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Rheological and thermal properties of epoxy resins obtained from epichlorohydrin and *m*- or *p*-aminophenol, cured with triethylenetetraamine

Summary — Synthesis of triglycidyl derivatives of *m*- or *p*-aminophenol and their crosslinking with triethyltetraamine (TETA) has been described. The obtained products have been characterized by IR and ¹H NMR methods and rheological properties. The curing reaction with TETA has been investigated by differential scanning calorimetry (DSC). Thermal stability of the cured products has been studied by thermogravimetric analysis (TGA).

Key words: *m*- and *p*-aminophenol, glycidyl derivatives, rheological properties, curing, epoxy resins, thermal properties.

Over the last few years, much attention has been devoted to the synthesis of tri- or tetrafunctional polymers constituting raw materials in the synthesis of new products [1–10]. These polymers may exhibit a number of useful properties, such as high thermal stability, chemical resistance, good dimensional and mechanical properties and excellent processability. Conventional epoxy resins (bifunctional) are unsatisfactory in meeting requirements in the field of advanced materials where certain thermal and mechanical properties are demanded. Epoxy resins, being multifunctional polymers, find important applications as adhesive and matrix resins in chemical processing, for electrical and electronic application, aviation and the hydrospace industries, coating industry *etc.* [11, 12].

The present paper reports synthesis of epoxy resins obtained from epichlorohydrin and *m*- or *p*-aminophenol and the rheological and thermal properties of the final cured products.

EXPERIMENTAL

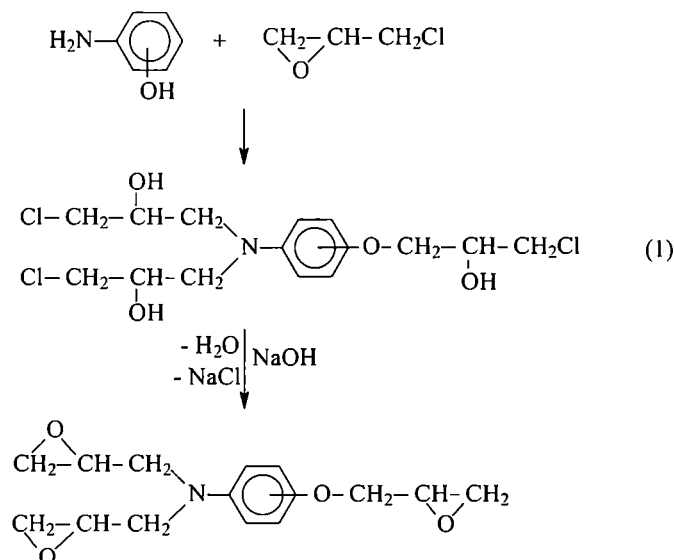
Materials

m- or *p*-Aminophenol (*m*AP, *p*AP; Fluka), sodium hydroxide (NaOH; Aldrich), pure for analysis, were used without further purification.

Epichlorohydrin, triethylenetetraamine (TETA) and organic solvents were reagent grade products and were distilled before use.

Synthesis of triglycidyl derivatives of *m*AP or *p*AP

A typical synthesis of the epoxy resins (Eq. 1) was as follows:



A 0.5 L 4-necked round-bottomed flask immersed in a water bath, equipped with mechanical stirrer, thermometer, dropping funnel, a Dean Stark trap and water condenser was charged with 54.5 g (0.5 mol) *m*AP or *p*AP, 277 g (3 mol) epichlorohydrin and 7 ml water. The mixture was slowly stirred (under nitrogen) at 30°C over 30 minutes to give a homogeneous solution. Next, it was heated at 60°C and maintained at this temperature for 6 hours. Subsequently, the reaction mass was cooled at 52–55°C and 60 g NaOH (1.5 mol) as 50% w/w aque-

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ous solution was added dropwise over a period of 3 hours. The mixture was kept for an additional 3 hours. The organic phase was separated, filtered and washed several times with distilled water to remove residual sodium chloride. After washing, the organic phase was heated under reflux to remove at first the azeotropic mixture (water and epichlorohydrin) and next, excess of epichlorohydrin. Finally, the raw product was distilled under vacuum to remove epichlorohydrin completely. A pale red brownish mass of triglycidyl (TG) resin was obtained (average epoxy equivalent weight = 118 g·eq⁻¹ for TGpAP and = 104 g·eq⁻¹ for TGmAP). The number-average molecular weights as determined by cryoscopic method (using DMSO as solvent) were 301 for TGmAP and 318 for TGpAP.

Curing procedure

The curing reaction was performed by mixing epoxy resins with TETA, in the ratio $r = 0.75$, where r = amine hydrogen/epoxy group. The mixture was placed into a vacuum oven at room temperature for 10 minutes to remove air bubbles and it was used for the DSC study. The remaining samples were cured at 120°C for 1 hour and at 150°C for another 2 hours. Cured products were powdered as fine grain and used for thermal analysis at a heating rate of 12°C/min in air.

Measurements

The chemical structure of the prepared products was identified using IR (Specord M80 Carl Zeiss, KBr pellets) and ¹H NMR (JEOL-JNMC 60HL, CDCl₃ as solvent, tetramethylsilane as internal standard) spectroscopic methods. The average epoxy equivalent weights (expressed in g·eq⁻¹) and the number-average molecular weight (determined by cryoscopy) were determined using a method described elsewhere [13, 14]. Thermal properties of epoxy resins were evaluated by means of a Mettler 12 E type differential scanning calorimeter (DSC); the instrument was calibrated using indium as a standard. Approximately 5–10 mg of the epoxy resin in mixture with the curing agent, in the proposed ratio, were scanned from 20 to 200°C, with different heating rates (5, 10 and 20°C/min), in a nitrogen atmosphere. Characteristics of cured products were obtained using thermogravimetric analysis (TGA) (MOM Budapest Paulik, Paulik-Erdey type derivatograph) at a heating rate of 12°C·min⁻¹, in air. Activation energy of the decomposition process for cured products was determined using the Coats and Redfern method for $n = 1$ [15]. Rheological behaviors were estimated using a Rheotest 2.1 type viscometer (Germany), equipped with cone and plate device (cone diameter = 36 mm, cone angle 0.3°, 1 s⁻¹ shear rate, the temperature range 40–90°C). Consistency index (K) (the zero shear viscosity) was measured by

direct extrapolation of straight lines from the logarithmic plots of shear stress versus shear rate. Flow index was determined from slope of these lines by using the Ostwald de Waele model [16]. Activation energy for viscous flow was calculated using the Arrhenius equation:

$$\eta = A \exp(E/RT) \quad (2)$$

where: E — activation energy for viscous flow; R — gas constant; A — constant characteristic of the sample; T — absolute temperature (K); η — viscosity.

RESULTS AND DISCUSSION

Chemical structure

Epoxy resins were synthesized from *m*- or *p*-aminophenol in a large excess of epichlorohydrin with the aim of obtaining low molecular weight products. However, the difference between experimental (118 or 104 g·eq⁻¹) and theoretical (92 g·eq⁻¹) values of average epoxy equivalent weights, suggest that the reaction mass contains oligomers in its composition.

Chemical structures were identified by IR and ¹H NMR spectra, namely:

IR peaks (KBr), cm⁻¹:

TGpAP: 1620 (phenyl), 1250–1270 (C-N aromatic), 1150–1200 (C-N aliphatic), 915 (oxirane ring), 840 (*p*-substituted benzene).

TGmAP: 1615 (phenyl), 1235 (C-N aromatic), 910 (oxirane ring), 830 and 755 (*p*-substituted benzene).

¹H NMR peaks (CDCl₃), ppm:

TGpAP: 2.65 (multiplet, CH₂ oxirane ring protons), 3.15 (singlet, CH oxirane ring proton), 3.6 (multiplet, NH proton), 6.70–7.1 (aromatic protons).

TGmAP: 2.81 (multiplet, CH₂ oxirane ring protons), 3.08 (singlet, CH oxirane ring proton), 3.6 (multiplet, NH proton), 4.05 (multiplet, N-CH₂ protons), 6.66–7.31 (aromatic protons).

So, peaks arising for the oxirane ring are observed at 910–915 cm⁻¹ in IR spectra and at 2.65–3.15 ppm in ¹H NMR spectra. Signal attributed to the benzene substitution is situated at 830–840 and at 755 cm⁻¹ in IR spectra and at 6.67–7.31 ppm in ¹H NMR spectra.

Rheological behavior

Typical logarithmic plots of shear stress versus shear rate for triglycidyl resins are given in Figure 1 and 2. The slope of extrapolated straight lines to $\dot{\gamma} = 0$ was used to calculate consistency index (K) and flow index (n) using the Ostwald de Waele model (Table 1). Activation energy of flowing was calculated on the basis of the Arrhenius equation and consistency index. As it can be seen in Table 1, flow indices attain values less than unity and this indicates that such resins exhibit non-Newtonian behavior of the pseudoplastic type.

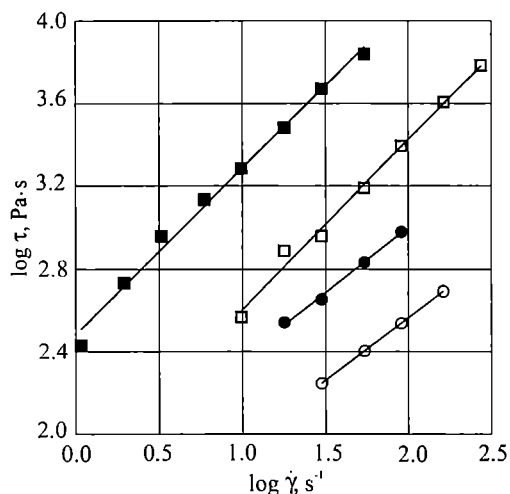


Fig. 1. Variation of the shear stress versus shear rate for the TGmAP resins; temperature: (■) 30°C; (□) 40°C; (●) 50°C; (○) 60°C

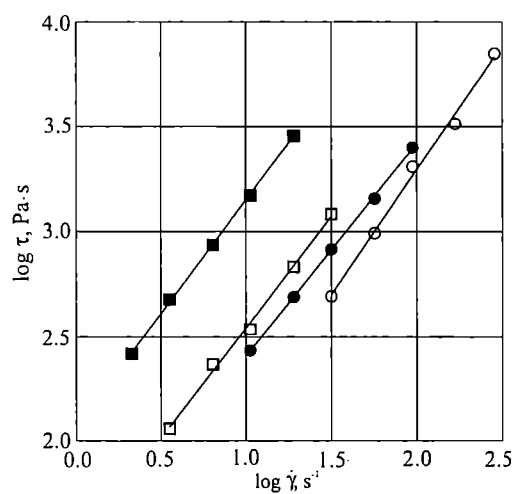


Fig. 2. Variation of the shear stress versus shear rate for the TGpAP resins; temperature: (■) 30°C; (□) 40°C; (●) 50°C; (○) 60°C

Table 1. Changes in the consistency index, flow index and activation energy of flowing in the temperature range 30–60 °C

Sample	Temperature, °C								Activation energy of flowing, kJ/mol
	30		40		50		60		
	K, Pa·s	n	K, Pa·s	n	K, Pa·s	n	K, Pa·s	n	
TGmAP	154.1	0.95	57.1	0.82	44.7	0.67	21.1	0.61	52.26
TGpAP	120.1	0.85	41.6	0.83	35.2	0.79	18.7	0.93	48.24

Thermal characterization of resins and cured products

Curing behavior of the resins was emphasized in DSC scans. Principal parameters of DSC scans are presented in Table 2. Log β (heating rate °C/min) was plotted versus peak temperature (K) using the Ozawa method [17]. Activation energy and frequency factor were obtained from the slope and intercept with the y-axis. A comparative observation in Table 2 reveals that values of activation energy of curing are in the same order of magnitude, probably due to the same chemical structure of the resins. These values are comparable with the data reported in literature for relatively similar systems [4].

In order to determine the thermal stability of the cured products activation energy of the degradation process determined using the Coats and Redfern

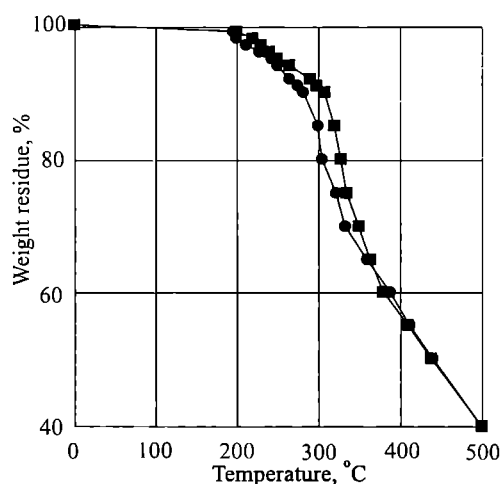


Fig. 3. TGA curves for decomposition in air of (■) TGmAP and (●)TGpAP resins cured with TETA

Table 2. Kinetic parameters of epoxy systems cured with TETA (from DSC scans)¹⁾

System	Heat rate, °C/min									Activation energy of curing kJ/mol	Frequency factor (average value, min ⁻¹)
	5			10			20				
	T _i	T _M	T _F	T _i	T _M	T _F	T _i	T _M	T _F		
TGmAP	28.7	70	162.5	30.1	86.3	169.2	35.5	95.3	185.4	57.3	5.18 · 10 ⁶
TGpAP	30.5	64	116.1	30.0	72	163.5	32.2	91.2	174.5	49.4	7.19 · 10 ⁵

¹⁾ T_i— initial temperature, °C; T_M— maximum peak temperature, °C; T_F— final temperature, °C.

Table 3. Thermal parameters of crosslinked resins.

Sample	Temperature (°C), at which weight loss is equal		Weight loss at 500°C %	Activation energies of degradation process ^a , kJ/mol
	10%	50%		
TGmAP	308	438	57	39.5
TGpAP	282	440	60	36.1

^a In temperature range 200–450 °C.

method. Thermogravimetric curves and the most important parameters are shown in Figure 3 and in Table 3, respectively. Initial decomposition temperatures (2% weight losses) of cured products were recorded at 200°C for TGmAP and for TGpAP. Cured products exhibit 5% weight losses at a relatively equal value of temperature. Values of the decomposition activation energy were similar for both products.

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KALENDARZ IMPREZ

7–10 kwietnia 2003 r. Cambridge, W. Brytania. 12. Międzynarodowa konferencja pn. „Deformation, Yield and Fracture of Polymers”.

Organizator: Institute of Materials (IOM) — wydawca czasopisma *Plastics, Rubber and Composites*.

Koordinatory: Plastics and Rubber Division of the Institute of Materials, Polymer Physics Group of the Institute of Physics, The British Society of Rheology, The Royal Society of Chemistry.

Zakres tematyczny: biopolimery, przetwórstwo, badania zmęczeniowe, udarowe i odpornościowe, mechanika spękań, żele, powierzchnie międzyfazowe, nowoczesne techniki, symulacja/modelowanie, lepkość.

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7–10 lipca 2003 r. Melbourne, Australia. 19. doroczne spotkanie dyskusyjne Stowarzyszenia Przetwórców Polimerów „Polymer Processing Society — PPS-19”.

Organizatorzy i sponsorzy: Polymer Processing Society, Rheology & Materials Processing Centre RMIT University CRS for Polymers, Australian Society of Rheology.

Tematyka: kompozyty, mieszaniny i stopy, reologia i reometria, mieszanie, formowanie z rozdmuchiwaniem, formo-

wanie termiczne, spienianie, morfologia/struktura i właściwości, modelowanie i symulacja, wytwarzanie folii i urządzeń, formowanie wytłoczone, powlekanie, nowe materiały i procesy.

Informacje: Secretariat, PPS-19 Meeting 2003, Rheology & Materials Processing Centre, School of Civil & Chemical Engineering, RMIT University, GPO Box 2476 V, Melbourne 3001, Australia. Tel.: +61-3-9925 3778, fax: +61-3-9925 2268, e-mail: pps 19@rmit.edu.au, internet: www.pps 19.nww.com.au

20–24 lipca 2004 r. Akron, Ohio, USA. 20. doroczne spotkanie dyskusyjne Stowarzyszenia Przetwórców Polimerów „Polymer Processing Society — PPS-20”.

Organizator: Polymer Processing Society.

Tematyka: adhezja, kleje i klejenie, mieszanie, technologie pokrywania, kompozyty, polimery przewodzące i do zastosowań w elektrooptyce, projektowanie i przewidywanie trwałości produktów polimerowych, technologie wtrysku i wytłaczania, włókna i powłoki, modelowanie i symulacja, nanotechnologie, monitoring procesów, reologia i reometria, przetwórstwo gumy i rozwój struktur w przetwarzaniu polimerów.

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