Polymer Degradation and Stability

The effect of a curing agent on the thermal degradation of fire retardant brominated epoxy resins

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Abstract

The diglycidyl ether of tetrabromobisphenol A, the diglycidyl ether of bisphenol A and their mixture was cured by 4,4′-diaminodiphenyl methane. The pyrolysis of the obtained epoxy resins was studied by TG, DSC, TG/FTIR as well as FTIR characterization of pyrolysis residues. The gaseous and high boiling pyrolysis products were collected, characterized by GC/MS and their formation is discussed. The brominated epoxy resins are thermally less stable than the non-brominated ones. This effect is caused by the amine-containing hardener. The degradation initiation reaction is associated with the formation of hydrogen bromide which further destabilizes the epoxy network. The effect of the curing agent can be used in recycling of epoxy resins to separate brominated pyrolysis products from non-brominated ones.
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Keywords: Brominated epoxy resin; Pyrolysis; GC/MS; FTIR; TG/FTIR; WEEE

1. Introduction

Epoxy resins are widely used in the production of electronic components (printed circuit boards), where flame retardant properties are required. Combustible epoxy resins are fire retarded with brominated systems due to their good flame retardant capacity and low cost. Here, tetrabromobisphenol A, which is easy to incorporate in the epoxy network, is applied as a reactive additive. However, the use of brominated compounds has also drawbacks because of the possible formation of polybrominated dibenzo-p-dioxins and -furans and the evolution of very corrosive bromine-containing gases in case of fire, incineration or recycling.

Fire retardant printed circuit boards are a major part of the waste from electrical and electronic equipment (WEEE). The recycling and utilization of WEEE has become an attractive and alternative method for their disposal, offering the advantages of lowering the volume of solid wastes. With respect to this, a pyrolytic approach is of importance because of the energy and material recovery. Therefore, a detailed knowledge of the pyrolytic mechanism of fire retardant epoxy resins is needed.

It is generally accepted [1,2] that degradation of epoxy resins starts by dehydration of secondary alcoholic groups followed by homolytic scission of the formed allylic bond. Repetition of bond scission of the epoxy network leads to the evaporation of the low molecular weight fragments (e.g., high boiling degradation products, HBPs), whereas polymerization of unsaturated bonds resulting from dehydration and subsequent aromatisation contributes to charring [2].

Brominated epoxy resins are thermally less stable than non-brominated ones [3,4] and there are still unanswered questions about the reason for this. In contrast to non-flame retardant epoxy resins, the pyrolysis of brominated epoxy resins yields very toxic products, as shown by micro scale pyrolysis [4], or pyrolysis and laser ablation mass spectrometry [5], and the important task of the pyrolytic approach is to


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minimize their formation by the variation of the pyrolysis temperature to obtain a "clean" oil. This was also pursued in the paper. The data presented should be helpful for the development of the pyrolytic recycling of WEEE.

2. Experimental

2.1. Materials

Commercial diglycidyl ether of tetrabromobisphenol A DGETBBA (I, DER 542, Dow Chemicals) and diglycidyl ether of bisphenol A DGEBA (II, DER 332, Dow Chemicals) were used as received as epoxy monomers. Brominated epoxy-polymer (BEP, III, F-2100, Dead Sea Bromine) was also used as received.
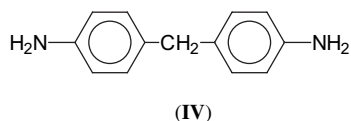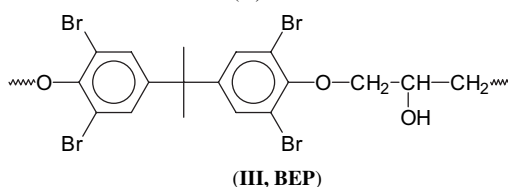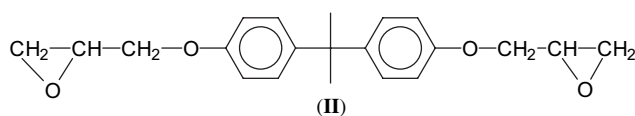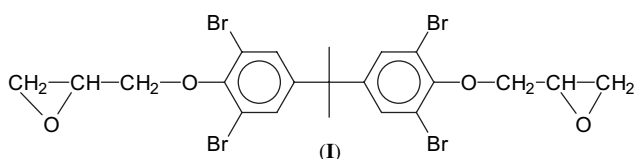
Stoichiometric amounts of 4,4′-diaminodiphenyl methane (DDM, IV, Aldrich) were dissolved in DGEBA or DGETBBA or the mixture DGEBA/DGETBBA on oil bath and subsequently cured under air in an oven heated for 1 h at 135 °C and for 0.5 h at 155 °C. Depending on the ratio between the monomers applied, the obtained epoxy resin contained 0% (ER), 43% (BER) or 20% (ER/BER) bromine (the bromine content was calculated using the value for DGETBBA given by the manufacturer).

2.2. Pyrolysis technique and products of thermal decomposition

For details of the thermal degradation procedure, the reader is referred to Ref. [6]. Briefly, high boiling degradation products (HBPs) were collected under argon or helium in a degradation tube in isothermal experiments, using samples of approximately 100 mg. In addition, low boiling degradation products (LBPs) were trapped at liquid nitrogen temperature and successively analyzed by GC/MS. The HBPs condensed in the upper part of the test tube cooled by running water were washed out by acetone. The acetone solution was analyzed by GC/MS (GC/MS model HP 6890/5972A) using a HP-1 60 m column, which was temperature programmed from 50 °C (3 min) to 290 °C (20 min) at a heating rate of 10 K/min. For analysis of LBPs, the 60 m HP-1 capillary column was also found to be an excellent column. The column was temperature programmed from −40 °C (3 min) to 250 °C at 10 K/min. The mass spectra were obtained by electron ionization at 70 eV keeping the source at about 180 °C. A mass spectrometric identification was carried out using WILEY and NBS libraries. In a few cases, when compounds were not included in the libraries, they were identified on the basis of both the molecular ion m/z value and the ion decomposition pattern constructed for the best fit with the mass spectrum.

Solid residues collected in the degradation tube at different residence times on isothermal heating were investigated by FTIR spectroscopy on ASI/Mettler-Toledo ReactIR-1000 FTIR System on the multi-reflexious diamante sensor.

In addition, solid residues collected in TG after the main stage of weight loss were subjected to the elemental analysis using a CHNS-932 apparatus made by LECO Instrumente GmbH Monchengladbach, Germany.

2.3. Thermal analysis

DSC measurements were performed by means of a simultaneous TG-DSC thermoanalyzer STA409 from Netzsch Gerätebau, Selb. Correction by reference data was done with empty crucible at measurement conditions identical to the sample measurement conditions. Experimental conditions: heating interval 25–600 °C, heating rate 5 °C/min, sample weight 30 mg, transfer gas nitrogen with 100 ml/min flow. Calculations were performed by Netzsch DSC-Software.

The temperature related release ("trace") of volatile substances during thermal treatment and the quantitative amount of released HBr were studied by coupled Thermoanalysis–FTIR-Spectroscopy (TG-FTIR) (Thermobalance STA409 by Netzsch Gerätebau, Selb; FTIR-Spectrometer Vector 22 by Bruker Optics, Rheinstetten). Thermogravimetric conditions: heating interval 25–600 °C, heating rate 5 °C/min, purge gas nitrogen, gas flow 100 ml/min. A 50 cm Teflon coupling heated to 200 °C was used to transfer the evolved substances into the FTIR cell.

The TG-FTIR method was improved by building an in-house designed FTIR cell, cylindrical, two CaF$_2$

windows, heated by a heating jacket made by Fa. Winkler, Heidelberg to 200 °C, with optical path 20 cm and volume 19.7 ml.

Used FTIR resolution: 2 cm^{-1}; scan rate 16; recording frequency of spectra: every 75 s. Evaluation by OPUS Bruker, Netzsch software and calculations in MS Excel.

Calculation of traces by using OPUS Bruker integration software under selection of characteristic vibrational bands (HBr: 2621 cm^{-1}). Quantification method by simultaneous control of the purge gas flow after external calibration [7]. Calibration by certified HBr in N_2 test gases of 1000, 2000 and 4000 mg HBr/ $N \text{ m}^3$ (test gases from Messer Griesheim, Karlsruhe), measured under conditions identical to the experimental setting.

2.4. Kinetic analysis

Kinetic analysis was carried out from the set of dynamic DTG curves obtained in a nitrogen atmosphere at heating rates 2.5, 5 and 10 °C/min. Dependence of the activation energy on the extent of conversion was calculated using the model-free isoconversional method and software therein [8]. Analysis of the resulting dependence provides important clues about changes in reaction mechanism.

3. Results

3.1. Spectroscopic characterization

The IR spectra of untreated DGETBBA, DGEBA and DDM are presented in Fig. 1. The IR spectrum of DGETBBA (spectrum a) exhibits strong absorption bands at 1460 cm^{-1} (arom. ring), 1264 cm^{-1} (C_{arom}–O), 990 cm^{-1} (O–C_{aliph}), and 737 cm^{-1} (H–C_{arom}). The corresponding absorption bands of DGEBA (spectrum b) are located at 1508 cm^{-1} (arom. ring), 1228 cm^{-1} (C_{arom}–O), 1032 cm^{-1} (O–C_{aliph}) and 827 cm^{-1} (H–C_{arom}) indicating that bromine atom influences the position of the main absorption bands. Both compounds show the characteristic absorption of the oxirane ring at $911–912 \text{ cm}^{-1}$. The main absorption bands of DDM (spectrum c) appear at 3432, 3332, 1625 cm^{-1} (NH_2), 1512 cm^{-1} (arom. ring), 1267 cm^{-1} (C–N), 809 cm^{-1} (H–C_{arom}).

After curing of the DGEBA/DGETBBA/DDM mixture, the IR spectrum of the resulted polymer (Fig. 2, spectrum a) keeps the main absorption bands of the components except those of the oxirane ring and amino group consumed during curing. In addition, new bands due to –OH (the broad one around 3400 cm^{-1} and the sharp one at 1104 cm^{-1}) appear indicating the
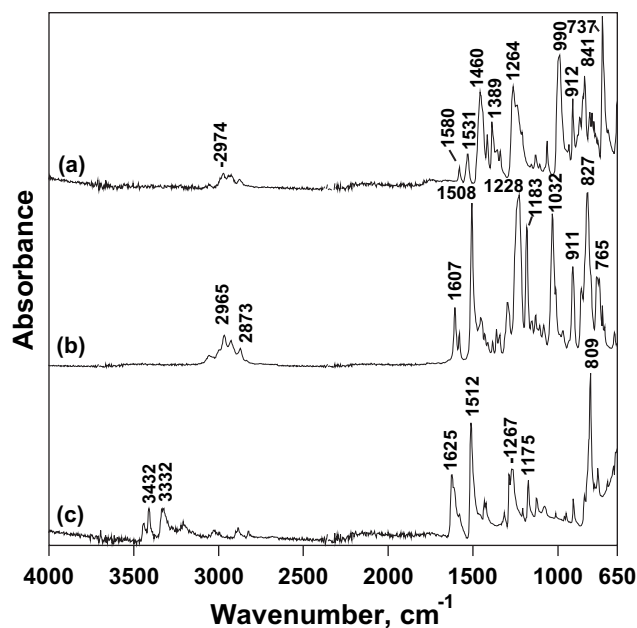

Fig. 1. Infrared spectra of initial: DGETBBA (a), DGEBA (b), DDM (c).

formation of the epoxy network. Because of the stoichiometry between the oxirane ring and amine group, mainly tertiary amine groups (Fig. 3) developed during the epoxide–primary amine reaction followed by
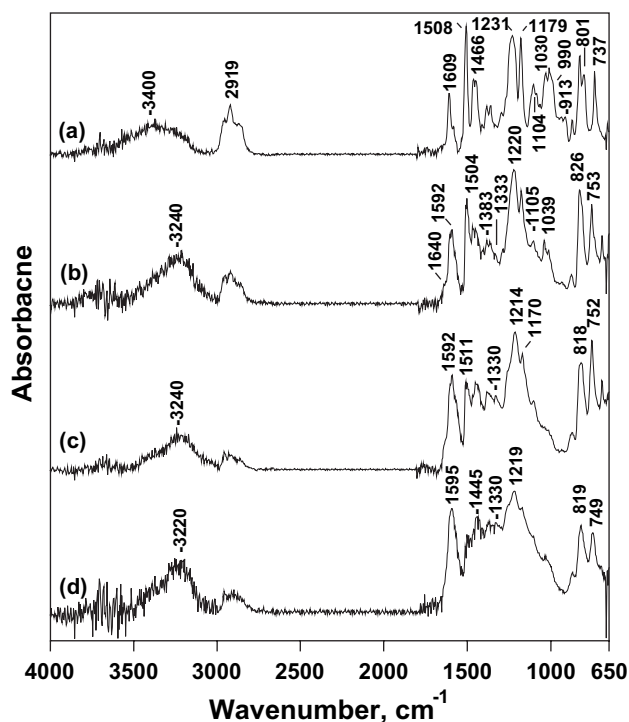

Fig. 2. Infrared spectra of initial ER/BER (a) and its solid products of the thermal degradation collected in the degradation apparatus in inert atmosphere on isothermal heating to 20% weight loss (b) and 40% weight loss (c) at 310 °C and to 60% weight loss at 400 °C.

X = Y = -H: 0% Br (**V**)   X = Y= -Br: 43% Br (**VI**)   X = -H, Y = -Br: 20% Br (**VII**)
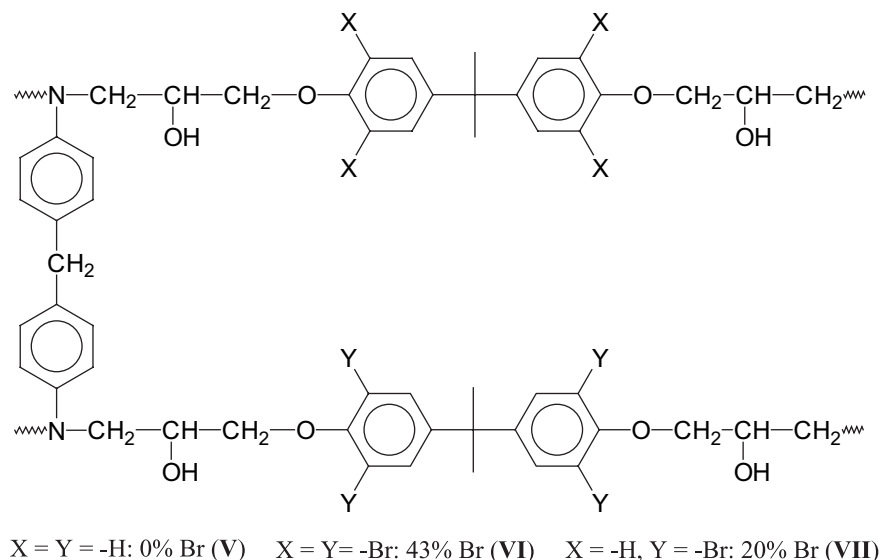
Fig. 3. Expected structures of the prepared epoxy resins.

the epoxide–secondary amine reaction are expected in the final network of ER (V), BER (VI) and ER/BER (VII). Due to the fact that the reactivities of the secondary amino hydrogens in the aromatic amines are lower than those of the primary amino hydrogens, the presence of some secondary amino groups in the network is also expected [9].

3.2. Thermal analysis

ER shows a weight loss in the temperature interval 330–400 °C followed by the more slow stage of weight loss in the broad temperature interval 400–600 °C leaving 26% solid residue when heated under nitrogen in

dynamic TG (Fig. 4). BER or ER/BER also exhibits a two step weight loss taking place to a marked degree at lower temperature than that of ER. Furthermore, BER or ER/BER are thermally much less stable than BEP. These results indicate that the lower thermal stability of BER or ER/BER compared with that of ER and BEP is related to the simultaneous presence of amine-containing curing agent and bromine atoms in the resins.

In DSC (Fig. 5), both BER and ER/BER exhibit an endothermal effect corresponding to the main stage of weight loss in TG. The effect is likely to be associated with the melting of low molecular products formed during the decomposition of the resins. In addition, ER/BER shows an exothermal effect in the temperature interval 430–560 °C.
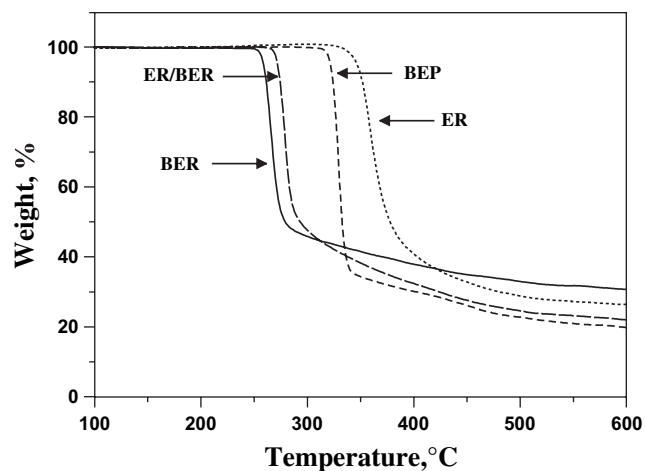

Fig. 4. Thermogravimetry of BER, ER/BER, BEP and ER. Heating rate 3 °C/min. Nitrogen flow 60 ml/min.
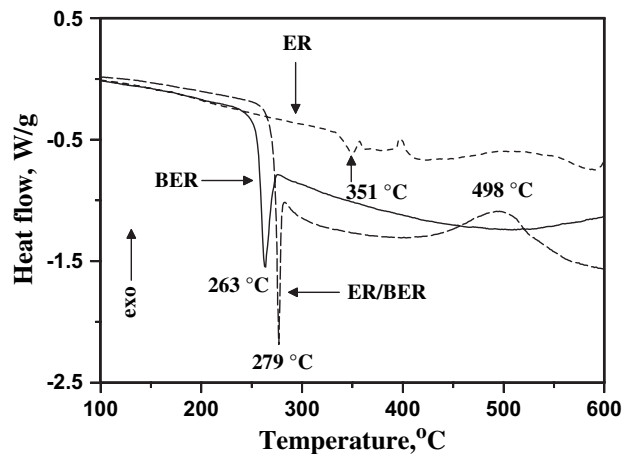

Fig. 5. DSC analysis of BER, ER/BER and ER. Heating rate 3 °C/min. Nitrogen flow 60 ml/min.

The DSC curve of ER is also presented in Fig. 5. It shows a complex endothermal effect which corresponds to the weight loss in TG.

3.3. FTIR study

Chemical modifications of ER/BER occurring on heating are shown in Fig. 2. The characteristic absorption pattern involving bromine atom (1466, 990, 737 cm^{-1}) decreases on heating to 20% weight loss indicating the dominating degradation of BER. Simultaneously, the absorption bands of secondary alcohols (3400, 1104 cm^{-1}) and aromatic–aliphatic ether (1030 cm^{-1}, 1231 cm^{-1} moves to 1220 cm^{-1}) diminish in intensity demonstrating degradation of the aliphatic part of the epoxy network. In addition, phenolic [10] and polyaromatic structures [11] appear in the residue as inferred from new absorption bands at 3240, 1220 cm^{-1} and 1592, 826–818, 753 cm^{-1} correspondingly. The band at 1640 cm^{-1} is associated with absorption of olefinic double bonds.

Further heating to 40% weight loss results in decreasing of the absorption bands of residual secondary alcohols and aromatic–aliphatic ether (spectrum c). Moreover, the band at 1504 cm^{-1} reduces relating to the degradation of non-brominated ER. The appearance of

a new band at 1330 cm^{-1} attributed to the stretching vibration of the C_{arom}–N bond [12] is indicative of reaction of bromine atoms with DDM.

The heating to 400 °C yields further degradation of ER as the absorption band at 1511 cm^{-1} decreases (spectrum d). The obtained solid residue is a polyaromatic char (1595, 819, 749 cm^{-1}) with phenolic (3220, 1445, 1219 cm^{-1}) groups containing aliphatic (broad absorption at 2800–2950 cm^{-1}) and C–N bridges (1330 cm^{-1}).

3.4. GC/MS study

The pyrolysis of BER yields HBr, CH_3Br, acetone, water, 3-bromo-2-propene, 1-bromobutane, and bromoacetone as the main gaseous products (Fig. 6a). The pyrolysis of ER/BER with the lower Br-content mainly produces CH_3Br, acetone, water and bromoethane (Fig. 6b). The remarkable point is that the addition of ER to BER strongly reduces the yield of HBr as it was detected only on the walls of the degradation tube by an analytical reaction with a water solution of $AgNO_3$. For comparison, Fig. 6c shows the gaseous pyrolysis products of ER. The main products are ethane, propene, chloromethane (presumably, from impurities), acetaldehyde, water and acetone.
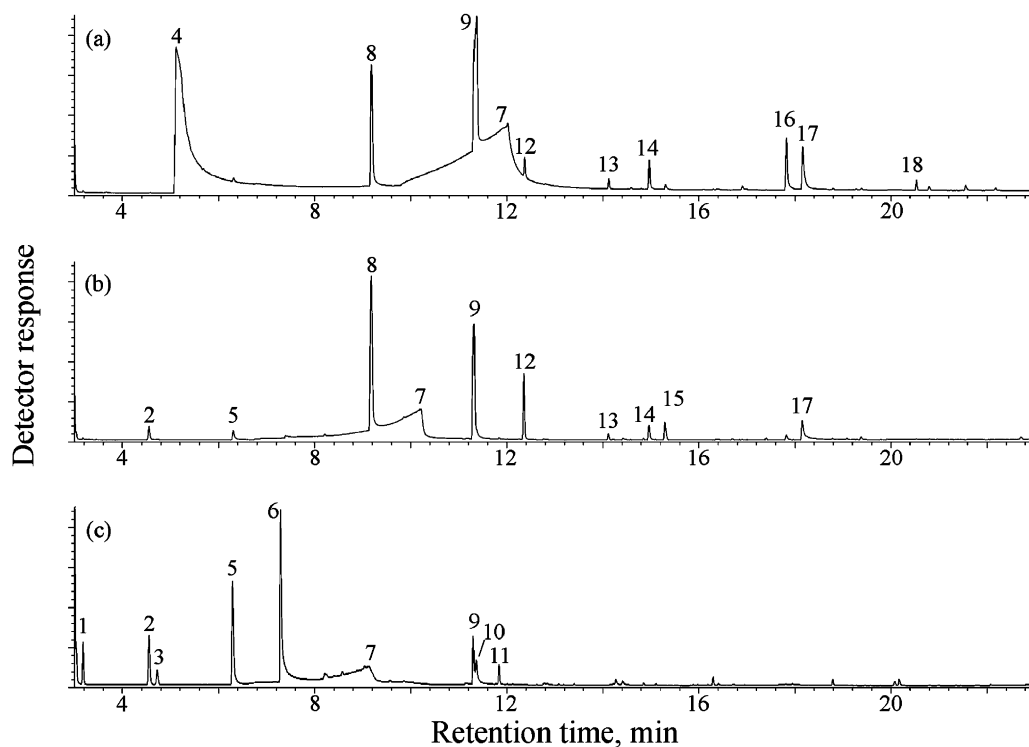

Fig. 6. Total ion gas chromatogram of the gaseous pyrolysis products of BER (a), ER/BER (b) and ER (c). Pyrolysis conditions: isothermal temperature 310 °C, 10 min (a, b), 400 °C, 10 min (c). 1—ethane, 2—propene, 3—propane, 4—HBr, 5—chloromethane, 6—acetaldehyde, 7—H_2O, 8—bromomethane, 9—acetone, 10—propanal, 11—furan, 12—bromoethane, 13—2-bromopropane, 14—3-bromo-2-propene, 15—1-bromopropane, 16—1-bromobutane, 17—bromoacetone, 18—1,2-dibromopropane.
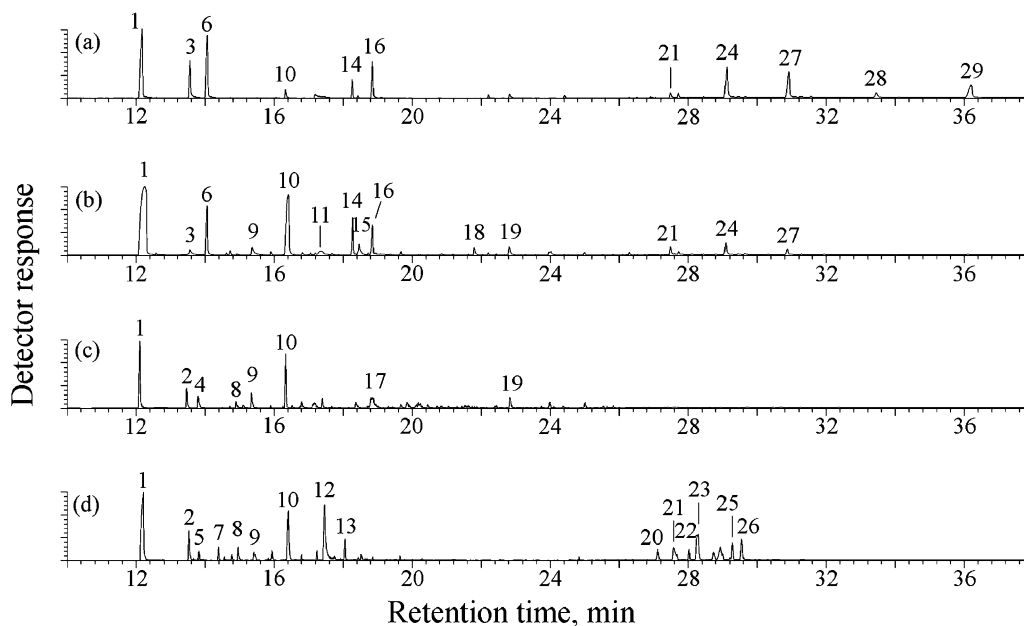
Fig. 7. Total ion gas chromatogram of the high boiling pyrolysis products of BER (a), ER/BER (b), pyrolysis residue after (c), ER (d). Pyrolysis conditions: isothermal temperature 310 °C, 10 min (a, b), 400 °C, 10 min (c, d). 1—phenol, 2—2-methylphenol, 3—1,3-dibromoisopropanol, 4—4-methylphenol, 5—N-methylaniline, 6—2-bromophenol, 7—N,N-dimethylaniline, 8—2-ethylphenol, 9—4-ethylphenol, 10—4-isopropylphenol, 11—isoquinoline, 12—4-isopropenylphenol, 13—2-(1-methylethenyl)benzofuran, 14—2-bromo-4-isopropylphenol, 15—3,4-dihydro-2H-benzopyran-3-ol, 16—2,6-dibromophenol, 17—methylquinoline, 18—2,6-dibromo-4-isopropylphenol, 19—p-hydroxybiphenyl, 20—bis(4-aminophenyl)methylene, 21—bisphenol A, 22—4-aminophenyl-4′-(N-methylaminophenyl)methylene, 23—bis(N-methyl-4-aminophenyl)methylene, 24—2-(3-bromo-4-hydroxyphenyl)-2-(4-hydroxyphenyl)propane, 25—4-(N-methylaminophenyl)-4′-(N,N-dimethylaminophenyl)methylene, 26—bis(N,N-dimethyl-4-aminophenyl)methylene, 27—2,2-bis(3-bromo-4-hydroxyphenyl)propane, 28—2-(3,5-dibromo-4-hydroxyphenyl)-2-(4-hydroxyphenyl)propane, 29—2-(3,5-dibromo-4-hydroxyphenyl)-2-(3-bromo-4-hydroxyphenyl)propane.

In Fig. 7 gas chromatograms of the HBPs of the epoxy resins under investigation are shown. The pyrolysis of BER produces mainly phenols contaminated by 1,3-dibromoisopropanol and brominated phenols and brominated derivatives of bisphenol A (Fig. 7a). The formation of phenol indicates that a debromination reaction occurs upon heating of BER.

The pyrolysis of ER/BER at 310 °C (Fig. 7b) mostly yields phenol and isopropylphenol together with poisonous 2-bromophenol, 2-bromo-4-isopropylphenol, 2,6-dibromophenol and mono- and dibromobisphenols A. If the residue obtained at 310 °C was pyrolyzed further at 400 °C (Fig. 7c), a "clean" oil was obtained as it does not contain brominated compounds.

It should be noted that pyrolysis of both BER and ER/BER does not produce aromatic amines in the HBPs neither at 310 °C nor at 400 °C indicating that they are blocked in the solid residue. This evidence is supported by FTIR data, as the C_{arom}—N bonds were detected in the spectra of the solid pyrolysis residues (Fig. 2), and by an elemental analysis of the residue, which revealed 4.2–5.8% nitrogen in the solid residue. In contrast to BER or ER/BER, the pyrolysis of ER at 400 °C yields aromatic amines. These data signify reaction between BER and DDM upon heating, leading to an incorporation of the aromatic amines in the residue.

3.5. TG-FTIR study

TG-FTIR investigations showed the strong release of HBr, phenol and bromophenols from both BER and ER/BER. In Fig. 8 a representative IR spectrum at the maximum rate of weight loss is presented with the well distinguished absorption bands of bromophenols (at 3654 cm^{-1}), phenol (at 3559 cm^{-1}), HBr (at 2400–2800 cm^{-1}) and ketones (at 1736 cm^{-1}). The absorption band at 2970 cm^{-1} is attributed to the asymmetric C—H stretching of —CH$_3$-containing systems. The 1600–1000 cm^{-1} region represents the absorption bands, typical for the aromatic rings and
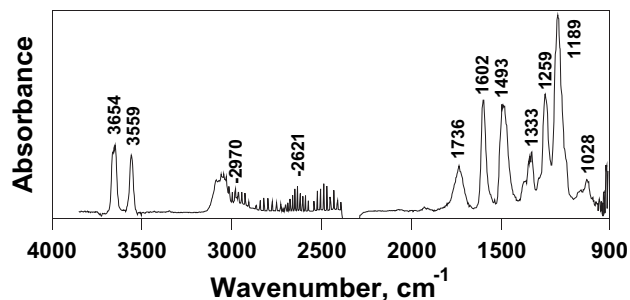

Fig. 8. Infrared spectrum of the pyrolysis products (LBPs + HBPs) of BER at the maximum rate of weight loss recorded in TG/FTIR.

C–O–H bonds of both phenol and bromophenols. Comparison of the TG-FTIR studies revealed that ER/BER releases more phenol than BER. Phenol was also detected as a product of the thermal degradation of ER.

The temperature related release of –CH$_3$-containing moieties, ketones, phenol, bromophenols and HBr from the substances under investigations was traced. Fig. 9 shows the molecular evolution profiles of the thermal degradation products of BER together with the DTG curve. At the beginning, the rate of the release of –CH$_3$-containing moieties (curve b) and ketones (bromoacetone or acetone) (curve c) is faster than that of phenol (curve d) and bromophenols (curve e). The latter, in its turn, is higher than that of HBr (curve f). These facts are likely to indicate the sequence of reaction originating from the thermal decomposition of BER: the initial formation of aliphatics and ketones followed by the evolution of phenol and bromophenols and finally the release of HBr. However, the maximum rate of the release of HBr coincides with that of phenol and bromophenols.
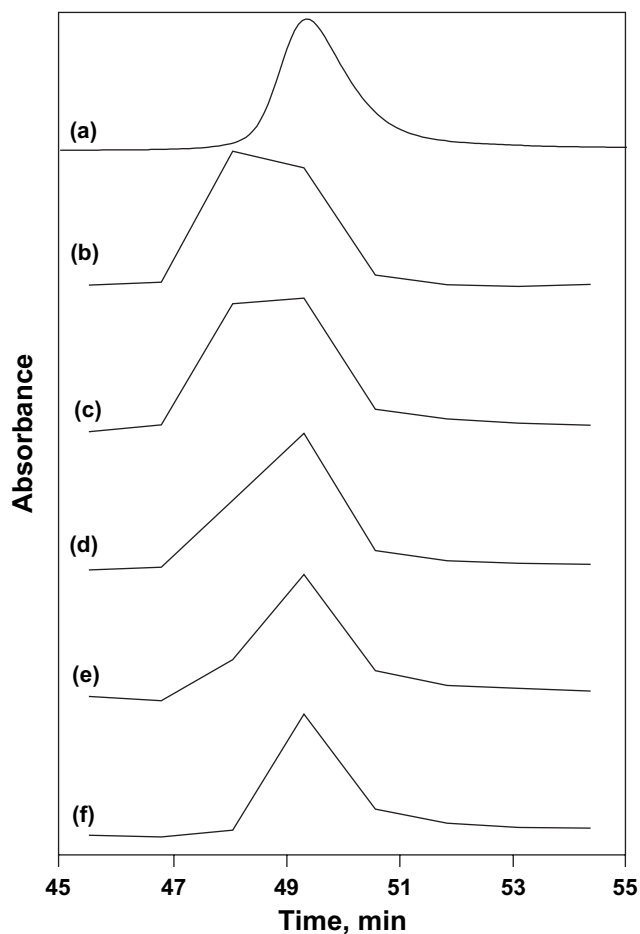
Comparison of TG-FTIR experiments showed that phenol traces of all substances (BER, ER/BER, ER) exhibits a maximum in accordance to the maximum of the DTG curves. The traces are sharp, especially the phenol trace of ER/BER. This indicates fast release in a small temperature interval. By increasing bromine content of the sample, phenol is evolved at lower temperatures. In addition, HBr and bromophenols are released from BER at lower temperature than from ER/BER. The release of bromophenols from both samples is very fast as well. The HBr release from ER/BER, on the contrary, takes place in a broader temperature interval than that of BER.

The HBr traces were used to quantify the amount of released HBr of BER and ER/BER. The results are given as the percentage of the bromine input of each sample. From ER/BER, 25% of the bromine input (20%) was released as HBr. The pyrolysis of BER resulted in a release of 40% of the bromine input of the sample (43%).

Hence, the addition of ER to BER reduces the yield of released HBr significantly. HBr yield from ER/BER is reduced to nearly 2/3 of that from BER. This result confirms the GC/MS estimation.

3.6. Kinetic analysis

Kinetic data reported for BER in Fig. 10 are calculated for the main first stage of weight loss (240–300 °C). Three sections can be distinguished in the dependence of the apparent activation energy on the degree of decomposition (α): the initial section up to $\alpha = 0.2$ where the activation energy is 95 kJ/mol; the middle section $0.2 < \alpha < 0.65$ where the activation energy increases to 103 kJ/mol; and, finally, the third section $\alpha > 0.65$ the activation energy decreases. This

Fig. 9. DTG curve of BER (a) and IR profiles of the BER thermal degradation products: 2970 cm^{-1} (–CH$_3$-containing products) (b); 1736 cm^{-1} (ketones) (c); 3559 cm^{-1} (phenol) (d); 3654 cm^{-1} (brominated phenols) (e); 2621 cm^{-1} (HBr) (f).
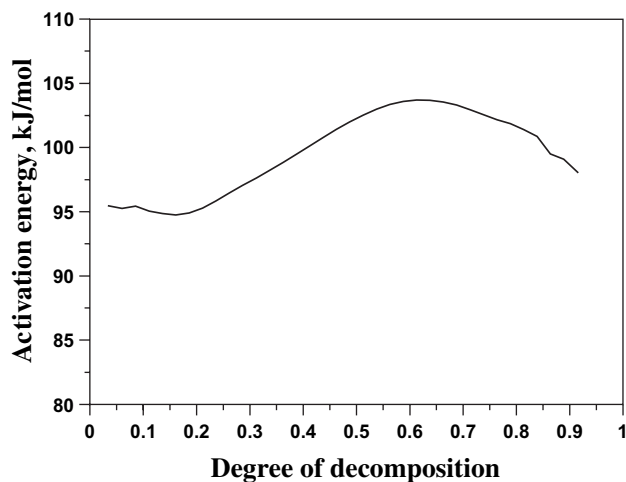

Fig. 10. Dependence of the activation energy on degree of decomposition of BER.
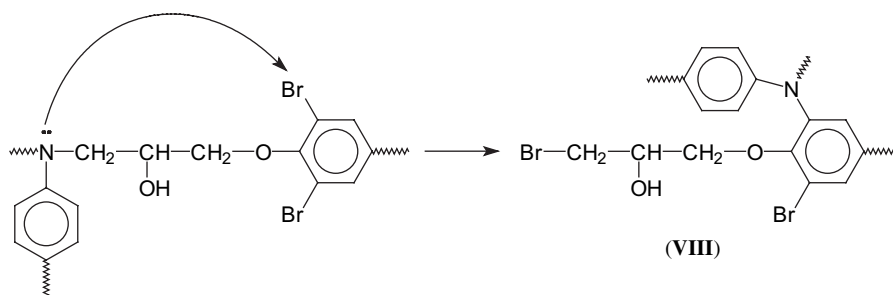
Fig. 11. Possible initiation degradation reaction of brominated epoxy resins by incorporated tertiary amine curing agent.

kinetic analysis confirms that the thermal decomposition of BER is a complex process, including several competing reactions [8]. The effective value of the activation energy 95 kJ/mol is the estimate of the activation energy of the reaction prevailing at the initial stage of the transformation [13]. According to the TG-FTIR data (Fig. 9) this reaction leads to the formation of aliphatics and ketones. Likewise, the value of the activation energy of the reaction prevailing at the middle stage of transformation is about 103 kJ/mol. In accordance with the TG-FTIR data (Fig. 9) this reaction leads to the evolution of bromophenols and phenol. At the final stage the reaction with lower activation energy prevails.

4. Discussion

The thermal degradation of non-brominated epoxy resins cured by amines is initiated by dehydration of secondary alcoholic groups [1,2]. In the case of the thermally less stable brominated epoxy resins, an initiation reaction should take another origin as inferred from the TGA data (Fig. 4). Obviously, the initiation reaction is related to the presence of amine groups and bromine atoms in the polymer network. Indeed, amines are good attacking nucleophiles and Br is a good leaving group [14]. A nucleophilic substitution within the aromatic ring of BER by amines is a possible initiation reaction of degradation as shown in Fig. 11. The

reaction is supported by the FTIR spectra of the solid residues and GC/MS data of the HBPs. It leads to the formation of the C_{arom}–N bonds and blocks aromatic amines from escaping in the gas phase. The initiation reaction by secondary amines [14] which are present in small amounts in the resin can lead to the evolution of HBr as presented in Fig. 12. This is in accordance with the data of Nakao et al. [15] who observed an acceleration of the degradation of brominated epoxy resin with added amines.

The reactions shown in Figs. 11 and 12 can also take place between the neighboring chains in the resin.

The initiation reaction leading to the HBr formation becomes less important, as the amount of HBr evolved increases in the middle stage of the thermolysis (Fig. 9). Nevertheless, HBr from the initiation reaction is able to further destabilize the resin. It is known [14] that HBr causes migration in arylalkylamines when they are heated at above 200 °C. The reaction called the Hofmann–Martius reaction [14] is shown for the particular case of BER in Fig. 13. This intermolecular reaction results in the formation of alkylsubstituted aromatics (X). Furthermore, the Hofmann–Martius reaction gives a side reaction, yielding alkyl halides [14]. The formation of an alkyl bromide (XI) from BER is shown in Fig. 14.

As shown in Fig. 15, the structures (XI) and (VIII) are likely to contribute to the evolution of bromomethane, bromoacetone or 1,3-dibromoisopropanol which prevail in the initial stage of the decomposition
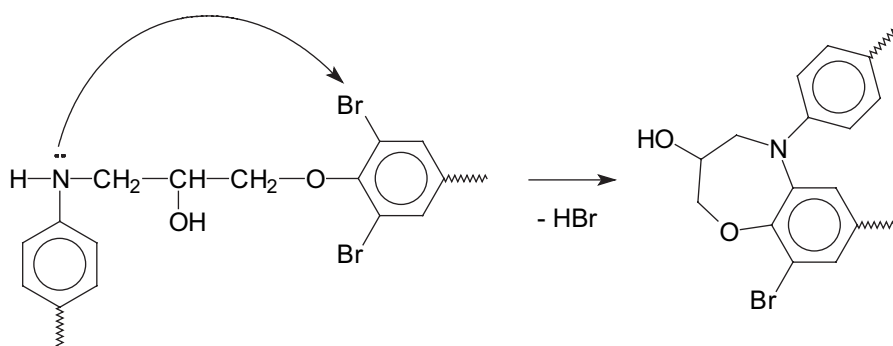

Fig. 12. Possible initiation degradation reaction of brominated epoxy resins by incorporated secondary amine curing agent.
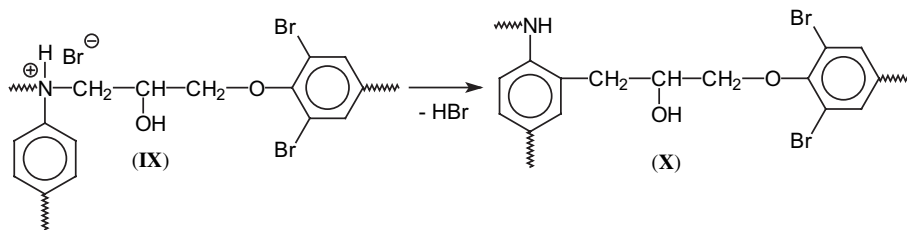
Fig. 13. Possible degradation reaction of brominated epoxy resins by incorporated amine curing agent.
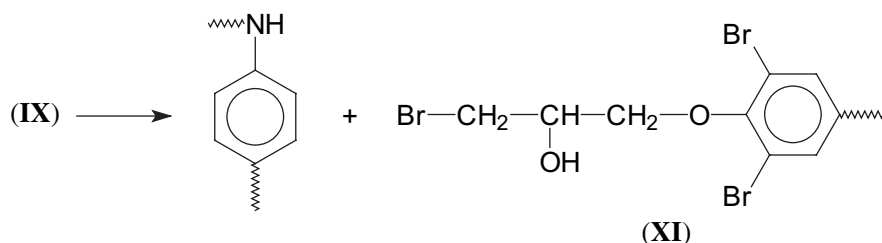

Fig. 14. Possible degradation reaction of brominated epoxy resins by incorporated amine curing agent.
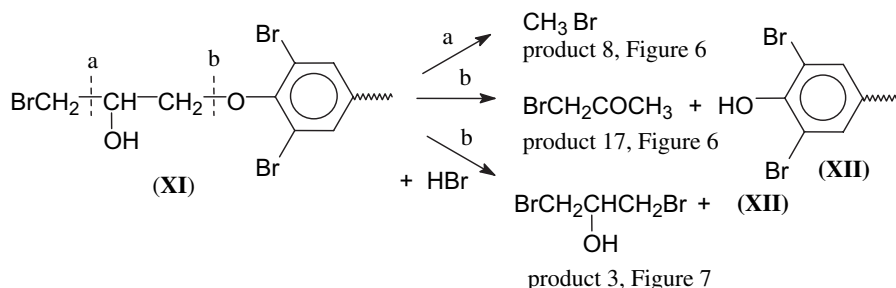

Fig. 15. Possible mechanism of the formation of bromomethane, bromoacetone or 1,3-dibromoisopropanol.
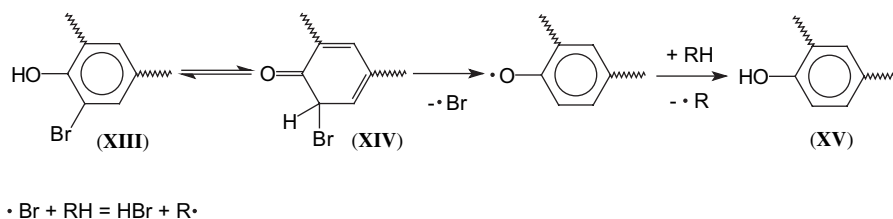

Fig. 16. Possible mechanism of the formation of HBr and phenols.

(Fig. 9). For the formation of 1,3-dibromoisopropanol, the cleavage of the ether (XI) by heating with HBr is known from literature as halo-de-alkoxylation [14]. The reaction also leads to the formation of brominated phenols (XII) in the residue. It is known [16,17] that brominated derivatives of bisphenol A are already unstable at 280 °C mainly producing phenol, mono- and dibrominated phenols and HBr. The corresponding reaction of the HBr formation is radical in origin [16,18] and related [18] to the tautomerisation of (XIII) to an unstable cyclohexadienone structure (XIV) as illustrated in Fig. 16. The formation of resulting phenols (XV) is in good agreement with the FTIR data (Fig. 2).

The very likely source for hydrogen abstraction by the radical, formed as shown in Fig. 16, are tertiary C–H bonds because of lower bond strength compared to secondary ones. As shown in Fig. 17, radicals can assist an initiation of degradation of non-brominated parts of the resin (XVI, X = H) being usually stable to higher temperatures (Fig. 4) or contribute to the degradation of brominated parts of the resin (XVI, X = Br). The scheme shown in Fig. 17 also illustrates the formation of acetone and brominated and non-brominated phenols.

From Figs. 11, 14 and 17 it is seen that the formation of structures (VIII) and (XI) precedes the formation
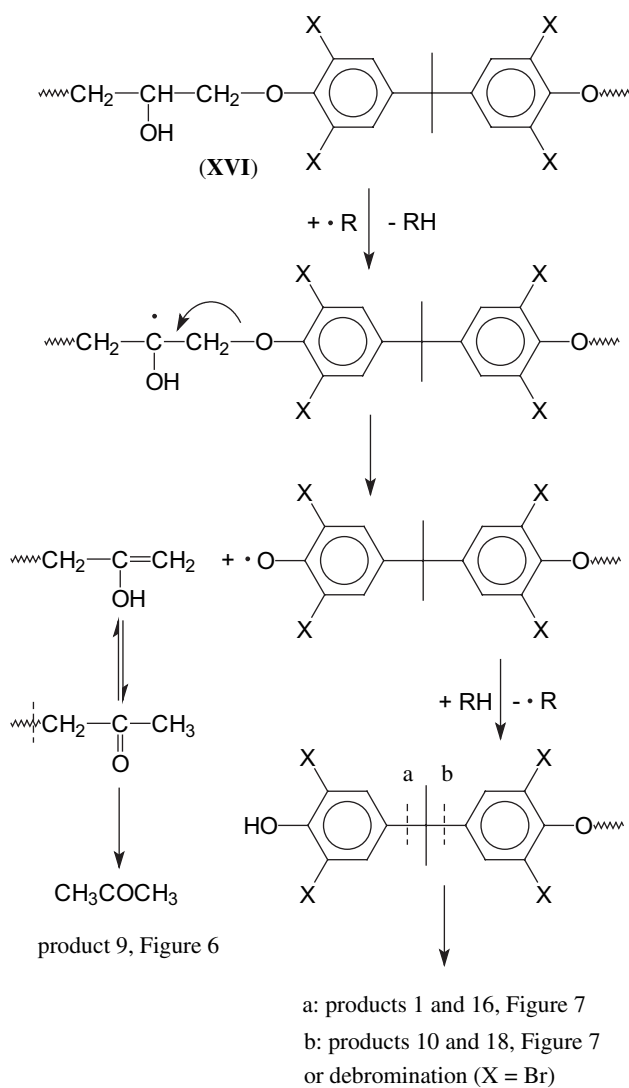
Fig. 17. Possible mechanism of the formation of acetone and brominated phenols.

a: products 1 and 16, Figure 7
b: products 10 and 18, Figure 7
or debromination (X = Br)

phenol-containing moieties. As a result, aliphatics and ketones evolve before phenols (Fig. 9).

As far as the ratio of N/Br in ER/BER is higher than that in BER, the higher number of Br-atoms can be substituted by N-atoms leading to the formation of a structure like VIII in Fig. 11. This may explain the higher yield of CH_3Br to that of HBr in ER/BER than that in BER (Fig. 6).

5. Conclusions

Amine-containing curing agent destabilizes brominated epoxy resin by a mechanism of the nucleophilic substitution of bromine. As a result, brominated epoxy resin produces gases and oil at the temperature of about 100 °C lower than non-brominated epoxy resin does. However, these pyrolysis volatiles are contaminated by brominated phenols, brominated alkanes and HBr. Nevertheless, the effect of an amine-containing curing agent to lower the pyrolysis temperature can be used to separate the contaminated oil from the non-contaminated one. Indeed, the residue coming from brominated resins on pyrolysis at low temperature (300–350 °C) can be subjected to further pyrolysis at higher temperature to obtain "clean" fuel-oil. This two-stage process called Haloclean [19] aimed at pyrolytic recycling of WEEE has been realized in the Research Center of Karlsruhe.

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