

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Synthesis and Characterization of a Novel Curing Agent for Epoxy Resin Based on Phosphazene Derivatives

Xiaojun Gu^a; Hao Wei^b; Xiaobin Huang^a; Xiaozhen Tang^c

^a School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai, China ^b

Department of Prosthodontics, Ninth People's Hospital, Shanghai Jiao Tong University School of

Medicine, Shanghai Key Laboratory of Stomatology, Shanghai, China ^c National Key Laboratory of

Metallic Matrix Composite Material, Shanghai Jiao Tong University, Shanghai, China

Online publication date: 05 July 2010

To cite this Article Gu, Xiaojun , Wei, Hao , Huang, Xiaobin and Tang, Xiaozhen(2010) 'Synthesis and Characterization of a Novel Curing Agent for Epoxy Resin Based on Phosphazene Derivatives', *Journal of Macromolecular Science, Part A*, 47: 8, 828 – 832

To link to this Article: DOI: 10.1080/10601325.2010.492257

URL: <http://dx.doi.org/10.1080/10601325.2010.492257>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Synthesis and Characterization of a Novel Curing Agent for Epoxy Resin Based on Phosphazene Derivatives

XIAOJUN GU¹, HAO WEI², XIAOBIN HUANG^{1,*} and XIAOZHEN TANG³

¹School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai, China

²Department of Prothodontics, Ninth People's Hospital, Shanghai Jiao Tong University School of Medicine, Shanghai Key Laboratory of Stomatology, Shanghai, China

³National Key Laboratory of Metallic Matrix Composite Material, Shanghai Jiao Tong University, Shanghai, China

Received January 2010, Accepted February 2010

In this work, a novel amine-terminated curing agent for epoxy resin based on hexachlorocyclotriphosphazene (HCCP) was synthesized through two steps of nucleophilic substitution reactions by phenol and 4-aminophenol. Its chemical structure was characterized by ¹H-NMR, Fourier transform infrared spectroscopy (FTIR) and mass spectrometry (MS). This curing agent was liquid at room temperature which made it easy to disperse in the epoxy resin. The rheological test showed the viscosity of the pre-polymer fluid decreased as the proportion of the curing agent increased so it improved the process performance. The curing reaction was studied by differential scanning calorimeter (DSC). The novel curing agent had a wider range of curing temperature and relatively lower curing temperature in comparison with the widely-using curing agent 4,4'-Diaminodiphenylmethane (DDM). The wider range of curing temperature helped lower the heat accumulation which was an important factor in curing process.

Keywords: Epoxy resin, curing agent, hexachlorocyclotriphosphazene

1 Introduction

Epoxy resin is one of the most important thermosetting polymers widely used in aerospace and electronic industries as surface coatings, structural adhesives, printed circuit boards, insulation materials for electronic devices and advanced composites matrices (1–4). Epoxy resin shows the excellent mechanical and chemical properties such as high tensile and compressive strength, good chemical resistance and high heat distortion temperature (5–7). However, it suffers from fire risks which restricts its application (8). There are two traditional approaches enhancing flame retardancy of epoxy resin called “addition” and “reaction”, and the latter shows more potential because of its permanent effect (9). Curing of a resin system is also a critical step in the fabrication of thermosetting polymer and epoxy resin always shows high viscosity thus making the curing process difficult. However, due to its solid state, the widely-using curing agents are difficult to disperse in the epoxy resin and tend to

increase the viscosity leading to a harder processing course. So it is of great significance to develop a novel curing agent with both flame retardancy and viscosity-decreasing effect.

Phosphazene-based materials attract more and more attention in these years due to its excellent comprehensive properties (10–11). Hexachlorocyclotriphosphazene (HCCP) is a usual starting oligomer for the synthesis of phosphazene-based polymers. The chlorine atoms attached to the phosphorus atoms are easy to substitute to form reactive cyclotriphosphazenes. The structure of alternating phosphorus and nitrogen atoms shows its inherent advantage in flame retardancy (12–15).

In this work, a liquid-state curing agent for epoxy resin based on HCCP was synthesized through two steps of nucleophilic substitution reactions and its curing properties were studied.

2 Experimental

2.1 Material

Hexachlorocyclotriphosphazene(HCCP) was synthesized as described in the literature (16). Tetrahydrofuran (THF) was obtained from Shanghai Chemical Reagents Corp. (Shanghai, China) and dried before use. Ethanol,

*Address correspondence to: Xiaobin Huang, School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China. Tel: +86 21 54743264; Fax: +86 21 54741297; E-mail: xbhuang@sjtu.edu.cn; digoman@163.com

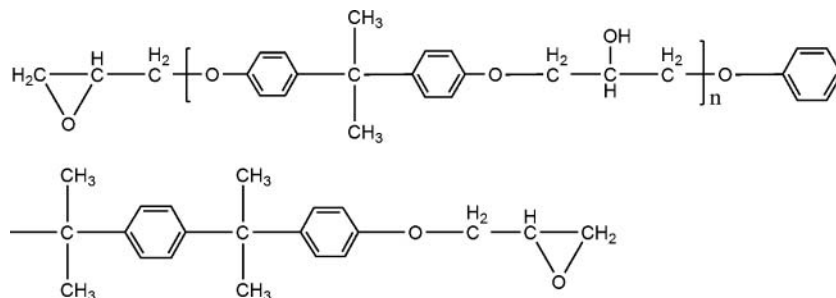


Fig. 1. Structure of EP618.

acetone, 4-aminophenol, phenol, DDM, sodium were purchased from Shanghai Chemical Reagents Corp. (Shanghai, China) and used without further purification. Epoxy resin 618 (EP618) was purchased from Shanghai Haiqu Chemical Industrial Corp. The structure of EP618 is shown in Figure 1 and its average epoxy value is 0.51 (The term “epoxy value” represents the fractional number of epoxy groups contained in 100 grams of resin).

2.2 Characterization

The FTIR measurement was conducted on a Perkin-Elmer Paragon 1000 Fourier transform spectrometer at room temperature. The sample of our synthesized curing agent was first dissolved in ethanol to easily spread on the KBr flake to form a thin layer of solution and then dried under infrared lamp.

The $^1\text{H-NMR}$ measurement was performed on a Perkin-Elmer advance 500AC 200P NMR spectrometer and CDCl_3 was used as a solvent. The mass spectrometry was performed on a Waters QTOF Premier MS device and the conditions were as follows: Capillary: 2.0 KV; Sampling cone: 45.0 V; Extraction cone: 4.0 V; Source temperature: 100°C ; Desolvation temperature: 200°C ; Desolvation gas flow: 600 t/hr.

2.3 Synthesis of Phosphazene-Based Curing Agent

2.3 g sodium was cut to shreds and added slowly into the solution of 9.4 g phenol in 100 mL THF in a 250 mL three-neck-flask under nitrogen protection. The reaction aiming to synthesizing sodium phenoxide lasted 3 h at room temperature. 8.7 g HCCP was dissolved in 100 mL THF in a 500 mL three-neck-flask, and the sodium phenoxide solution was added dropwise into it over a period of 30 min. The reaction was maintained in the reflux condition for 3 h and then refrigerated to room temperature. Subsequently, 1.38 g sodium was cut to shreds and added slowly into the solution of 6.54 g 4-aminophenol in 100 mL THF in a 250 mL three-neck-flask under nitrogen protection. The reaction at room temperature was aimed to synthesizing sodium p-aminophenolate.

Then, the solution of partly-substituted HCCP was slowly added into the flask with the solution of sodium p-aminophenolate over a period of 30 min. The reaction was maintained in the reflux condition for 5 h. The resulting product was washed by acetone, ethanol and water and then dried at 100°C in a vacuum oven. The curing agent finally obtained was puce and showed relatively low viscosity at room temperature.

2.4 Rheological Test

The rheological test was performed on a Gemini 200 HR rheometer manufactured by Bohlin Instruments, UK. At the temperature of 30°C , 6 samples with different proportion of curing agent were tested. The shear rate increased from 0 to 180 1/s and the viscosity of the samples were detected.

2.5 Study on Curing Reaction

The study on curing processes was carried out by DSC. The synthesized curing agent and DDM was respectively mixed with the EP618 at the mass ratio of 1:6, (Fig. 1) the mixtures were stirred manually to be homogeneous and subsequently

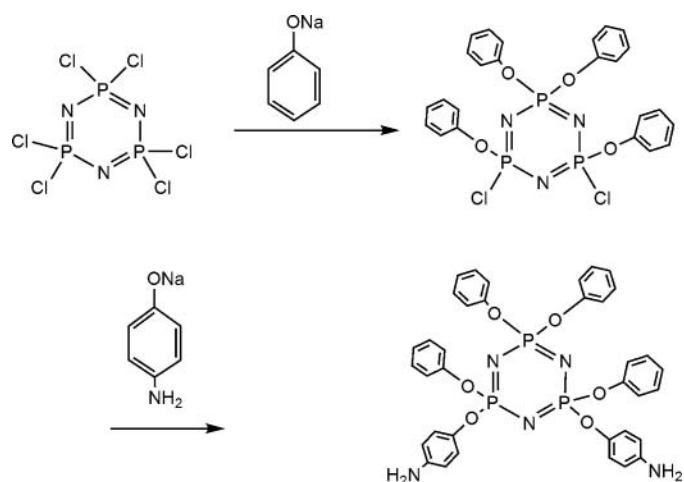


Fig. 2. Schematic procedure of synthesis of curing agent.

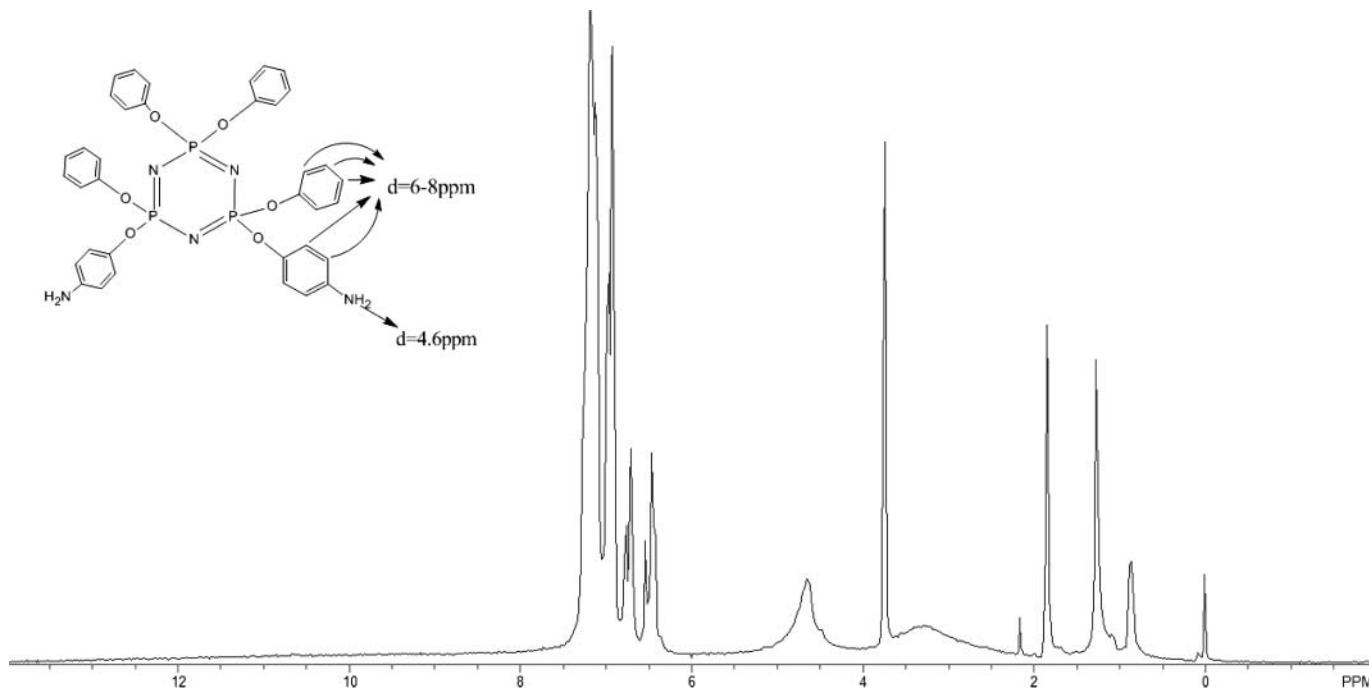


Fig. 3. $^1\text{H-NMR}$ spectrum of our synthesized curing agent.

determined in the DSC instrument at a heating rate of $10^\circ\text{C}/\text{min}$ from 0°C to 200°C at a N_2 atmosphere.

3 Results and Discussion

3.1 Synthesis of Phosphazene-Based Curing Agent

The procedure of synthesis is shown in Figure 2. When synthesizing the curing agent, we made HCCP partly-substituted by sodium phenoxide first and then added the sodium p-aminophenolate instead of 4-aminophenol to avoid the active amido reacting directly with HCCP.

The chemical structure of the curing agent synthesized in our work was characterized by $^1\text{H-NMR}$, FTIR spectroscopy and MS. The $^1\text{H-NMR}$ spectrum is shown in Figure 3. The peak at $\delta = 4.6$ ppm corresponds to amino protons thus indicating the successful synthesis of the curing agent; the peaks at $\delta = 6\sim 8$ ppm correspond to the phenyl protons; the peaks at $\delta = 1.8$ ppm and 3.7 ppm correspond to protons of THF; the peaks at $\delta = 2.2$ ppm correspond to protons of acetone; the peaks at $\delta = 1.3$ correspond to protons of ethanol. We can make a conclusion that the chlorine atoms in HCCP have been substituted by 4-aminophenol and phenol.

The FTIR spectrum is shown in Figure 4. The absorption peaks at 1640 cm^{-1} and 3400 cm^{-1} indicate the presence of $-\text{NH}_2$. The peak at 1260 cm^{-1} corresponds to $\text{P}=\text{N}$; the peaks at 1480 cm^{-1} and 1590 cm^{-1} correspond to benzene ring; the peak at 940 cm^{-1} corresponds to P-O-Ar ; the peak at 875 cm^{-1} corresponds to P-N .

The mass spectrum is shown in Figure 5. The base peak is the molecular ion at m/z 724.1660 and it is our synthesized curing agent. The three most intense fragment ions are m/z 630.1204 (loss of $\text{C}_6\text{H}_5\text{O}\cdot$), m/z 615.1212 (loss of $\text{C}_6\text{H}_6\text{NO}\cdot$) and m/z 536.0662 (loss of $\text{C}_6\text{H}_5\text{O}\cdot$ from 630.1204). The mass spectrum further confirms the structure of the molecular.

FTIR, $^1\text{H-NMR}$ and mass spectra indicate that we have obtained the expected curing agent.

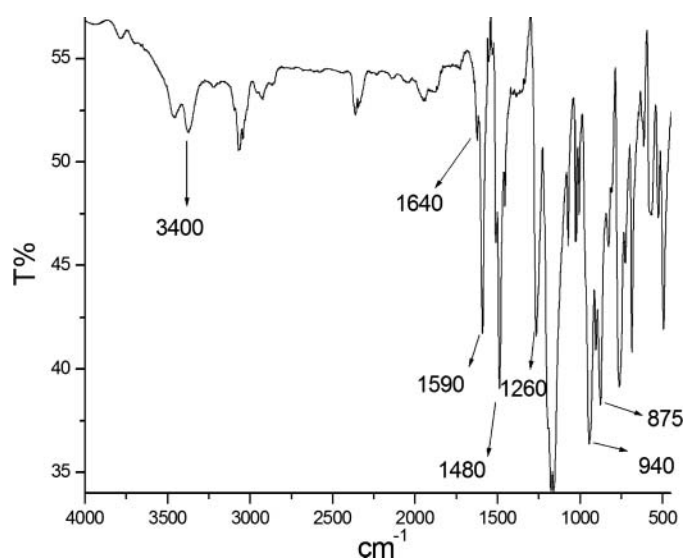


Fig. 4. FTIR spectrum of our synthesized curing agent.

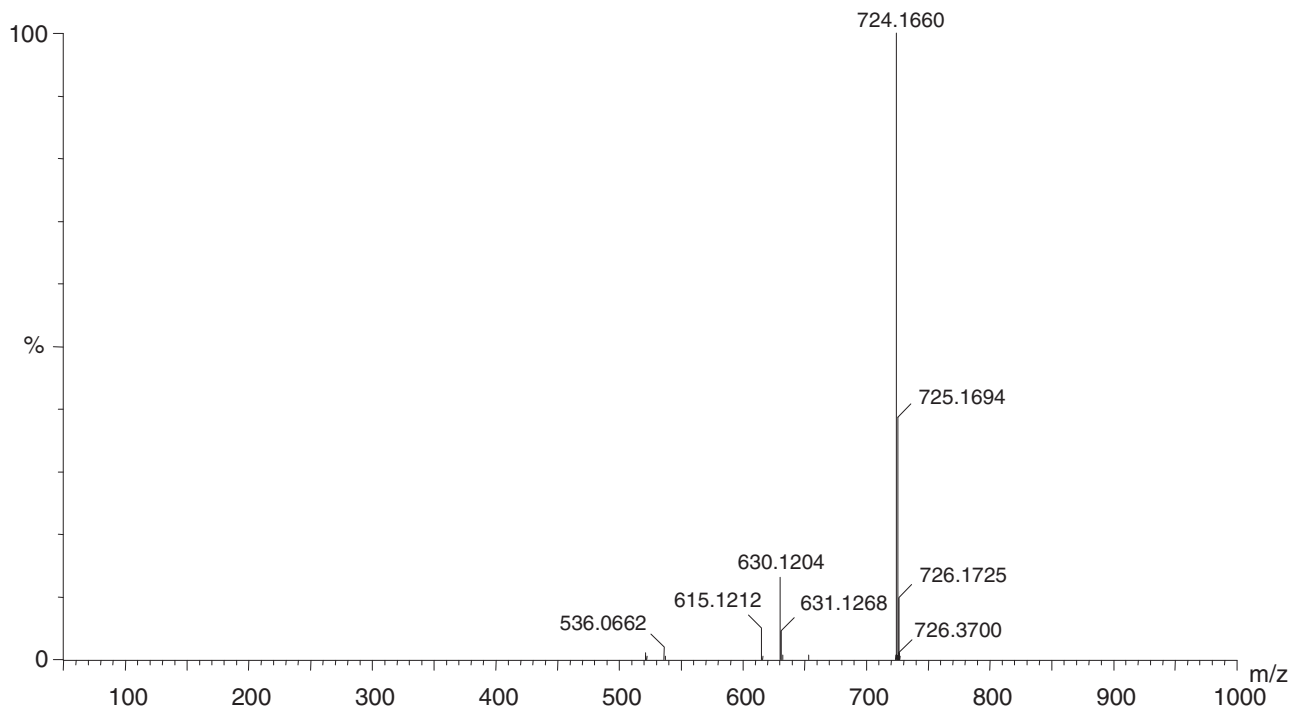


Fig. 5. MS spectrum of our synthesized curing agent.

3.2 Rheological Test

The synthesized curing agent is in liquid state at room temperature which may solve the problem of inhomogeneous dispersion of traditional powder-state curing agent in the epoxy resin. It was found that when our curing agent was added into the epoxy resin, the system viscosity decreased as the proportion of curing agent increased. Figure 6 showed the viscosity of the pre-polymer fluid with different proportion of curing agent when the shear rate changed. The viscosity of EP618 reached about 7Pas however the viscosity of the sample 2 ($m_{EP618} : m_{curing\ agent} = 6:1$), sample 3 ($m_{EP618} : m_{curing\ agent} = 5:1$), sample 4 ($m_{EP618} : m_{curing\ agent} =$

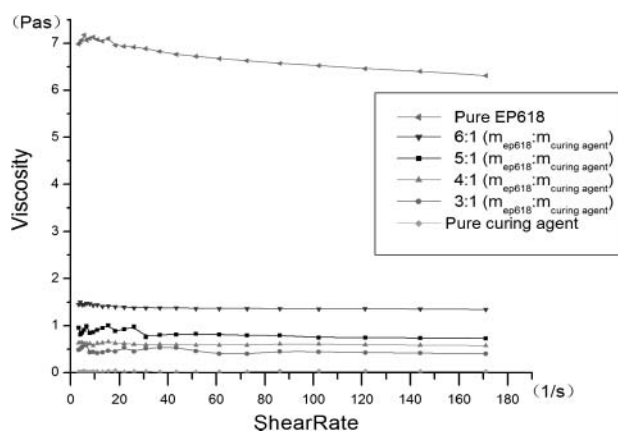


Fig. 6. Viscosity of pre-polymer fluid with different proportion of curing agent.

4:1), sample 5 ($m_{EP618} : m_{curing\ agent} = 3:1$) dropped to 1.5Pas, 0.9Pas, 0.6Pas, 0.4Pas. The pure synthesized curing agent was about 0.02Pas.

3.3 Study on Curing Reaction

Curing reactions of EP618 with phosphazene-based curing agent and DDM were respectively studied by DSC. The

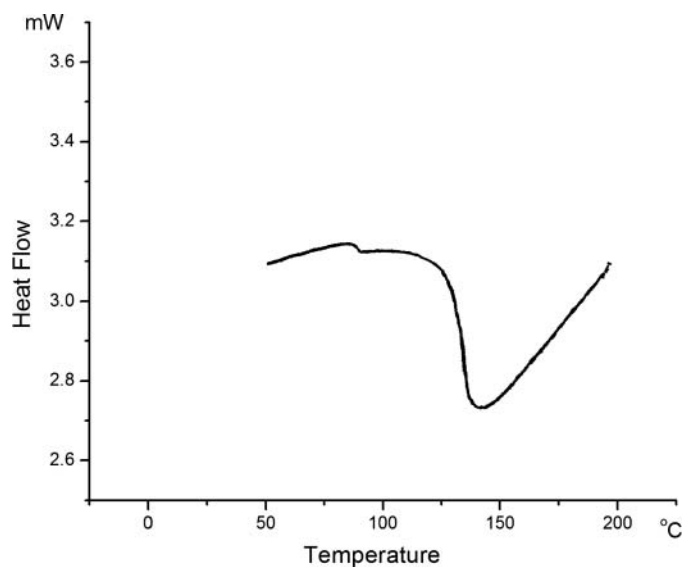


Fig. 7. DSC thermo gram of the curing reaction of phosphazene-based curing agent with EP618.

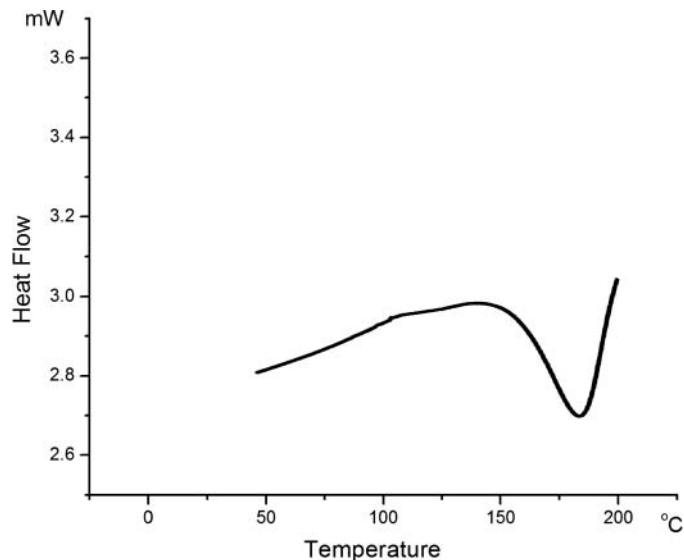


Fig. 8. DSC thermo gram of the curing reaction of DDM with EP618.

thermo grams in Figures 7 and Figure 8 show that the initial curing temperature of phosphazene-based curing agent is 90°C and it is lower than that of the traditional curing agent DDM which is detected as 130°C. This indicates the reactivity of our curing agent is higher than that of DDM. It also can be observed that the curing temperature of our curing agent has a wider range compared with that of DDM. The relatively broad heat-releasing peak can make it easy to reduce the internal stress of the EP materials.

Our preliminary test showed that the cured EP system by our curing agent has an enhanced flame retardant property and the mechanical properties are studied at present.

4 Conclusions

A novel amine-terminated curing agent for epoxy resin based on hexachlorocyclotriphosphazene (HCCP) was synthesized. The curing agent was in liquid state at room

temperature which would help the homogeneous dispersion of curing agent in the epoxy resin. The rheological test showed the viscosity of the system decreased a lot as the curing agent was mixed in the resin. The study on its curing reaction by DSC showed a lower starting curing temperature and a wider range of curing temperature compared to DDM especially the latter advantage can help reduce the internal stress of EP materials. Its backbone of alternating phosphorus and nitrogen atoms was expected to be an effective flame retardant system because studies had indicated that the flame-retardant efficiency increased when phosphorus and nitrogen existed simultaneously in the curing system of epoxy resin. This may broaden the potential application of EP in many fields.

References

1. Rwei, S.P., Cheng, C.Y., Liou, G.S. and Cheng, K.C. (2005) *Polym. Eng. Sci.*, 45(4), 478.
2. Cooper, C.A., Young, R.J. and Halsall, M. (2000) *Composite Part A*, 32, 401.
3. Wang, C.S. and Lee, M.C. (2000) *Polymer*, 41(10), 3631.
4. Pan, G., Du, Z., Zhang, C., Li, C., Yang, X. and Li, H. (2007) *Polymer*, 48, 3686.
5. Park, S.J. and Jin, F.L. (2004) *Polym. Degrad. Stab.*, 86, 515.
6. Jain, P., Choudhary, V. and Varma, I.K. (2003) *Eur. Polym.*, 39, 181.
7. Wang, F., Xiao, J., Wang, J.W. and Li, S.Q. (2008) *J Appl. Polym. Sci.* 107, 223.
8. Hauk, A., Sklorz, M., Bergmann, G. and Hutzinger, O. (1995) *J. Anal. Appl. Pyrolysis*, 31(2), 141.
9. Mauerer, O. (2005) *Polym. Degrad. Stab.*, 88(1), 70.
10. Orme, C.J., Klaehn, J.R., Harrup, M.K., Lash, R.P. and Stewart, F.F. (2005) *J. Appl. Polym. Sci.*, 97, 939.
11. Zhu, L., Zhu, Y., Pan, Y., Huang, Y.W., Huang, X.B. and Tang, X.Z. (2007) *Macromol. React. Eng.*, 1, 45.
12. Gao, F., Tong, L.F. and Fang, Z.P. (2006) *Polym. Degrad. Stab.*, 91(6), 1295.
13. Yuan, C.Y., Chen, S.Y., Tsia, C.H. and Chiu, Y.S. (2005) *Polym. Adv. Technol.*, 16(5), 393.
14. Chen-Yang, Y.W., Yuan, C.Y., Li, C.H. and Yang, H.C. (2003) *J Appl. Polym. Sci.*, 90(5), 1357.
15. Chen-Yang, Y.W., Lee, H.F. and Yuan, C.Y., (2000) *J. Polym. Sci. Polym. Chem.*, 38(6), 972.
16. Jaeger, R.D. and Gleria, M. (1998) *Prog. Polym. Sci.*, 23, 179.