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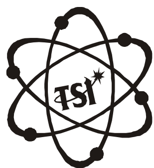

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Synthesis of novel epoxy hardeners and properties of cured products

Xiaoliang Zeng, Jia Liu, Junren Chen, Hanping Liu, Xinnian Xia*

College of Chemistry and Chemical Engineering, Hunan University, Changsha, 410082, (P.R. CHINA)

E-mail : xiaxinnian@126.com

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ABSTRACT

A series of phenol-HPM-dicyclopentadiene (PHD) resins were synthesized through the Friedel-Crafts reaction of phenol, N-(4-hydroxy phenyl) maleimide (HPM) and dicyclopentadiene. The PHD resins were characterized by FTIR, ^{1}HNMR, Gel Permeation Chromatography (GPC) and Elemental analyses. The PHD resins were used as curing agents for o-cresol formaldehyde novoloc epoxy (CNE) resin. The thermal stability of cured epoxy resins was determined by termogravimetric analysis (TGA). The obtained results showed that the cured epoxy resins exhibited good thermal stability (5% degradation temperature > 330 ºC) and high char yield (800 ºC, 47.2%). The moisture absorptions of cured epoxy resins were also tested. The results showed that the cured epoxy resins had lower moisture absorption (1.13%-1.54%) than that of the epoxy resin cured by phenol formaldehyde novolac (PN) resin (1.72%). Moreover, the thermal stability and moisture absorption of the cured epoxy resins were found to be increased with the increase of HPM content.

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KEYWORDS

Curing agent;
Epoxy resin;
Imide;
Dicyclopentadiene;
Thermal properties.

INTRODUCTION

Epoxy resins are extensively used in industry fields as coatings, adhesives, insulating and substrate materials due to their good thermal and dimensional stability, excellent chemical and corrosion resistance, etc[1]. However, the conventional epoxy resins and curing agents are unable to meet the requirements of some applications such as integrated circuit packaging and advanced materials which require higher thermal resistant properties and lower moisture absorption[2]. So it is necessary to develop higher thermal stability and lower moisture-absorbing resin systems for these applications.

Imide compounds and polymers, which contain aromatic or heterocyclic groups, can offer desirable high temperature stability[3]. Therefore, using imide groups to modify the structure of epoxy resin to enhance its thermal resistance has attracted great attention. One method to improve the thermal resistance of epoxy resin is introducting imide groups into the backbones of epoxy compounds. Y.L.Liu[4] synthesized a hybrid monomer of 4-(N-maleimidophenyl) lycidylether. The diglycidyl ester compound further reacted with amine compounds to result in crosslinking networks. The resulted resins exhibited good thermal stability and high glass transition temperature. Developing novel imide containing epoxy curing agents is also an effective way to increase thermal stability of the cured polymers[5-11]. Dicyclopentadiene (DCPD) is a byproduct of C_5 streams in oil refineries. It is a raw material for producing low dielectric polymers

due to their low polarity, low moisture absorption and relatively low cost. This hydrophobic, nonpolar bridging group contributes excellent moisture resistance and a dramatic reduction in the dielectric constant without determinately affecting thermal performance[12]. Many experiments focused on reaction DCPD with phenol and naphthol. The experimental results showed that DCPD-containing compounds exhibited low moisture absorption[13-18]. However, the synthesis of epoxy curing agent containing both imide structure and DCPD moiety has not been reported.

In order to improve both the thermal stability and moisture absorption, the objective of the present study is to synthesize a novel novolac epoxy curing agent containing both a imide structure and a DCPD moiety. The thermal stability and moisture absorption of the cured epoxy resin were investigated and compared with the epoxy curing agent PN.

EXPERIMENTAL

Materials

4-aminophenol, maleic anhydride, *p*-toluenesulfonic acid (*p*-TSA), aluminum chloride, phenol, dicyclopentadiene and triphenylphosphine were purchased from Shanghai Chemicals China. The epoxy resin used was *o*-cresol formaldehyde novoloc epoxy (CNE, epoxy equivalent weight, EEW=207 g/eq). A phenol formaldehyde novolac resin (PN) with a hydroxyl equivalent weight of about 126 g/eq was used as curing agent. Both CNE and PN were kindly supplied by Ba Ling Petrochemical of China. All reagents and solvents were used without further purification.

Synthesis of HPM

HPM was synthesized by two-step reaction procedure from 4-aminophenol and maleic anhydride as previously described[19]. First, the N-(4-hydroxyphenyl) maleamic acid (HPMAc) was prepared by the reaction of 4-aminophenol with maleic anhydride in acetone and obtained a yellow powder product. The *p*-TSA was used for the cyclodehydration of HPMAc. The product was recrystallized from a mixed solvent of water-isopropanol (1:1, V/V) to give an orange crystalline needle product (yield 65%). FTIR (KBr, cm^{-1}): 3481(Ph-OH), 1705(C=O, symmetrical stretching), 1369(C-N stretching), 714 (C=O bending), 688 (C=C bending).

Synthesis of phenol-HPM-dicyclopentadiene (PHD) resins

The PHD resins containing various proportions of HPM were synthesized by the Friedel-Crafts reaction of phenol, HPM and DCPD at 110°C for 10 h, using aluminum chloride as the catalyst. The Synthetic route of PHD resins was showed in Scheme 1. In a typical experiment, a mixture of phenol (90 g, 0.85 mol), HPM (10 g, 0.106 mol), and aluminum chloride (5 g) were heated in a four-necked flask equipped with a heating oil bath, stirrer, reflux condenser and nitrogen inlet. In order to dissolute HPM in phenol absolutely, the reactant mixture was heated to 90°C. The DCPD was added gradually over a period of 1 h and then the mixture was heated to 110°C and maintained for 10 h. When the excessive phenol and DCPD were removed under vacuum, the product then dried at 50°C under vacuum for 4 h and gave a brown color resin (yield 60.2%; softening point 60.6-67.5 °C; hydroxyl equivalent weight=125.7 g/eq). FTIR (KBr, cm^{-1}): 3390 cm^{-1} (Ph-OH), 2945 cm^{-1} (-CH_2- for DCPD ring), 1707 cm^{-1} (C=O, symmetrical stretching), 1242 cm^{-1} (C-N-C), 692 cm^{-1} (=C-H group of maleimide). ^{1}HNMR (TMS) δ ppm: 1.0-3.0 ppm (saturated protons in the DCPD ring), 3.0-3.5 (imide protons), 6.7-7.2 ppm (aromatic protons), 8.1ppm (-OH).

Preparation of cured epoxy resins

The cured epoxy resins were obtained via thermally curing of PHD resins with CNE. In order to obtain a highly crosslinked polymer with good thermal stability, one epoxy equivalent weight of the epoxy resin was cured with one functional equivalent weight of the novolac curing agents. The resin was then cured at 80 ºC for 1 h, 150 ºC for 2 h, 180 ºC for 2 h, and 200 ºC for 2 h, respectively.

Instruments

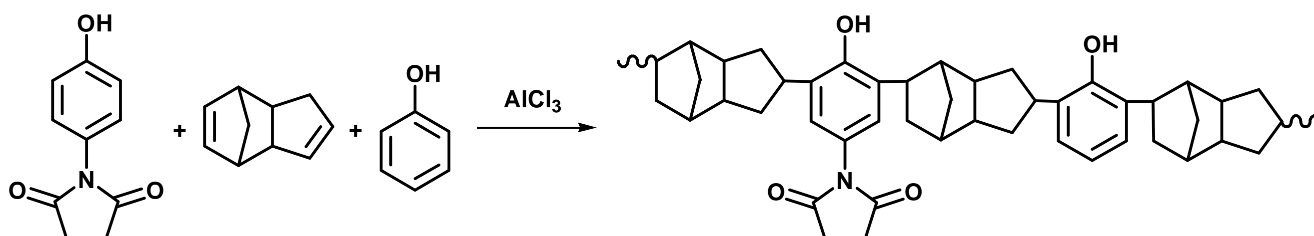
Fourier transform infrared spectroscopy (FTIR) was recorded using a WQF-410 spectrophotometer. ^{1}HNMR spectra was obtained with an INOVA-400 ^{1}HNMR spectrometer using tetramethylsilane (TMS) as internal standard. Gel Permeation Chromatography (GPC) was performed on a Waters 1525/2414 GPC

instrument using tetrahydrofuran as eluent. Elemental analyses was performed using a Heraeus CHN-O-S-Rapid elemental analyzer. TGA data were obtained using a STA-449C Thermogravimetric Analyzer at a heating rate of 10 °C/min under nitrogen atmosphere. Moisture absorption was tested as follows: Samples of the cured epoxy resins (1×1×0.1 cm) were dried under vacuum at 100 °C for 24 h until traces water was expelled. Then the samples were cooled to room temperature and weighed. After placing in boiling water for 24 h, the samples were reweighed. The moisture absorption was calculated as percent weight gain = $(W/W_0-1)\times100\%$, where W was the weight of sample after placing in boiling water for 24 h, and W_0 was the weight of sample before placing in water.

RESULTS AND DISCUSSION

Synthesis and characterization

The PHD resins containing various proportions of HPM were synthesized by the Friedel-Crafts reaction of phenol, HPM and dicyclopentadiene according to Scheme 1. HPM was soluble in phenol up to a solid loading of 50 wt %, beyond which an appreciable amount of the monomer remained solid, making the reaction system heterogeneous. Therefore, only



Scheme 1: Synthetic route of PHD resins.

TABLE 1 : Characteristics of the purified PDH resins.

Polymer number	Wt%HPM in the feed	Wt%HPM in the polymer	Molecular weight (GPC)			
			Mn[a]	Mw[b]	Mp[c]	Mw/Mn[d]
PHD-0	0	0	1056	1676	992	1.63
PHD-10	10	7	900	1275	732	1.42
PHD-30	30	16	540	855	483	1.58
PHD-50	50	29	660	1002	480	1.52

[a]Number average molecular weight, [b]Weight average molecular weight, [c]Peak molecular weight, [d]Polydispersity.

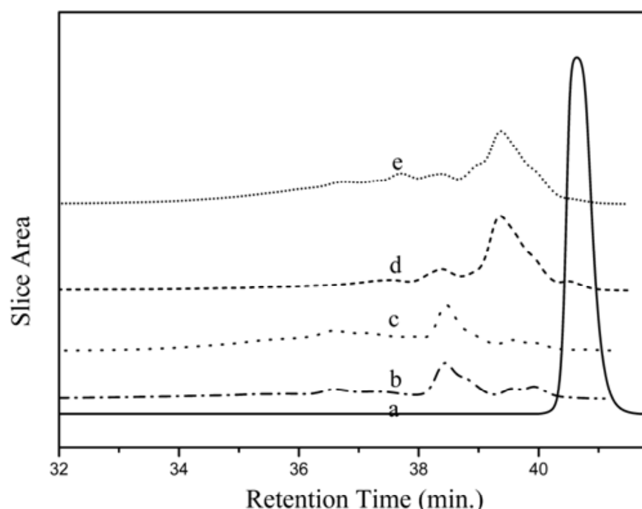


Figure 1 : GPC traces of purified PHD resins (a - HPM, b - PHD-0, c - PHD-10, d - PHD-30, e - PHD-50).

the compositions that were less than 50 wt % HPM in the feed were used. The GPC patterns were shown in Figure 1. The GPC results showed the absence of free HPM in the purified PHD resins. The GPC data of the purified PHD resins containing various proportions of HPM were given in TABLE 1. As can been seen from TABLE 1, the number average molecular weight of PHD resins decreased as the HPM content increased in the feed. The reason was that HPM contained a relatively bulky maleimide group which can hinder its reactivity to some extent. The diminished reactivity of HPM also accounted for the reduction in the nitrogen content of PHD resins compairing with the nitrogen content in the feed.

The PHD resins were characterized by FTIR (Figure 2) and ^{1}HNMR (Figure 3), respectively. The FTIR spectra of PDH-10 displayed characteristic absorption bands at 1707 cm^{-1} (C=O, symmetrical stretching), 1242 cm^{-1} (C-N-C) and 692 cm^{-1} (=C-H group of maleimide). It proposed that the PHD-10 contained HPM. The absorption bands at 2945 cm^{-1} corresponded to $-CH_2-$ for DCPD ring. The characteristic absorption bands of –CH=CH- at 1650, 1609 and 700-740 cm^{-1} (from DCPD) disappeared, and the OH absorption

peaks of novolac at 3390 cm^{-1} are observed, implying that all – CH=CH- functional groups had reacted with phenol or HPM. The ^{1}HNMR signal at 5.4 and 5.9 ppm disappears due to the protons of the – HC=CH – functional groups (from DCPD) reacting with phenol or HPM. The characteristic peaks of aromatic ring at 6.7-7.2 ppm, peaks of imide protons at 3.0-3.5 ppm and the OH absorption peaks at 8.1 ppm are all observed. These results were found to be coincident with the expected chemical structure.

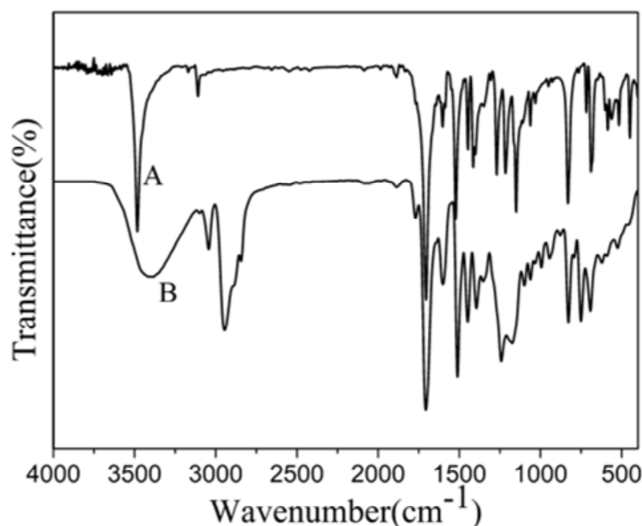


Figure 2 : FTIR spectra of (A) HPM and (B) PHD-10.

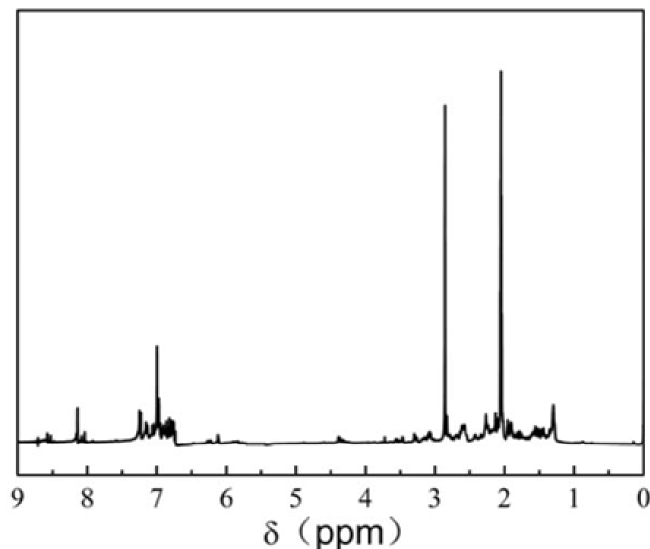


Figure 3 : ^{1}HNMR spectra of PHD-10.

Thermal properties of the cured epoxy resins

The thermal stability of the cured epoxy resins was examined with TGA measurements (Figure 4). The TGA data of cured epoxy resins were listed in TABLE 2. As can been seen from TABLE 2, the CNE epoxy resin cured with PN exhibited 5% degradation temperature ($T_{d5\%}$) at 312.7 ºC, 10% degradation temperature ($T_{d10\%}$) at 346.6 ºC in N_2. However, the CNE epoxy resin cured with PHD resins exhibited higher thermal stability. The CNE epoxy resin cured with PHD resins exhibited the $T_{d5\%}$ ranging between 335.0 ºC and 337.6 ºC, the $T_{d10\%}$ ranging between 354.2 ºC and 376.3 ºC, the char yield at 800 ºC ranging between 15.69% and 47.2%. Moreover, the results indicated that the $T_{d5\%}$, $T_{d10\%}$ and the char yield at 800 ºC shifted toward the higher temperature as the amount of HPM increased. The higher thermal stability was attributed to the higher content of HPM in the polymer chain.

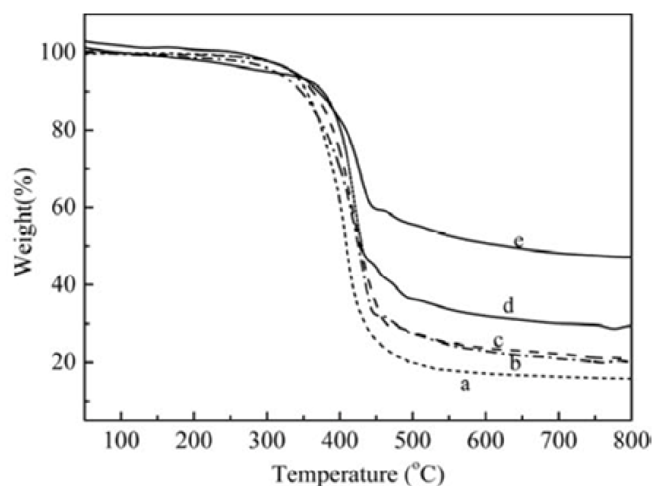


Figure 4 : TGA thermograms of cured epoxy resins in N_2 (a - CNE/PHD-0, b - CNE/PN, c - CNE/PHD-10, d - CNE/PHD-30, e - CNE/PHD-50).

TABLE 2 : Thermal properties of cured epoxy resins.

Sample number	$^aT_{d5\%}$ (ºC)	$^bT_{d10\%}$ (ºC)	$^bW_{800\,°C}$ (%)
CNE/PN	312.7	346.6	20.07
CNE/PHD-0	335.0	354.2	15.69
CNE/PHD-10	336.4	363.0	21.01
CNE/PHD-30	337.8	376.3	29.51
CNE/PHD-50	337.7	370.0	47.2

[a]The temperature 5% of the mass was volatilized, [b]The temperature 10% of the mass was volatilized, [c]Char yield at 800 ºC.

Moisture absorption

The moisture absorptions of cured epoxy resins were given in TABLE 3. As seen in TABLE 3, the moisture absorptions of the cured CNE/PHD resins exhibited lower mositure absorption (1.13%-1.54%) than that of the epoxy resin cured by PN (1.72%). It was due to the hydrophobic, nonpolar bridging DCPD group

which contributed to the excellent moisture resistance without detrimentally affecting thermal performance. Furthermore, the moisture absorptions of cured epoxy resins were found to be enhanced by increasing the HPM content. The reason was that the crosslinking density of cured epoxy resins can be improved by increasing HPM content. As a result, moisture absorption was enhanced by increasing crosslinking density[20].

TABLE 3 : Moisture absorption of the cured epoxy resins

Samples	Moisture absoption (%)
CNE/PN	1.72
CNE/PHD-0	1.13
CNE/PHD-10	1.25
CNE/PHD-30	1.34
CNE/PHD-50	1.54

CONCLUSIONS

A series of imide-DCPD-based PHD resins were synthesized and were used as curing agents for CNE epoxy resin. The cured epoxy resins showed good thermal stability (5% degradation temperature> 330 ºC) and high char yield (800 ºC, 47.2%). The moisture absorptions of cured epoxy resins were also tested. The results showed lower moisture absorption (1.13%-1.54%) than the epoxy resin cured by PN (1.72%). Moreover, thermal stability and moisture absorptions of cured epoxy resins were found to be increased with the increase of the HPM content. The combination of good thermal stability and outstanding resistance to moisture absorption make the CNE/PHD resins attractive candidate in printed circuit board application.

ACKNOWLEDGEMENTS

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REFERENCES

[1] C.A.May, G.Y.Tanka; 'Epoxy Resin: Chemistry and Technology', Marcel Decker, New York, **(1973)**.
[2] G.C.Henningsen, S.A.Gause; 'Printed Circuits Handbook', McGraw-Hill, New York, **(1996)**.
[3] W.K.Chin, M.D.Shau, J.C.Salamone; 'Polymeric Materials Encyclopedia', CRC Press, London, **(1996)**.
[4] Y.L.Liu, Y.J.Chen, W.L.Wei; Polymer, **44**, 6465 **(2003)**.
[5] T.Lchino, Y.Hasuda; J.Appl.Polym.Sci., **34**, 1667 **(1987)**.
[6] S.Sasaki, Y.Hasuda; J.Polym.Sci.Part C: Polym. Lett., **25**, 377 **(1987)**.
[7] C.Gouri, C.P.Reghunadhan Nair, R.Ramaswamy; J.Appl.Polym.Sci., **73**, 695 **(1999)**.
[8] A.Serra, V.Cadiz, A.Mantecan; Angew.Makromol. Chem., **155**, 93 **(1987)**.
[9] K.Adhinarayanan, S.Packirisamy, R.S.George, R.V.Lakshmana, R.Ramaswamy; J.Appl.Polym. Sci., **43**, 783 **(1991)**.
[10] W.K.Chin, M.D.Shau, W.C.Tsai; J.Polym.Sci., Part A: Polym.Chem., **33**, 373 **(1994)**.
[11] P.Sharma, V.Choudhary, A.K.Narula; J.Appl. Polym.Sci., **101**, 3503 **(2006)**.
[12] J.Y.Shieh, C.Y.Lin, C.L.Huang, C.S.Wang; J.Appl. Polym.Sci., **101**, 342 **(2006)**.
[13] H.J.Hwang, J.Y.Shieh, C.H.Li, C.S.Wang; J.Appl. Polym.Sci., **103**, 1942 **(2007)**.
[14] H.Ren, J.Z.Sun, B.J.Wu, Q.Y.Zhou; Polymer, **47**, 8309 **(2006)**.
[15] T.Wang, P.Y.Wan, Q.P.Yu, M.Yu; Polym.Bull., **59**, 787 **(2008)**.
[16] G.H.Hsiue, H.F.Wei, S.J.Shiao, W.J.Kuo, Y.A.Sha; Polym.Degrad.Stab., **73**, 309 **(2001)**.
[17] G.H.Lin, J.C.Chiang, C.S.Wang; J.Appl.Polym.Sci., **88**, 2607 **(2003)**.
[18] F.P.Tseng, F.C.Chang, J.J.Lin; J.Appl.Polym.Sci., **74**, 2196 **(1999)**.
[19] R.L.Bindu, N.C.P.Reghunadhan, K.N.Ninan; J.Polym.Sci., Part A: Polym.Chem., **38**, 641 **(2000)**.
[20] M.Ogata, N.Kinjo, T.Kawata; J.Appl.Polym.Sci., **48**, 583 **(1993)**.