Study on the Synthesis of Brominated Epoxy Resins

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ABSTRACT: The GC/MS/Py method, thermogravimetric analysis (TG), MALDI-TOF spectrometry, and IR spectra were utilized to investigate structures and thermal stability of brominated epoxy resins synthesized in the reaction of epichlorohydrin (ECH) and tetrabromobisphenol A (TBBA), with varied molar rates of monomers and varied condensation temperatures. A Rheotest viscometer was employed to test rheological properties of the resins, while their mechanical properties were determined after hardening with phthalic anhydride. The research work revealed that the optimum synthesis conditions were ECH : TBBA = 5 : 1, and the condensation temperature reasonably low (e.g., 40°C). The basic properties of the synthesized resins were found to be comparable to those of the commercial product D.E.R. 542 offered by Dow Plastics. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3122–3134, 2003

Key words: MALDI, mechanical properties; thermal properties

INTRODUCTION

Brominated epoxy resins make part of widely employed hardening plastics wherein bromine atoms play the role of active fire-retardant additives responsible for the self-extinguishing performance. Those bromine atoms are fixed by means of hydrolysis resistant C—Br bonds with diglycidyl ether groups within bisphenol A (DGEBA). Irrespective of bromine, some small amounts of organic chlorine are also present in those plastics, and in some grades chlorine compounds serve the function of chemical hardeners or specific filler materials; waste chlorinated rubber can make the example of the latter case.[1]

From among numerous slow-burning epoxy resins, the practical outlets could be found predominantly for those obtained from tetrabromobisphenol A (TBBA), because only those resins can offer bromine bonding, which is satisfactorily robust at the temperatures exceeding 150°C.

The epoxy sealants and putties make the most popular encapsulation materials for integrated circuits and semiconductor-based electronic systems at present. Their task is to protect the electric circuits against environment moisture under (frequently) rugged operation conditions as well as against ionic contamination derived from potential hydrolysis products of organic dielectrics, which are in contact with the integrated circuit components. What is usually important is hard-to-forecast and changing environment conditions, like air humidity and temperature, and changing mechanical loads, for example, vibrations resulting from specific operating conditions of machines and/or equipment, to which the electronic components can be exposed. Having in mind the above reasons, the epoxy-based encapsulating materials must offer good hydrolytic, thermal, and mechanical stability.

The brominated epoxy resins have been utilized in particular in printed circuit boards, in laminated elements for electrical appliances, and in encapsulation compounds, which are frequently expected to additionally offer fire-resistive performance. Moreover, these materials make valuable admixtures that improve the fire resistance of other polymers employed in electronic engineering, for example, polyurethanes. Unfortunately, that type of resin can contain numerous unstable and readily hydrolysable bromides — their contents will dramatically increase when a sealant is held at a high temperature. The bromides and chlorides formed during hydrolysis and thermolysis make ionic contaminations of epoxy encapsulation materials, and they are responsible for corrosion and reduced serviceability of electronic systems. Moreover, additional problems are posed when a self-extinguishing material is still set on fire. The burning process will release toxic and corrosive fumes that will contain HBr and HCl, which puts additional limits to the applicability of such materials in the automotive and aircraft industries, for example. One of the methods to reduce the inflammability of encapsulation resins is the pro-

duction of composite materials with good heat resistance and low thermal conductivity.[2] That can be achieved by incorporating additional inorganic fillers (aluminium, magnesium, and antimony oxides), novolak resin(s) and other additive(s) that consolidate the structure through introducing benzene rings or increasing the crosslinking density of hardening plastics. Also, epoxy-based composite materials are produced, which find their outlets in, for example, glass-reinforced laminates, wherein the polymer matrix is made by brominated novolak resins and polyfunctional epoxy resins. These materials offer good adhesion to metal foil, considerable thermal stability, and their mechanical strength even approaches the performance of some grades of steel.[3-7] Silica, antimony, and aluminium hydroxide have also been introduced to epoxy-based systems.[8,9]

Increased flame resistance of epoxide resins can also be attained by introducing phosphorus com-

pounds to the matrix[10,11] or by introducing a stable dispersion of polysiloxane particles to the epoxy–phenol–arylalkid resin. Plastics with improved mechanical and thermal performance can be produced in that way that perfectly encapsulate electronic elements.[12]

The present study also enters the trend of research as described above. Its purpose is to highlight some aspects of the manufacturing processes and applications of brominated epoxy resins that can be hardened to form a solid layer of engineering polymer.

The basic commercial method for the production of epoxy resins — inclusive of their brominated versions — is a two-stage epoxidation process that involves epichlorohydrin (ECH) and compounds that contain active hydrogen atoms. Epoxy rings usually make chain terminal groups. The structure of expected resin can diagrammatically be presented as follows:
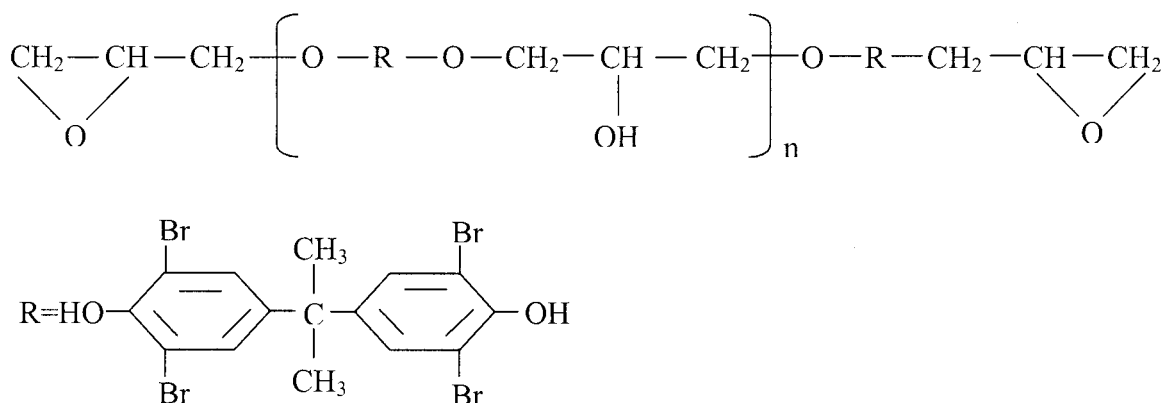
where $n = 1$–10.

The polymer chains could be terminated by: α-glycol groups (a), α-chlorohydrin groups (b), or β-chlorohydrin groups (c), and by oligochlorooxypropylene groups as well, or even by the

products of further and generally disadvantageous oligomerisation of ECH, which can be present in the reaction mixture.[13]

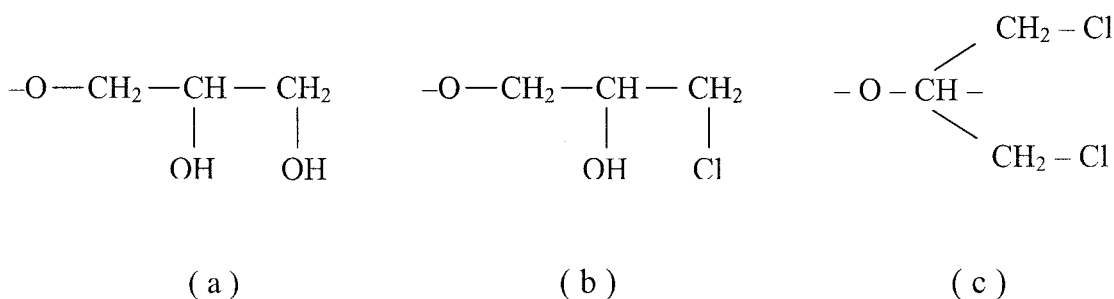Those structures affect thermal stability of the resin and thus its flammability.

(a)   (b)   (c)

TABLE I
Effect of the Amount of Epichlorohydrin on the Properties of Brominated Epoxy Resin

Sample No.	ECH:TBBA Ratio (mol/mol)	Epoxy Number (mol/100 g)	Organic Chlorine Content (wt %)	Bromine Content (wt %)	Melting Point (°C)	Yield of Reaction (%)
1	8	0.276	0.47	49.1	59	52.5
2	5	0.271	0.42	49.1	62	66.0
3	4	0.277	0.12	49.1	63	67.0

Our special attention has been given just to those aspects in our research.

EXPERIMENTAL

Raw materials

1. Epichlorohydrin for industrial use, from ZCh "ZACHEM" S.A. in Bydgoszcz, which has been subjected to atmospheric distillation prior to use (b.p. = 117°C),
2. tetrabromobisphenol A, reagent from "Aldrich,"
3. isopropanol for industrial use, from "POCh" S.A., Gliwice,
4. sodium hydroxide, analytically pure, from PPH "Standard", Lublin,
5. phthalic anhydride, from "POCh" S.A., Gliwice.

Synthesis of low molecular-weight brominated epoxy resin

Adequate volumes of ECH, TBBA, and isopropanol as an inert process solvent were placed in a 750 cm³ three-necked flask provided with a reflux condenser, thermometer, and dropping funnel. The ratio of monomers was changed for various synthesis experiments. The reaction mixture was heated up to dissolve the substrates. The first volume of NaOH in the form of a 32 wt % solution was added drop by drop at the reaction temperature of 50°C, for 15 min. Then, condensation followed — the balance volume of NaOH was added dropwise at 40–60°C. After the condensation reaction was completed, hot water was added to the mixture to dissolve NaCl, and the postreaction liquor was separated. The purified volatile products, inclusive of unconverted ECH and isopropanol, were expelled by means of vacuum distillation then. The distillation cycle took 1 h at 130°C under about 2 kPa. The resin was obtained as a distillation residue. After cooling down, it had a form of pale yellow and brittle solid, which melted above 50°C.

Hardening of brominated epoxy resin

The low molecular-weight brominated solid resins were hardened at 120°C by adding 30% phthalic an-

hydride, over 24 h in a drier. Test pieces were produced in PTFE molds.

Methods for the characterization of products

The IR spectra of resin samples were taken with the use of SPECORD M80 spectrometer within 4000–650 cm^{-1}, and the samples were prepared as KBr pellets.

The elementary bromine content was determined according to a standard method.[14] The samples to be analyzed were burnt in an atmosphere of oxygen, the combustion products were absorbed, and the potentiometric titration method was employed to determine their bromide contents.

The epoxy number was determined after acid hydrolysis of epoxy groups in the HCl$_{cone}$/dioxane solution, by titration of unreacted HCl with methanolic NaOH; cresol red was used as an indicator.[15]

The organic chlorine content was determined according to a standard method.[16] The samples were subjected to distillation in the presence of a known volume of 0.1 mol/L alcoholic KOH. The amount of KOH consumed for hydrolysis of C—Cl bonds reflects the organic chlorine content in the resin.

The flow curves and absolute viscosity specifications for liquid resins at 80°C were found by means of a Rheotest viscometer, in accordance with a standard method.[17] The determination consists in measuring the torque at the wall of a cylinder immersed in the
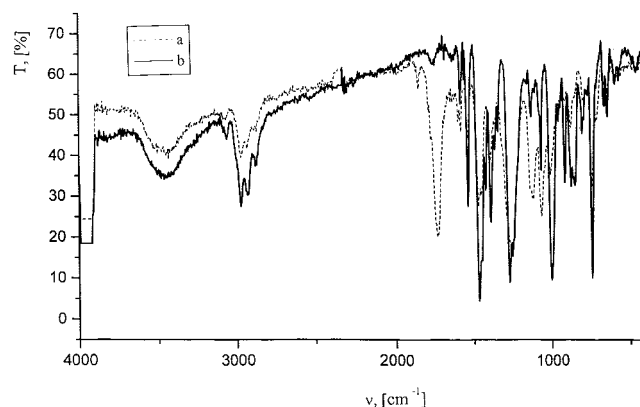

Figure 1 IR spectra of brominated epoxy resins. (a) Low molecular-weight product; (b) product after its hardening.

TABLE II
Physical-chemical Properties of Brominated Epoxy Resin vs Condensation Temperature

Sample No.	Condensation Temperature (°C)	Epoxy Number (mol/100 g)	Organic Chlorine Content (wt %)	Bromine Content (wt %)	Melting Point (°C)	Glass Transition Temperature (°C)
4	40	0.265	0.013	52.4	66	67.8
5	50	0.271	0.42	49.1	62	70.4
6	60	0.263	1.38	48.7	56	78.0

liquid tested. The liquid is subjected to shearing in a gap between two cylinders, the internal cylinder being mobile while the external one was stationary.

Thermal stability of the resins synthesised was investigated by thermogravimetric analysis (TG). The determination utilised a F. Paulik, J. Paulik, L. Erdey derivatograph from MOM (Hungary); 100–500-mg samples were held at 20–600°C over 100 min and mass decrements were recorded against temperature.

Differential microcalorimetry was employed to examine the glass transition temperature (T_g) and thermal effects, which can be observed when resin samples are heated up; a DSC 822 apparatus from Mettler Toledo with STARe software was used for that pur-

pose. The samples of about 10 mg were heated up at the rate of 2 deg/min.

The softening point was determined by a "ring-and-ball" method: a sample is heated up under controlled conditions until the softening resin, under a load of a steel ball, moves and touches the footing of the apparatus.[18]

The mechanical properties of hardened brominated epoxy resins — bending strength and compression strength — were studied according to methods described in standards,[19,20] with the use of a motor-driven FK-100 testing machine (Germany), which provides the fixture traveling speed of 5 mm/min. Increasing elongations of test pieces were automatically recorded vs load. The material hardness was determined by means of a Brinell testing machine that indented a ball into a sample.[21]

The chemical composition of pyrolytic gases released during decomposition of resin samples in the atmosphere of helium was analyzed by Py-GC-MS. Samples were subjected to thermal decomposition in a 0316M pyrolytic attachment from Fischer (Germany) installed directly at a "split/splitless" sample injector of a gas chromatograph. Solid samples of 10–50 mg were deposited on a pyrolizer heating element made of a ferromagnetic alloy. The heating element with the
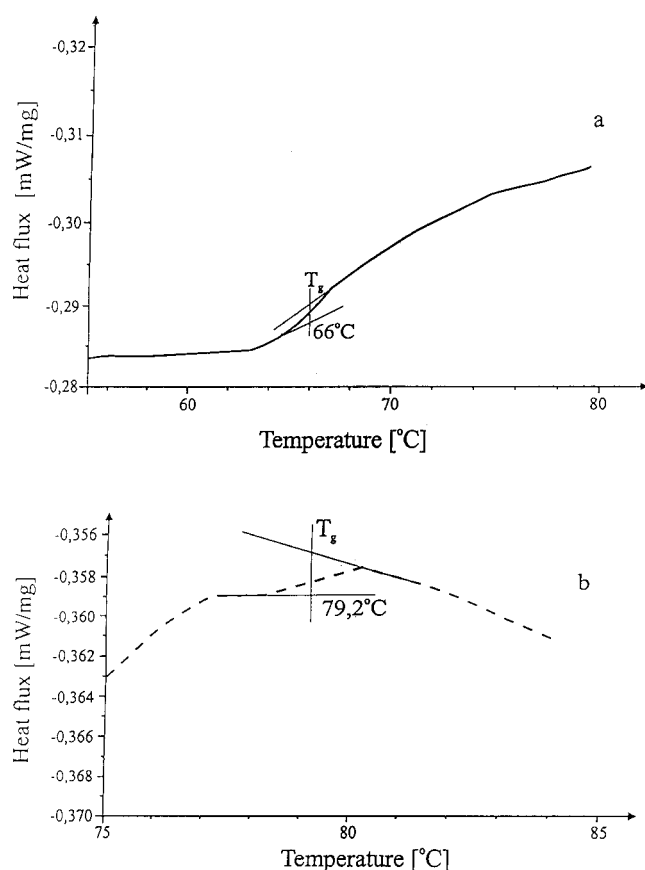

Figure 2 DSC thermograms of brominated epoxy resins. (a) Condensation temperature 40°C; (b) condensation temperature 60°C.
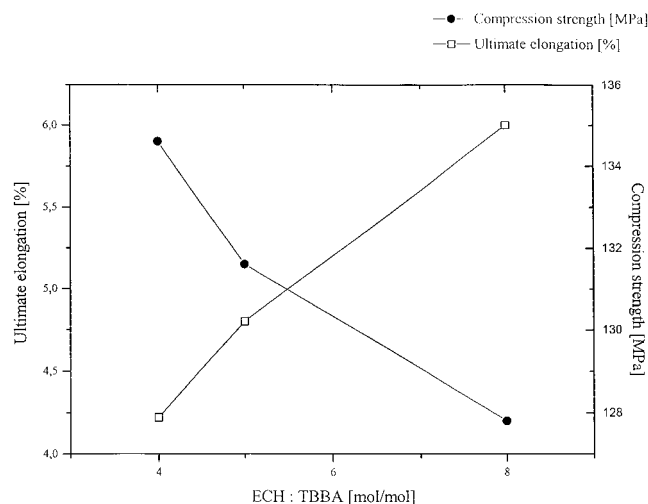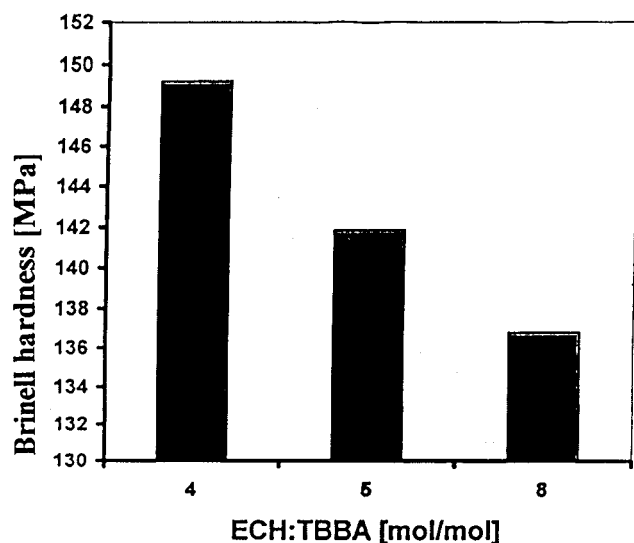

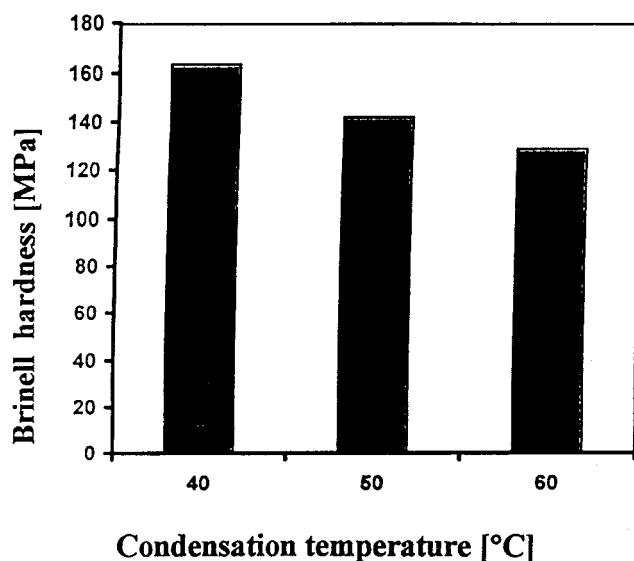**Figure 3** Ultimate elongation and compression strength of hardened resins vs ECH : TBBA molar ratio.

chromatograph (GC) equipped with a HP 5971 detector from Hewlett-Packard (Palo Alto, CA). The samples were dissolved in $CHCl_3$. The components of analyzed samples were chromatographically separated in a capillary column made of fused silica, with the length of 25 m and internal diameter of 0.2 mm, wherein a 0.2-μm film was formed of HP-5MS methylphenylsilicone stationary phase. The column was heated up within 70–290°C at the rate of 10 deg/min, with linear programming. The temperature of the "split/splitless" sample injector was 300°C, and the carrier gas flow rate was adjusted at 0.5 cm^3/min. Low-resolution mass spectra (MS) were then taken for individual components leaving the column. The following conditions were adopted for the mass sensitive detector (MSD): temperature of GC/MS transfer line = 280°C, temperature of ion source = 180°C, ionization energy for electron beam = 70 eV, ion accelerating voltage = 1600 V. The data from the Py/GC/MS system were collected and processed by a ChemStation computer set, type Vectra XM, series 4, from Hewlett-Packard (USA). That method made it possible to record ions with m/z within 14–550 amu.

Compositions of resin-derived high molecular-weight products were analyzed by MALDI-TOF spectroscopy, i.e., matrix-assisted laser desorption of molecular ions that are then extracted in the time-of-flight (TOF) analyzer. The mass spectra were taken by means of a Voyager-Elite spectrometer from Perseptive Biosystems (USA). The resin samples with the initial concentration of 1 mg/cm^3 in methanol were prepared for taking the measurements. The matrix was made 2,5-dihydroxybenzoic acid (DHB) with M = 153 g/mol and concentration of 10 mg/cm^3 in THF. The molecular ions of oligomers with the additional

Figure 4 Brinell hardness of brominated epoxy resins, (a) Versus ECH : TBBA molar ratio; (b) vs condensation temperature.

sample on it was then placed in a pyrolizer chamber made of quartz glass that had been preliminarily heated up to 225°C to prevent condensation of higher molecular-weight products. After adjusting the flow rate of carrier gas (helium) through the pyrolizer-chromatograph-mass detector system, the sample induction heating system was activated to produce the sample pyrolysis products. The pyrolysis temperature was 770°C in every case. The pyrolysis products thus obtained from the test samples were transferred in the carrier gas stream through the sample injector to a chromatographic capillary column. The pyrolysis products were separated in a HP 5890 Series II gas
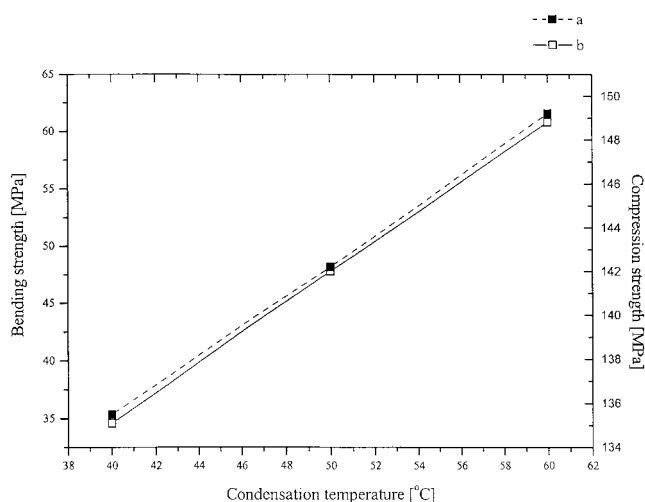

Figure 5 Bending strength and compression strength of brominated epoxy resins vs condensation temperature. (a) Condensation temperature 40°C; (b) condensation temperature 60°C.

TABLE III
Comparison of Properties of Synthesised Brominated Epoxy Resin and Those of Commercial Product D.E.R.542

Type of Resin	Epoxy Number (mol/100 g)	Organic Chlorine Content (wt %)	Bromine Content (wt %)	Melting Point (°C)
Sample No. 4	0.265	0.013	52.4	66
D.E.R.542	0.305–0.355	0.05	46–51	52–62

atomic weight of Na^+ (23 g/mol) or molecular weight of methanol (32 g/mol) were recorded in the spectra.

RESULTS AND DISCUSSION

Characterization of brominated epoxy resins obtained at changing ECH : TBBA molar ratio

The basic process criterion that is decisive for the economics of the manufacture of epoxy resins, inclusive of their brominated versions, is the ECH-to-TBBA molar ratio. To obtain the principal component of the low molecular-weight resin, i.e., DGEBA, as mentioned above, some specific excess of ECH is required due to losses of that monomer in side reactions. However, that excessive volume has to be controlled because unreacted ECH needs to be distilled off, which involves additional energy.[22] Having the above in mind, the brominated epoxy resins were synthesized with the changing ECH : TBBA molar ratio and that fact — like the condensation temperature in further tests — was taken into consideration when investigating physical-chemical properties of the products obtained (Table I).

What becomes apparent from the data presented is that a reduction of the ECH : TBBA ratio lowers the organic chlorine content and increases the product

melting point. Moreover — which is very important — the reaction yield increases considerably, which is calculated as a percentage of the product weight in relation to the substrate weight.

Running the synthesis process at lower and lower volumes of ECH leads, as can be seen, to the formation of high molecular-weight products — which accounts for their increased melting points observed. Running the synthesis at the lower and lower ECH content results in formation of products with increased molecular weights, which accounts for the observed increase in the melting point. The epoxy numbers vary within a narrow range only. The bromine content undergoes no change in practice because bromine is introduced in the TBBA monomer and (if thermal degradation is negligible) it is not directly involved in any resin-forming reactions. The amount of ECH used for the synthesis can be reduced to the minimum molar ratio of 5 : 1. The physical-chemical specification of the resin remains unchanged then. Further reduction of ECH volumes is no longer advantageous, as it increases the share of high molecular-weight products;- these are probably ECH oligomers that expand the DGEBA chains.

IR spectra of brominated epoxy resins (Fig. 1) confirm the generally expected structures of products before they have been hardened and after their hardening. Bands have been observed that are specific for hydroxyl, methyl, methylene, and ether groups, for substitution at the aromatic ring, and for epoxy groups. The valence vibrations band for —OH groups is located within 3500–3400 cm^{-1}, the stretching vibrations of C—H can be found within 3000–2700 cm^{-1}, asymmetric stretching vibrations of —CH_3 groups are shown within 2975–2950 cm^{-1}, while symmetric vibrations are at 2800–2900 cm^{-1}. The corresponding bands for the —CH_2— group have been recorded within 2950–2900 and 2850–2800 cm^{-1}, respectively. The absorption bands specific for the aromatic nucleus arrive in a few regions along the spectrum. The medium-intensity bands for stretching vibrations of C_{Ar}—H occur within the range of 3100–3000 cm^{-1}. The skeletal vibrations of the C=zC bond can be observed at 1600–1400 cm^{-1}, and stretching vibrations of C—Br at the aromatic ring are present between 700 and 650 cm^{-1}. The bands for asymmetric valence vibrations of the epoxy ring are represented within 914–830 cm^{-1}, the absorption band specific for
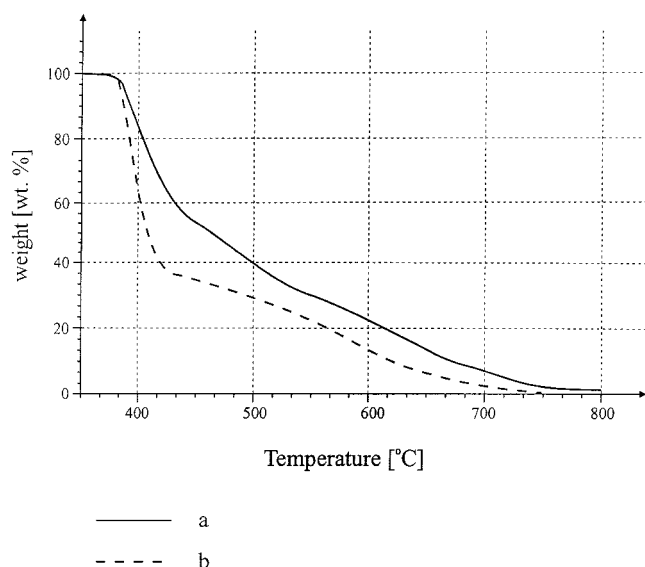

Figure 6 TG thermograms of brominated epoxy resins. (a) Condensation temperature 40°C; (b) condensation temperature 60°C.

TABLE IV
Thermal Decomposition Temperatures of Brominated Epoxy Resin Samples

Sample No.	Initial Decomposition Temperature (°C)	5% Loss in Weight Temperature (°C)	20% Loss in Weight Temperature (°C)	50% Loss in Weight Temperature (°C)	Decomposition End Point (°C)
4	379	383	417	460	800
6	375	379	392	408	750

asymmetric valence vibrations of aryl ether groups at 1250 cm^{-1}, and for alkyl ethers, at about 1000 cm^{-1}.

A considerable decay of the epoxy group band at 914 cm^{-1} was observed in the spectrum of the resin hardened with phthalic anhydride, which proves complete crosslinking. A strong band appeared within 1800–1700 cm^{-1}, which corresponds to asymmetric stretching vibrations of carbonyl groups, while at 1200–1100 cm^{-1} a band was recorded that is specific for stretching and bending vibrations of C—O present in esters.

Testing physical-mechanical properties of brominated epoxy resins vs temperature of condensation reaction

The condensation temperature, which is vital for the quality of resins, was analyzed from a broad viewpoint of chemical composition and selected physical-chemical properties, at the optimum ECH : TBBA molar ratio of 5 : 1 (Table II). The increased condensation temperature was found to considerably increase the organic chlorine content, from 0.013 to 1.38 wt %. Such a high difference in the organic chlorine content was found to result in increased T_g values what is due to the presence of polar C—Cl bonds. However, the phase transition points — although typical for that process — are not so clearly outlined, which can be observed in DSC curves (Fig. 2), and the accompanying changes in heat capacity of samples are small. The samples synthesised at 40°C (No, 4) and at 60°C (No, 6) also reveal a considerable difference in their softening points determined by a ring-and-ball method. No peak of expected endothermic process can be found in the DSC thermogram, which would correspond to the softening point. The ring-and-ball method, which provides only the information on resin melting and does not get to the core of thermodynamics of the process, is apparently more versatile for resins.

After having analyzed samples No, 4 and No, 6, it becomes noticeable that milder synthesis conditions are favorable for the formation of more orderly resin structures, which are responsible for higher melting and/or softening points. Also, the increasing rigidity of the polymer chain increases the melting point of

crystalline phase, if it only has time to be formed during slow solidification of resin in a mold.

Valuable application information was obtained after subjecting to mechanical tests the resins that had been hardened. The findings from mechanical examinations were presented in Figure 3, with due consideration given to the ratio of raw materials, which is important from the viewpoint of the process. As comes from the profiles, increased share of ECH in relation to TBBA results in lower compression strength. On the other hand, considerable excess of ECH over TBBA is favorable for increased elongation, which can be accounted for by the presence of ether groups within the resin chains that foster molecular flexibility. The analytical review of the profiles presented in Figure 4 suggests that hardness of brominated resin can be increased considerably by reducing the volume of ECH employed for the synthesis, while the impact from the condensation temperature is not as clearly outlined, and even some reduction in hardness can be observed.

Further investigations verified the effect of condensation temperature on the properties of brominated epoxy resin after it had been hardened. The findings were presented in Figure 5. It is apparent that the compression strength and bending strength for resin samples after hardening are clearly improved by increasing the condensation temperature.

The properties of brominated epoxy resins synthesized under mild temperature conditions and with lowered ECH amounts were compared to those of the commercial product from Dow Plastics.[23] The properties analyzed were found to be comparable to those specific for the commercially available product D.E.R.542 (Table III).

Investigation of thermal stability, rheological properties, and structures of brominated epoxy resins

Further investigations analyzed the effect of monomer condensation temperature on thermal stability of brominated epoxy resins. The studies involved the resins produced at 40°C (No, 4) and 60°C (No, 6). The findings have been presented in Figure 6. The presented thermogram shows that the higher thermal stability — just as better phase order — is offered by the resin
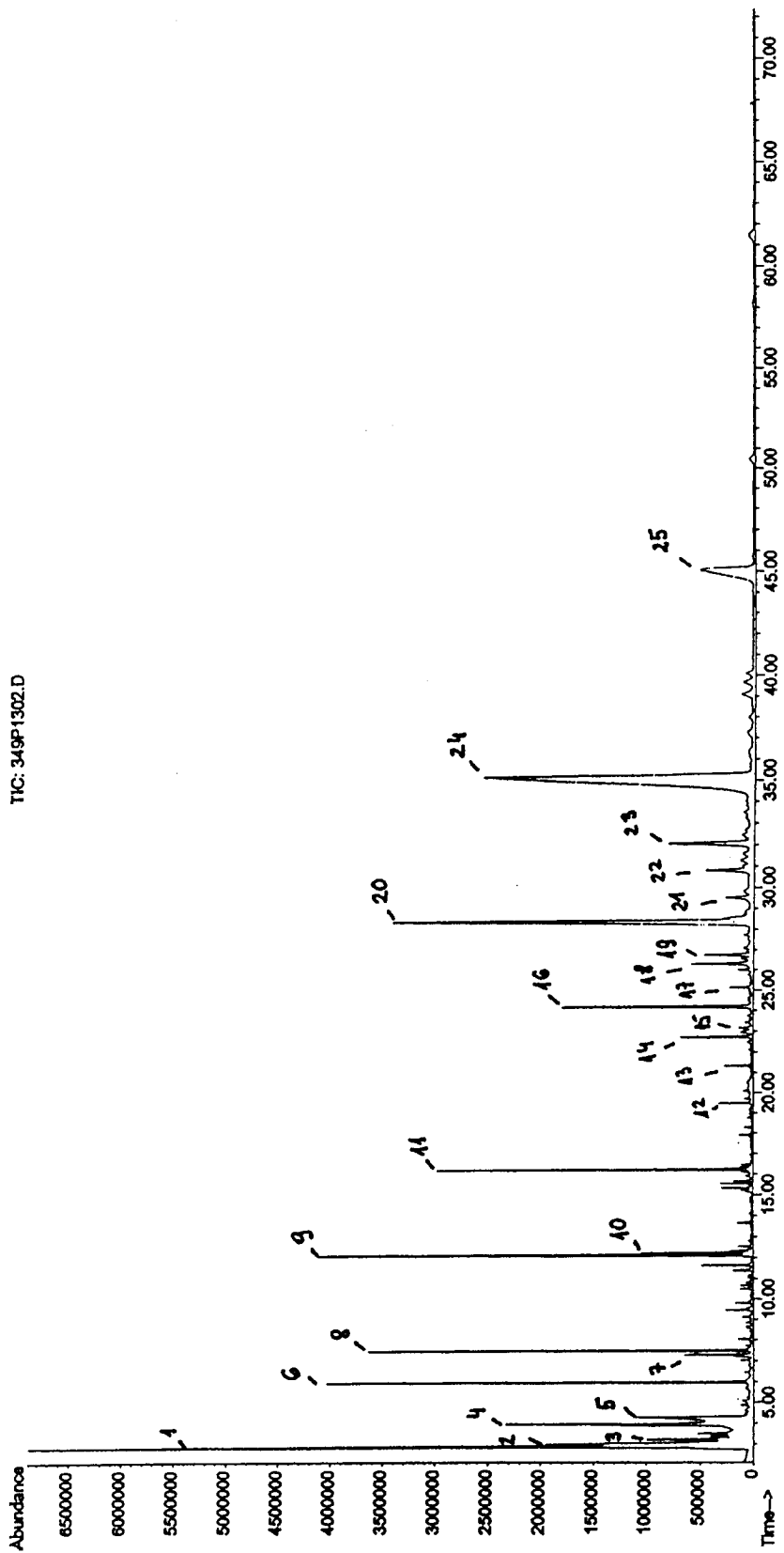
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Figure 7 Pyrogram of brominated epoxy resins.
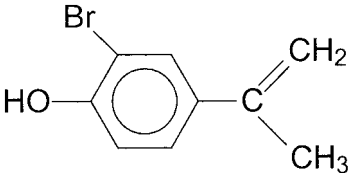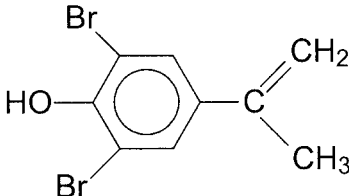
TABLE V
Identification of Pyrolysis Products for Resins Nos. 4 and 6

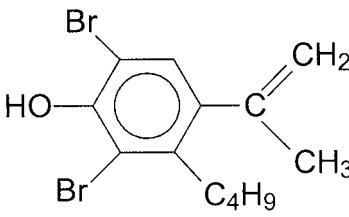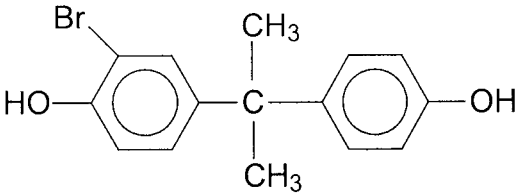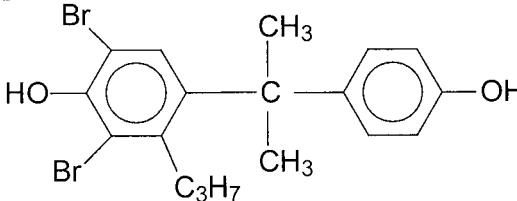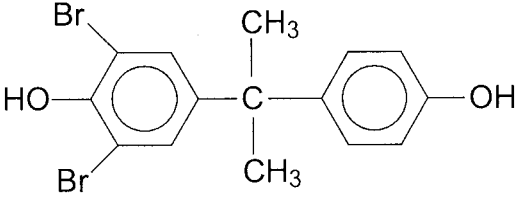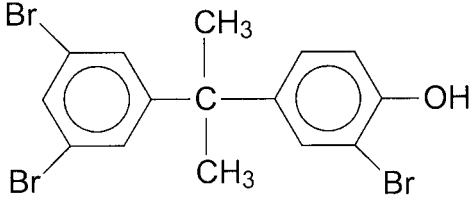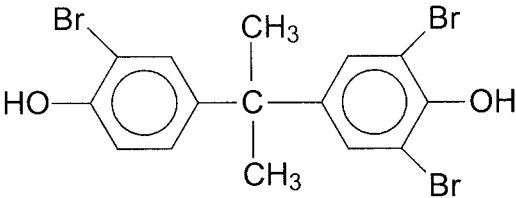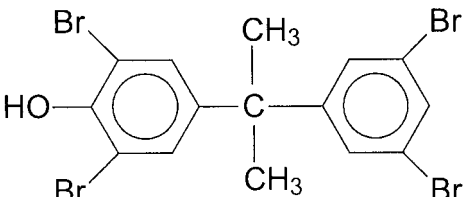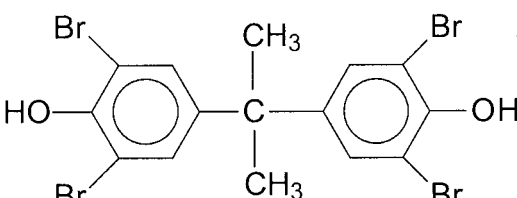| Component no. (fig. 8)	Type of component	Retention time for component (min)	Specific fragmentation ions (m/z)
1.	HBr	2.82	$[M]^+$ (80)
2.	Allyl alcohol	2.99	$[M]^+$ (58), $[M-H]^+$ (57)
3.	2-Bromopropen-1	3.20	$[M]^+$ (120), $[M-Br]^+$ (41)
4.	Bromobutane	3.88	$[M]^+$ (136), $[M-C_3H_7]^+$ (93)
5.	Isomer of component 4	4.25	$[M]^+$ (136), $[M-Br]^+$ (93)
6.	Phenol	5.96	$[M]^+$ (94), $[C_5H_6]^+$ (66)
7.	1,3-Dibromo-propane-2-ol	7.26	$[M]^+$ (216), $[M-CH_2Br]^+$ (123)
8.	2-Bromophenol	7.48	$[M]^+$ (172), $[M-Br]^+$ (93)
9.	2,6-Dibromophenol	12.11	$[M]^+$ (250), $[M-HBr]^+$ (170)
10.		12.22	$[M]^+$ (212), $[M-CH_3]^+$ (197)
11.		16.20	$[M]^+$ (290), $[M-CH_3]^+$ (275), $[M-2Br]^+$ (132)
12.		19.48	$[M]^+$ (346), $[M-Br]^+$ (267), $[M-C_3H_5]^+$ (305)
13.	Unidentified compound containing 2 Br atoms	21.32	$[M]^+$ (326)
14.		22.71	$[M]^+$ (306), $[M-CH_3]^+$ (291), $[M-CH_3-Br]^+$ (212)
15.		23.14	$[M]^+$ (426), $[M-HOC_6H_4C(CH_3)_2]^+$ (290)

TABLE V *Continued*

Component No. (Fig. 8)	Type of component	Retention time for component (min)	Specific fragmentation ions (m/z)
16.		24.15	$[M]^+$ (384), $[M-CH_3]^+$ (369)
17.		25.10	$[M]^+$ (446), $[M-CH_3]^+$ (431)
18.	Isomer of component 16	26.27	$[M]^+$ (384)
19.		26.72	$[M]^+$ (462), $[M-CH_3]^+$ (447)
20.	Isomer of component 19	28.36	$[M]^+$ (462), $[M-CH_3]^+$ (447)
21.		29.48	$[M]^+$ (524), $[M-CH_3]^+$ (509)
22.	Unidentified compound with molecular weight of 502	30.77	$[M]^+$ (502)
23.		32.03	$[M]^+$ (540), $[M-CH_3]^+$ (525)
24.	Isomer of compound 23	35.05	$[M]^+$ (540)
25.	Brominated organic compound with molecular weight >520	35.16	

sample *No,* 4 obtained at 40°C. Moreover, it contains much less organic chlorine. Table IV provides the temperatures found from thermograms, which correspond to mass losses of the polymers studied in percentage terms. The increasing condensation temperature has been found to increase the differences in mass losses of both polymers. For example, 50% mass loss for resin *No,* 4 is experienced at 460°C, while the temperature for sample *No,* 6 is much lower, i.e., 408°C. Also, total decomposition temperatures of resin samples confirm superior thermal stability of polymers synthesized under milder process conditions.
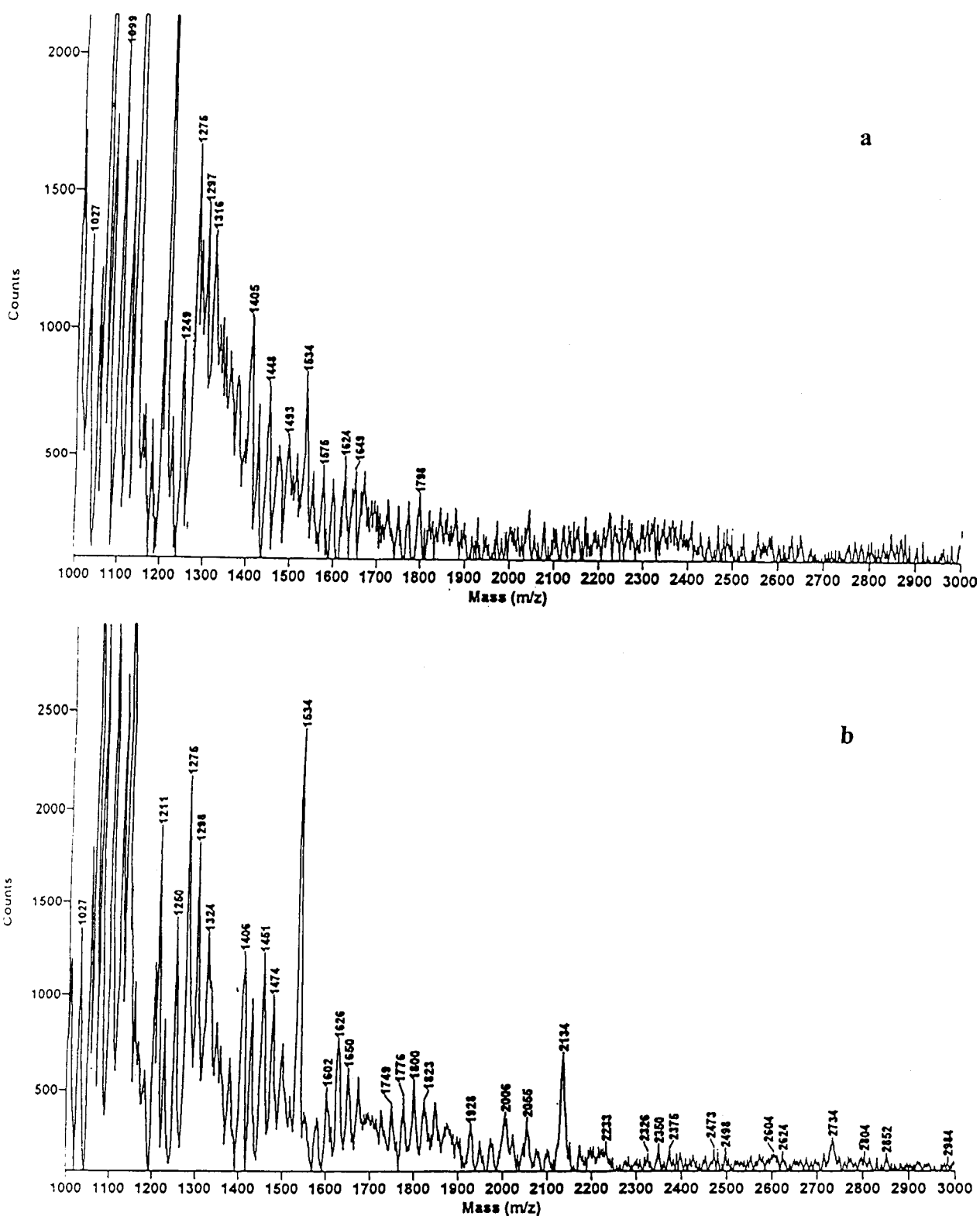
Figure 8 MALDI-TOF mass spectra of brominated epoxy resins. (a) Synthesized at condensation temperature 40°C; (b) synthesized at condensation temperature 60°C.

The additional structural information was acquired from the Py/GC/MS analysis. The investigations covered the brominated resin samples *No,* 4 and *No,* 6.

There is no practical difference in chemical compositions of both pyrolyzates. Figure 7 presents an exemplary pyrolysis chart for sample *No.* 4. On the basis of
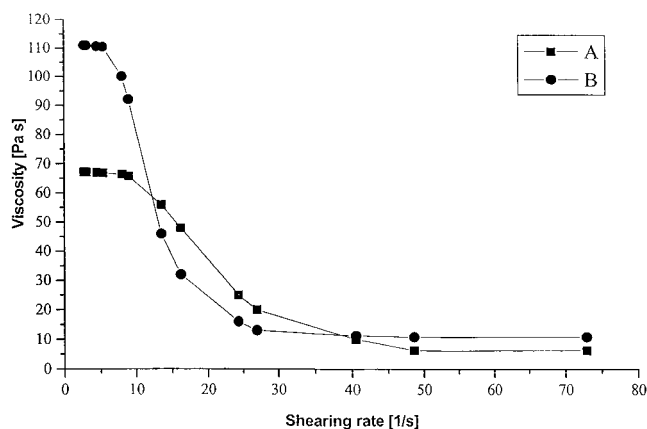
Figure 9 Flow curves for brominated low molecular-weight epoxy resins at 80°C. (a) Condensation temperature 40°C; (b) condensation temperature 60°C.

detailed interpretation of obtained MS spectra, it was possible to unequivocally identify the chemical structures of 25 organic compounds — most of them were brominated derivatives of phenol and bisphenol A (Table V). Because the Py/GC/MS method allows for the analysis of volatile organic compounds only with the molecular weight of below 650 amu, no heavier oligomer compounds could be recorded.

The compounds of that type were isolated in the soluble resin-derived products, which were obtained directly after synthesis; the MALDI-TOF spectrometry method was employed for that purpose. The spectra presented in Figure 8 prove that the resins synthesised at lower temperatures contain more high molecular-weight components.

The flow curves were taken at 80°C, i.e., at the temperature at which the synthesized samples underwent melting. The curves represent the profiles that are specific for Bingham plastics (Fig. 9). The resin produced at the condensation temperature of 40°C (*No, 4*) shows a higher viscosity value, which can be accounted for by its more orderly chemical structure. That material contains macromolecules with linear structures; hence, their packing density can be higher. On the other hand, the viscosity specification of the resin sample *No, 6* is lower, which suggests that the structure must be less orderly and that branched chlorine-containing substituents must be present in the chains that additionally can be formed as hanks and kinks. Resin *No, 6* (in Table II) is characterized by a much higher chlorine content because of adverse side reactions that occurred. When the shearing rate increases, more and more macromolecules are arranged along the stream in nonlaminar flow. Hence, their interactions are reduced, the internal friction is reduced, and consequently, the liquid viscosity is reduced. At some specific — reasonably high — shearing rate, viscosity is no longer dependent on the shar-

ing rate, and the flow curves have the profiles specific for Newtonian fluids.

Good correlation can be observed between the findings from rheology measurements and chemical compositions and melting points for individual samples of low molecular-weight resins. That confirms the generally known relationship between viscosity and molecular weight, and the latter, in turn, results from the process parameters adopted for the resin synthesis.[24]

CONCLUSIONS

The brominated epoxy resins have been synthesised, as expected. From their examinations we arrived at the following conclusions:

1. Reduced volumes of epichlorohydrin introduced to the synthesis increase the reaction yield factor and the resin melting point, while the organic chlorine content is reduced at the same time.
2. BPA-based brominated low molecular-weight resins are non-Newtonian fluids after melting. Their chemical structures are complicated. The structures of resins synthesized at lower temperatures are more orderly.
3. The bending strength and elongation of the resins hardened with phthalic anhydride increase for increased share of ECH. On the other hand, their compression strength is reduced at the same time.
4. Considerable reduction of ECH content yields high molecular-weight products. Hardness of hardened resin is increased while elongation and bending strength are decreased.
5. Higher condensation temperatures result in increased organic chlorine content, in reduced melting point, and in increased glass transition temperature as well.
6. Running the condensation reaction at 60°C adversely affects thermal stability of resin, changes its rheology, and considerably increases its glass transition temperature. However, the compression strength and bending strength are increased at the same time.
7. The Py-GC-MS investigations found out that pyrolysis under helium releases considerable amounts of low molecular-weight degradation products — 25 of them were identified.
8. Physical-chemical properties of the brominated epoxy resin synthesized at 40°C are comparable to those offered by the commercially available produce D.E.R.542 from Dow Plastics.

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