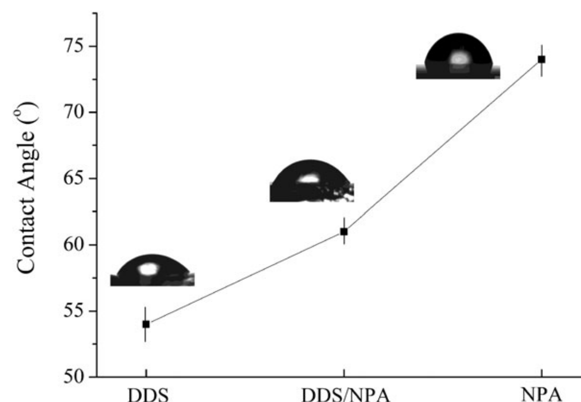

Figure 13. CA of the surface of cured resins obtained from E618 cured by DDS, NPA and their mixture (1 : 1).

Table III. Flame-Retardant Properties of the Cured Epoxy Resins

Sample	Total afterflame time (10 times)	Afterflame time for each individual specimen	Cotton indicator ignited by flaming particles or drops	Rating
DDS/E618	>250 s	>10 s	Yes	Fail
NPA/E618	<20 s	<2 s	No	V-0

temperature for 5% and 10% weight loss valued as 287 and 328°C. The temperatures become higher as the NPA is added and when NPA is solely used, the temperatures increase by 31 and 48°C respectively. The climb of weight loss temperature owes to heat resistant structures in NPA especially the high content of bi-naphthalene and the thermal-stable phosphazene rings. The values of residue at 800°C also demonstrate the high thermal resistance of the phosphazene and bi-naphthalene structures. The increase of the residue agrees with some reports on phosphazene-containing materials and this will improve the flame retardancy.[27]

Moisture Resistance. The result of water absorption experiments is shown in Figure 12 to illustrate the moisture resistance of the samples. The DDS-cured sample has a saturated absorption of 1.88%. The addition of NPA improves the moisture resistance and the DDS/NPA-cured sample absorbs 1.7% of water. The NPA-cured sample only absorbs 0.57% water which is much lower than the former samples. The moisture resistant property largely depends on the content of hydrophobic structures. For NPA, the nitrogen and phosphorus atoms play an important role and meanwhile the nonpolar bi-naphthalene structures show the resistance to water.

The surface of the sample is also an important factor for moisture resistance because water penetrates to the inner material through the surface except those contained in the matrix. The CA of the surface was tested and the result is shown in Figure 13. The CA of DDS-cured sample is 54° and it rises to 61° and 74° when NPA is added or solely used. The nonpolarity of bi-naphthalene structure and the low surface energy of phosphazene structure help increase the CA.[28]

Flame Retardancy. Studies have indicated that the flame retardant efficiency increases when phosphorus and nitrogen exist simultaneously in the epoxy resin system, thus the curing agent based on phosphazene has inherent advantage in flame retardancy. The samples were tested according to the UL94 standard and the result is listed in Table III.

Table IV. Electrical Property of the Cured Epoxy Resins

Sample	Volume resistivity (Ω cm^{-1})
DDS/E618	1.12×10^{16}
NPA/E618	9.52×10^{16}
DDS/E618 (saturated water absorption)	0.97×10^{16}
NPA/E618 (saturated water absorption)	8.73×10^{16}

The DDS-cured sample failed to meet the requirement of V-2 (the lowest rating) in UL94 test indicating the flammability of the resin. When NPA were used, the sample achieved V-0 rating in the test (the best rating). It is mainly due to the high content of nitrogen and phosphorus in phosphazene. These two elements showed synergistic fire-resistant effect when the material burned. The bi-naphthalene structure was also helpful because it tended to form residue in the process.

Electrical Property. Epoxy resin must possess superior electrical resistance as it is used as encapsulating material. The electrical resistivity of the samples was tested and the values are listed in Table IV. The increase in resistivity (from 1.12×10^{16} Ω cm^{-1} to 9.52×10^{16} Ω cm^{-1}) when NPA was used as curing agent can be explained by the inorganic ring of alternating phosphorus and nitrogen atoms in the molecular backbone of phosphazene. The skeleton of cyclotriphosphazene is not a conjugated structure and no electron current carrier is supplied.[29] It can be seen from the result that the resistivity of DDS-cured sample had a 13.4% drop after the saturated water absorption and the drop was lower for the NPA-cured sample which was valued as 8.3% (still higher than DDS-cured sample with no water absorption). This indicated that the NPA-cured resin has a good electrical property even in a moist condition.

CONCLUSIONS

A novel amine-terminated curing agent (NPA) for epoxy resin based on HCCP and bi-naphthalene was synthesized. The temperatures of pre-curing, constant-curing, and post-curing were determined as 86, 163, and 216°C. The cured resin obtained the best moisture-resistance and heat-resistance properties when the functional ratio of amino protons and epoxy group was 1.2 : 1. The temperature reached 318 and 376°C when the weight loss was 5 and 10% meanwhile the residue at 800°C was above 64%. The hydrophobicity of the resin surface was improved and the saturated water absorption was only 0.57%. The resin cured by NPA achieved UL94 V-0 rating indicating it had great flame retardancy. The electrical resistivity was also improved especially when it was compared in a wet condition after the saturated water absorption. This NPA-cured epoxy material with heat-moisture resistance, flame retardancy and electrical insulation had potential application in electronic packaging.

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