Pyrolysis of fire retardant anhydride-cured epoxy resins

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Abstract

Anhydride cured epoxies are in general the preferred in epoxy sealants and putties as encapsulation materials for integrated circuits and semiconductor-based electronic systems. Thermal recycling of brominated plastics is an eco-efficient waste management options available for end-of-life WEEE items. Thermal behaviour of epoxy ester resins prepared on purpose using brominated and unbrominated epoxy monomers based on bisphenol A and phthalic anhydride as hardener has been investigated in thermogravimetry and in Py-GC/MS. Similarly to what observed in amine hardened epoxies, the presence of bromine reduces the thermal stability of the network. First reactions to occur is the ester pyrolysis followed by hardener evaporation, and volatilization or rearrangement or loss of the glycidyl end groups from the glycidyl species. Debromination of aromatic structures and scission of the isopropyl bridge of bisphenol A take place at higher temperatures.

Keywords Epoxy resins, phthalic anhydride, Pyrolysis, Py-GC/MS, WEEE, pyrolysis,

Introduction

Epoxy resins (ER) are the preferred for encapsulants and laminates used to construct and protect electronic products. In these applications ER must comply with the industry flammability standard, Underwriters Laboratories (UL) 94 V-0 [1].

Brominated epoxy resins (BER) make part of widely employed hardening plastics wherein bromine atoms play the role of active fire-retardant. From slow-burning epoxy resins, the practical outlets could be found predominantly for those obtained from tetrabromobisphenol A diglycidyl ether (DGETBBA) and a number of hardeners amongst which the most popular are amines -aliphatic and aromatic- and anhydrides. In comparison to amines, anhydride cured epoxies in general provide longer pot lives, lower viscosity at the processing temperatures and curing with very slight exotherm. As a consequence they are preferred in epoxy sealants and putties as encapsulation materials for integrated circuits and semiconductor-based electronic systems. Resistance to photo and thermal oxidation is reported to be improved in epoxy ester resins [2].

Electric and electronic equipments (EEE) have been identified as producing one of the fastest-growing waste stream in the EU: they constitute 4% of municipal waste today and are increasing three times as fast as the growth of average municipal waste. Concern about environment prompts European Commission to issue specific legislation [3-4], aimed to reduce the amount of WEEE going to landfill and restrict the use of certain toxic substances, such as lead and some brominated fire retardant additives. As a consequence several ecofriendly strategies of fire retardancy of ER have been exploited, including incorporation of metal oxides, phosphorous and phosphorous-nitrogen compounds showing advantages and drawbacks.

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Organic phosphorus compounds can act as plasticizers, negatively affecting the thermomechanical properties of some encapsulants and their reliability in high humidity environments. Red phosphorus can redeposit a corrosive film resulting in failure because an unwanted current path [5]; Cyclotriphosphazenes are incorporated into the network of thermoset polymers, to increase the thermal properties and flame retardancy of the polymers [6]. Reliability performance of other formulations, such as metal oxides/metal hydrates blends and metal hydroxide/metal oxide blends, are not yet widely available [5].
On the other hand in 2008, SCHER (European Commission's Scientific Committee on Health and Environmental Risks) conclude no risk for tetrabromobisphenol A (TBBPA) when used as a reactive such as in the epoxy resins of printed circuit boards and does not foresee restrictions on TBBPA marketing and use [7] .
Therefore the market has still not selected a standard replacement for bromine-based flame retardants and new developments are in progress in the field of TBPPA based fire retardancy.
To reduce blooming phenomena and deterioration in mechanical properties of TBPPA based ER the immobilization of flame retardant onto hyperbranched poly(amidoamine) (PAMAM)-grafted silica was investigated [8]. Zinc stannates and hydroxystannate are used components within synergistic fire retardant systems usually in conjunction with halogenated species in a number of polymers in substitution of antimony III oxide but they are non-toxic, smoke suppressant and specific in their synergistic activity [9].
Implementation of the EU Directive on the management of WEEE will require diversion from landfill and the achievement of specific recycling and recovery targets. In many instances, mechanical recycling of WEEE is not eco-efficient due to local market circumstances and environmental requirements. In this view, pyrolytic thermal recycling is an attractive economical revenue for end-of-life EEE permitting recovery of chemicals, combustible pyrolysis oil and precious metals used in printed circuit boards. With the separate collection of WEEE, full-scale commercial operations can be assured a regular raw material supply. Thus thermal recycling of brominated plastics adds an important new dimension to the existing range of eco-efficient waste management options available for end-of-life WEEE items [10]. Thermal degradation of amino hardened BER starts at 300-350 °C giving about 30% of charred residue and a pyrolysis oil containing several brominated and unbrominated phenols; mineralization of bromine also occurs in the residue. However DGETBBA impairs thermal resistance of amine cured BER of about 100°C in comparison to that of similar non brominated ER [11, 12].
The knowledge of thermal stability and of the degradation products are of relevance on the set up of temperature and residence time of WEEE in pyrolysis operations, directing recycling toward the most beneficial revenue taking in account environmental and economic instances.
The purpose of the present study is to highlight some aspects of the thermal degradation of the brominated epoxy ester resins cured by anhydrides; the marking out of the mechanism of thermal degradation of such plastics also could assist in designing-for-recycling of new fire retarded resins.

Materials

Phthalic anhydride (PHT) was purchased by Aldrich and used as delivered. Fresh product has been used to avoid hydrolytic degradation to phthalic acid.
The epoxy monomers used were:
Commercial bisphenol A diglycidyl ether (DGEBA) Epikote 828 EL, Hexion, weight per epoxide 186-190 g/eq and commercial tetrabromobisphenol A diglycidyl ether (DGETBBA) Epon 1163, Hexion, weight per epoxide 380-410 g/eq., 50%w/w of Bromine.
GC/MS of both DGEBA and DGETBBA are shown in the upper line of fig.1 and their MS spectra in fig 2.

Epoxies resins have been prepared on purposes at Anhydride/Epoxy ratio of 0.5, as usual in general application: non brominated epoxy resin (ER-PHT) were obtained by mixing PHT with DGEBA; brominated epoxy resin (BER-PHT) by mixing PHT with a equimolecular mixture DGEBA/DGETBBA. In both cases curing was carried out by pouring the mixtures in a small open aluminum mould hold at 120°C for 3 h without catalyst. According to the recipe the amount of bromine in BER-PHT is about 23%.

Techniques

Spectroscopy

FT-IR spectra have been performed with a Perkin Elmer Spectrum 100 Instrument in transmission or in ATR mode using Universal ATR sampling accessory. Spectra on solid samples, acquired in ATR mode, were corrected with ATR correction procedure using 0° as a correction factor.

Thermal analysis

All data of thermal analysis were processed with TA instrument software Universal Analysis 2000

Thermogravimetric analyses (TGA) were carried out by a heating ramp of 20°C/min in an inertial atmosphere on TGA Q 500 TA Instrument. Usually 10-15 mg of sample and silica sample pans were used.

Differential scanning calorimetry (DSC) was performed on DSC Q200, TA Instruments in inertial atmosphere and in sealed sample holder. Glass transition temperature (Tg) was measured in three stages program involving a first heating ramp (20°C/min from -10 to 200°C), a cooling ramp of 2°C/min from 200°C down to -10°C and eventually a second heating ramp of 20°C/min from -10°C up to 200°C. Curing process was followed by heating at 20°C/min from room temperature to 300°C.

Py-GC-MS analysis were carried out on a Curie Point Pyrolyser 1040 PSC (Fischer, GSG) connected with a GC/MS HP 6890/5972A equipped with a HP-5 30 m column (outside diameter 0.25mm, phase thickness 0.25 μm). The GC conditions were as follows: injector: 260°C; split ratio: 40; oven: 40°C (4 min), T rate: 10°C/min, 320 °C (10 min);(slow program). A faster heating program (15°C/min) was sometime adopted in order to confirm peak attribution (fast program). The temperature of pyrolysis was set by the Curie Point of the material of which the sample holder selected was made. Analyses were carried out at 386, 423, 500, 590 and 670°C on about 1mg of sample, using a pyrolysis time of 15 sec. Most of the products were identified by MS data base Wiley138 and NBS75k or literature data. Others were attributed on the basis of the molecular ion, degradation pattern and number of bromine atoms, if this was the case.

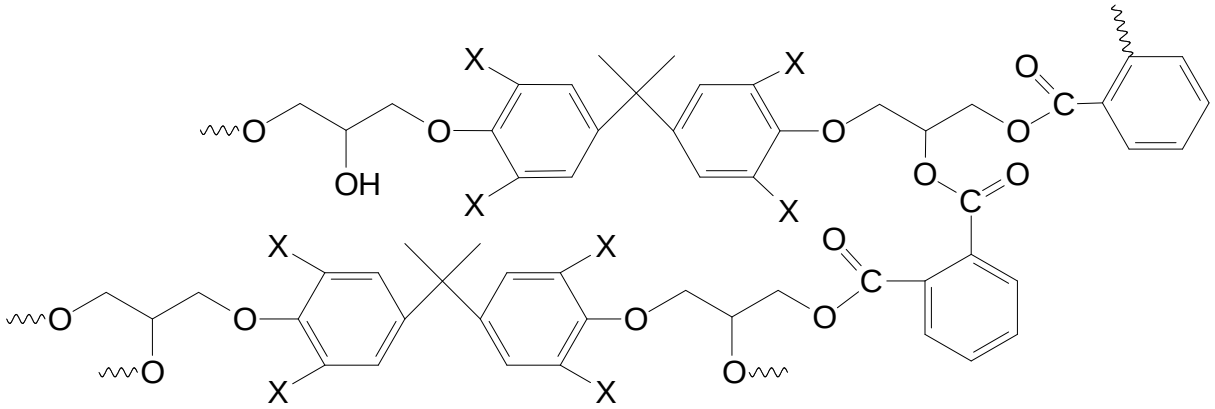
Results

Curing

Phthalic anhydride exhibits melting at 131°C. In order to select the curing parameters DGEBA and PHT were thoroughly mixed at room temperature and then the mixture was heated in the DSC apparatus at 20°C/min. DSC thermogram showed no endotherm at 131°C indicating a complete dissolution of PHT in DGEBA and a small exotherm starting at about 110°C due to the curing (63J/g) (Fig.3). Crosslinking is complete because exotherm vanishes in the second heating. Accordingly 120°C were chosen as a compromise to make higher the rate of crosslinking and lower the PHT volatility. Curing time was 3h.
The DCS of the crosslinked samples (Fig. 4) show in the first heating a relaxation peak at

about 60°C. Glass transition temperature, highlighted in the second heating, in located at 55-56°C. This supports for both the systems a similar segmental mobility and degree of crosslinking.
The structure of crosslinked resins was ascertained by IR.
Apart from small wavelength shift due to the stiffening of the systems, curing of BER-PHT results in bands at 3467 cm^{-1} (-OH), 1728 cm^{-1} (C=O in aromatic ester), 1120 cm^{-1}(ν (CO)-O in esters), 1065 cm^{-1} (ν_{oop} C-C-O in alcohol), and in a decreasing of oxirane (3056 and 912-915 cm^{-1}) and anhydride (cyclic symmetric anhydrides: ν_s C=O: 1852 cm^{-1}, ν_{as} C=O: 1788-1764 cm^{-1}, ν C-O-C and C–C-O: 901 cm^{-1} and 707 cm^{-1}) (Fig. 5).
ER-PHT mixture shows a similar behavior, increasing in curing absorption at 3503 cm^{-1}(ν –O-H), developing new absorptions at 1724 cm^{-1} (ν C=O in esters), 1119 and 1068 cm^{-1} (ν (CO)-O in esters and ν_{oop} C-C-O in alcohol) and decreasing oxirane (3056 and 913 cm^{-1}) and anhydride (cyclic symmetric anhydrides ν_s C=O: 1851 cm^{-1}, ν_{as} C=O: 1788-1774 cm^{-1}, ν C-O-C and C–C-O: 901 cm^{-1} and 713 cm^{-1}) (Fig. 6).

With reference to the figure 5 and 6, absorptions at 1607, 1509 cm^{-1} (ν aromatic ring), 1184 cm^{-1}, 1035 cm^{-1} (ν ArO-C), and 830 cm^{-1} (δ Ar-H, *para* substitution) pertain to DGEBA and those at 1531, 1458 cm^{-1} (ν aromatic ring), 997 cm^{-1} (ν ArO-C) and 737 cm^{-1} (δ Ar-H, isolated H) to DGETBBA: they mark their original structure in the IR spectra of the crosslinked products. Peaks at 1388 and 1361 cm^{-1} (δ geminal CH_3) are distinctive of both the structures. The Ar-O bond, absorbing 1247 cm^{-1} in DGEBA and at 1265 cm^{-1} in DGETBBA, results at 1236 and 1249 cm^{-1} in ER-PHT and BER-PHT respectively. The absorptions in the range 1800-1700 and 1300-1000 cm^{-1} undergo major changes in curing, due to the disappearance of anhydride and formation of new ester.
In curing process anhydride first is converted to monoester/monoacid by reaction with secondary OH of polymeric epoxy monomers; then the acid opens the oxirane ring forming a primary alkyl ester and a secondary alcohol which in turn reacts with PHT. Care should be taken in order minimize evaporation of PHT which would result in an uncrosslinked structure. Due to the insufficient stoichiometry some free secondary –OH appear.
According to that the crosslinked structure of scheme 1 is proposed:



Scheme 1 X= H (DGEBA units) or = Br (DGETBBA units).

Thermal stability
Thermal analysis. The curves of weight loss of BER-PHT and ER PHT overlap up to 340° C (6% weight loss). After that, BER-PHT loses weight more steeply than ER-PHT. In parallel to what observed in amine hardened epoxies [11-12], the presence of brominated DGETTBA units reduces thermal stability and increases the amount of residue: in BER-PHT main weight

loss in the TGA occurs at 382°C leaving 17% of residue at 550°C, conversely in ER-PHT two steps of weigh loss are located at 418 and 450°C with 7% of residue at 550°C. For comparison purposes neat diglycidyl monomers were subjected to TGA in similar conditions: onset of the evaporation step of DGEBA and DGETBBA is about 255 and 274°C with a maximum rate of evolution located around 337 and 339°C respectively, additional stages occurs at 378°C in DGTEBBA and at 445°C in DGEBA (Fig. 7).

IR Investigations. To follow the residue evolution, the systems were heated in TGA equipment in separate experiments up to the temperatures corresponding to the relevant points in TGA derivative of figure 7 and IR spectra have been performed on the residues of various temperatures (Fig 8).

Esters content (1724, 1065 cm^{-1}) decreases at 400°C in ER-PHT. DGEBA structure (1607, 1507, 1182, 1036 and 826 cm^{-1}) is preserved up to 425°C in ER-PHT and up to 368°C in BER-PHT . Similarly DGETBBA maintains its structure (1531, 1458 and 737 cm^{-1}) up to 368°C in the residue of BER-PHT. Collapses of the structure of the whole samples occurs at 390 and 500°C in BER-PHT and ER-PHT respectively resulting in charring: 1604 cm^{-1}, 873 (ω aryl CH), 812 $cm^{-}1$ (ω two-adjacent aryl CH) and 746 cm^{-1} (δ_{oop} C–H of the substituted aromatic) [13].

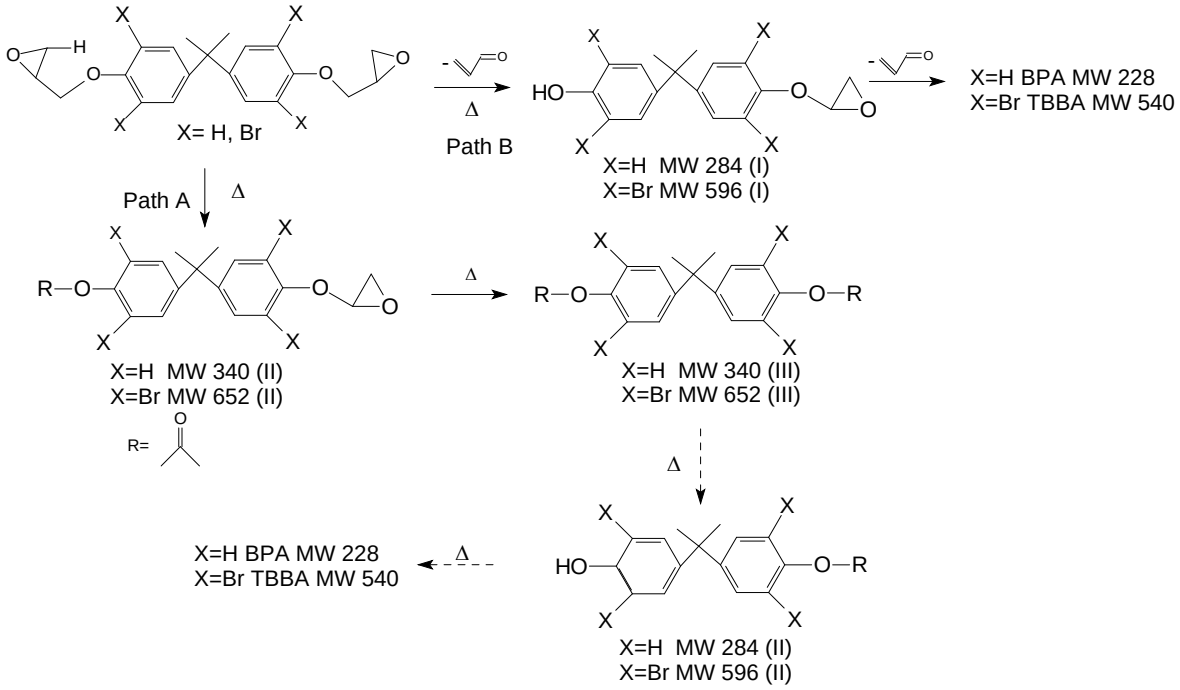
Pyrolysis experiments. In view of elucidating degradation mechanism, fast pyrolysis of the epoxies have been carried out at 386, 423, 500, 590 and 670°C in a Curie point Py-GC/MS equipment on BER-PHT, ER-PHT, DGEBA and DGETBBA. The minimum allowed sample (< 1mg) was used to highlight only the reactions occurring at a remarkable rate at the selected temperature and minimize secondary degradation reactions.

Apart for products whose MS spectrum is in reported in fig. 2, all others compounds have been identified by current MS libraries with high score value (>91) and by published MS spectra [14-17]; for instance MS spectrum of DGEBA closely matches reference n° 134714 in Wiley MS library; In ref. [14] some structures for isomers at MW 340 and 284 are suggested.

To assign the products 340(II) and 340(III) the mass spectrum of DGEBA was taken into consideration (Fig.2) which shows the loss of 15 amu due to methyl group followed by two consecutive losses of 56 amu due to the glycidyl group to produce OH groups probably through a cyclic transition state. Direct scission of the O-CH_2 bond is observed as well to give the ion at 57 amu. Therefore, the presence of an ion at 57 amu and a transition of 56 amu was taken as evidence of the existence of a glycidyl group. The 340(II) product shows a loss of 15 amu followed by a single transition of 56 amu indicating availability of an isopropyl bridge and a glycidyl group. The next clue is the ion at 43 amu that is not accompanied by ions at 42 and 41 amu, therefore attributed to the CH_3CO^+ ion. Thus, the compound 340(II) is concluded to be acetonylglycidyl ether of bisphenol A. The compound 340(III) shows a less prominent 325 – 269 transition, a negligible ion at 57 amu and a more intense ion at 43 amu. With the above discussion, the compound is attributed to diacetonyl ether of bisphenol A. Similar considerations lead to the conclusion that the compound 284(I) is monoglycidyl ether of bisphenol A whereas that 284(II) is monoacetonyl ether of bisphenol A. The 190 compound exhibits the loss of 56 which together ion at 57 amu support the structure of the glycidyl ether of isopropenylphenol.

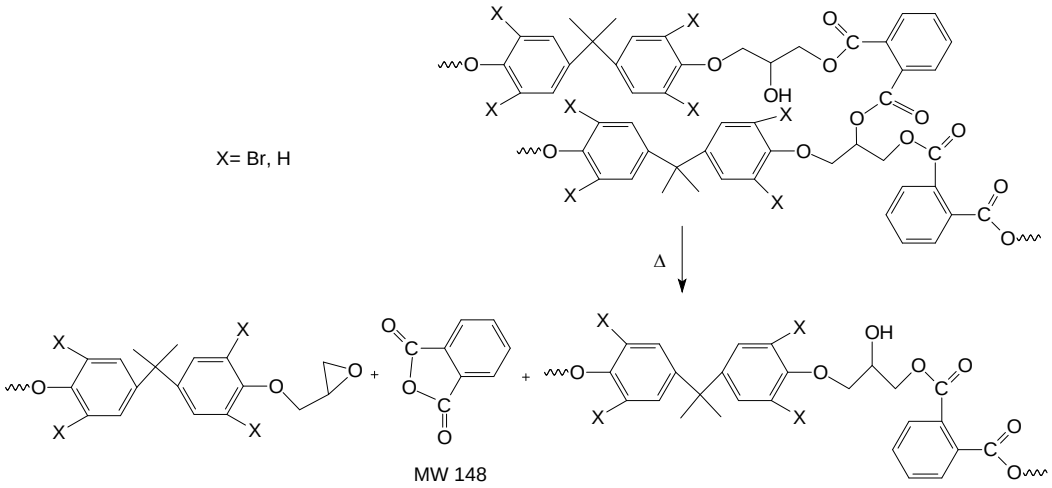
The above discussion is also valid to the bromine-containing products in Fig.2. Here, the ratio between ions at 43 and 57 amu is more demonstrative. As a result, the attribution of the products is as follows: acetonylglycidyl ether of tetrabromobisphenol A (652(II)), diacetonyl ether of bisphenol A (652(III)), monoglycidyl ether of tetrabromobisphenol A (596(I)), monoacetonyl ether of bisphenol A (596(II)). The mass spectra also show the influence of bromine atoms on the fragmentation reaction as the loss of methyl group is not always the most favorite process. According to that, attribution of the main degradation products is proposed in table 1.

MS spectra and GC retention times of the main pyrolysis product of DGEBA and DGETBBA at 386 °C both correspond to those of standard DGEBA and DGETBBA (fig.1 and 2), either using slow or fast GC heating programs. Therefore DGEBA and DGETBBA largely volatilize when pyrolyzed at 386°C (fig 1, bottom line). Other products formed in minor amount are MW340 (II), MW340 (III) in DGEBA and MW652 (II), MW596 (I), MW540 in DGETBBA. Very low amount of MW652 (III) and MW596 (II) are also found in pyrolysis of DGETBBA. They all can be formed according to scheme 2 which involves rearrangement of the epoxy end groups (path A) and loss of terminal glycidyl (path B);
The only relevant product in PY-GC/MS of ER-PHT and BER-PHT at 386°C is PHT, volatile at that temperature, likely to arise from small amount of unreacted PHT or just from initial pyrolysis of the ester groups (see below).



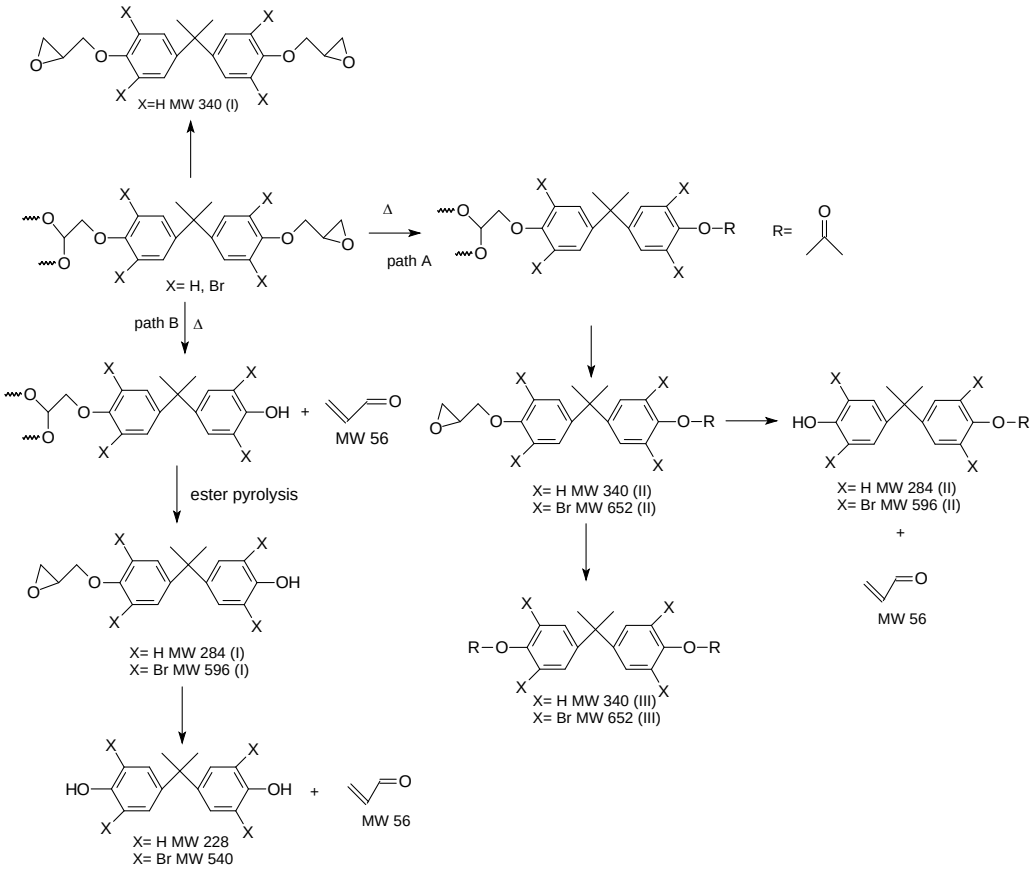
Scheme 2

DGEBA mainly volatilizes by PY-GC/MS at 423°C (Fig. 9, upper right pyrogram); a lower amount of MW340 (II) and MW340 (III) is also produced in agreement to what found at 386°C. When DGETBBA is pyrolysed at 423°C it is converted to product MW652 (III) and further degradation products such as acrolein (MW 56), propen-1-ol MW58 (I), TBBA (MW540) and MW596 (II) according to scheme 2. (Fig. 9, bottom right pyrogram). Amongst these processes volatilization and oxirane rearrangement prevail in DGEBA and deglycicylization in DGETBBA pyrolysis. This behavior can be attributed to the higher volatility of DGEBA and its derivatives in comparison to DGETBBA and its isomers.
At 423°C major products degradation of ER-PHT are PHT (MW 148) and epoxy monomer DGEBA which are formed by pyrolysis of the ester bond. This is in agreement to the IR of the residues at 400 and 425°C (Fig. 8) which showed decreasing of the 1065 and 1728 cm^{-1} bands (Scheme 3, X=H). Minor products are acrolein, MW340 (II), MW340 (III), MW284 (II) and MW 228, (Fig. 9 upper left pyrogram). In comparison PY-GC/MS at 423°C of BER-PHT (Fig. 9, bottom left pyrogram) originates acrolein (MW 56) propen-1-ol (MW 58), PHT (MW 148), MW 228, MW 284 (II) MW340 (II) and TBBA.
On the basis of these evidences, the main process occurring in the pyrolyser at 423°C is the pyrolysis of the ester bond reforming PHT and epoxy terminals (scheme 3).



Scheme 3

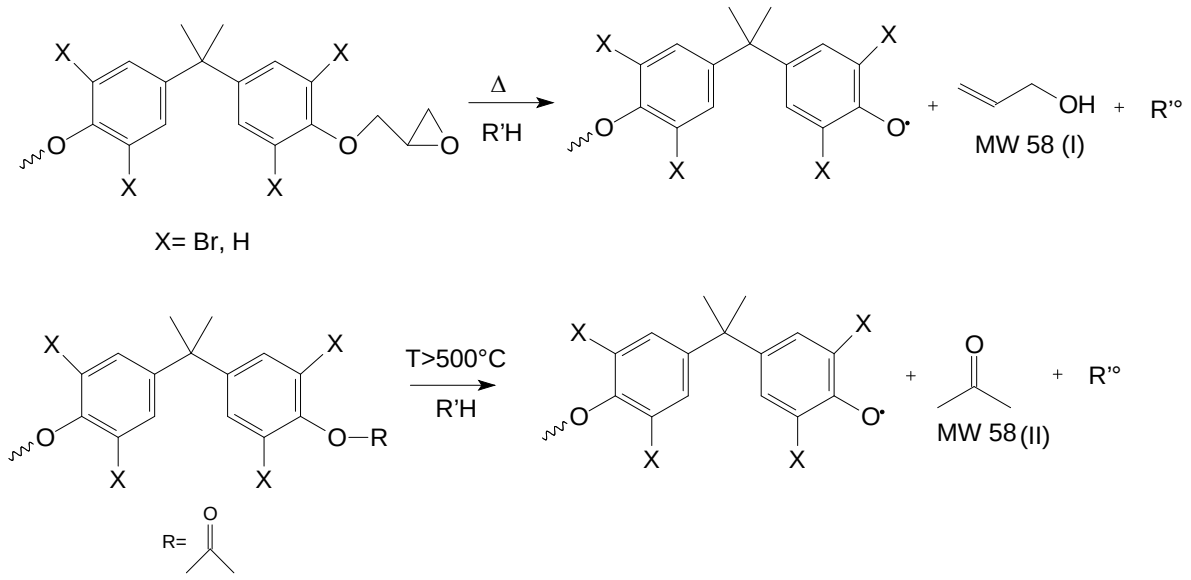
Under conditions of fast removal of the degradation products epoxy monomer can be recovered in the pyrolysis oil; this occurs with DGEBA because of it greater volatility in comparison to DGETBBA. However, because of the persistence of the degrading network in the hot spot of pyrolyzer, the process of rearrangement and of scission of the glycidyl end groups is likely to take place, originating the above mentioned products (scheme 4).



Scheme 4

The relatively small amount of propen-1-ol MW 58 (I) evolved from 423 °C pyrolysis of BER-PHT and DGETBBA possibly suggests the occurrence of a radical process, concurrent

to those above, involving H abstraction (Scheme 5); Phenolic –O-H (formed as in scheme 4) is likely to be the favorite candidate for H abstraction.



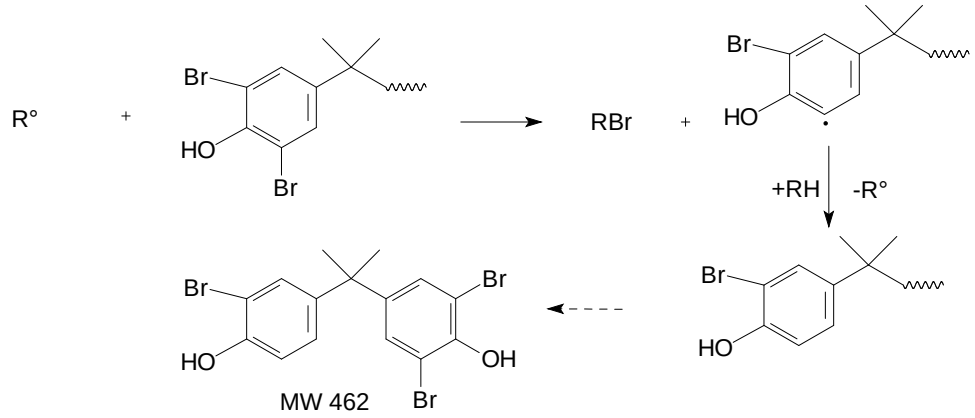
Scheme 5

Pyrolysis at 500 °C of ER-PHT and of DGEBA, besides traces of water, CO_2 and CO, results formation of acrolein (MW 56), propen-1-ol MW 58 (I), traces of acetone MW 58 (II), PHT (MW 148), bisphenol A (MW 228), MW284 (II), MW340 (II) and MW340 (III) according to reactions of schemes 2, 3, 4 and 5. Degradation is more extensive in ER-PHT than in DGEBA (Fig.10 upper pyrograms).

In contrast, pyrolysis of BER-PHT and DGETBBA at 500 °C yields additional products. Pyrograms of BER-PHT in fig. 10 shows formation of brominated low molecular weight products such as bromomethane (MW 94 (I)), 3-bromopropene (MW120) and bromoacetone (MW 136) together with acrolein (MW 56), propen-1-ol (MW 58), acetone (MW 58), phenol (MW 94 (II)), PHT (MW 148), dibromophenol (MW 250), dibromo(methylethenyl)phenol (MW 290) bisphenol A (MW 228), MW 284 (II), Tribromobisphenol A (MW 462), TBBA (MW 540), MW 596 (II) and MW 652 (III). Bromoacetone attribution was confirmed from SDBS spectral database of organic compounds [15] and in [16]; MS spectrum attributed to Tribromobisphenol A corresponds to that reported by Blazso [16] and that of dibromo(methyl ethenyl) phenol to that reported in ref. 17. Pyrogram at 500°C of DGETBBA shows similar features but a lower extent of degradation.

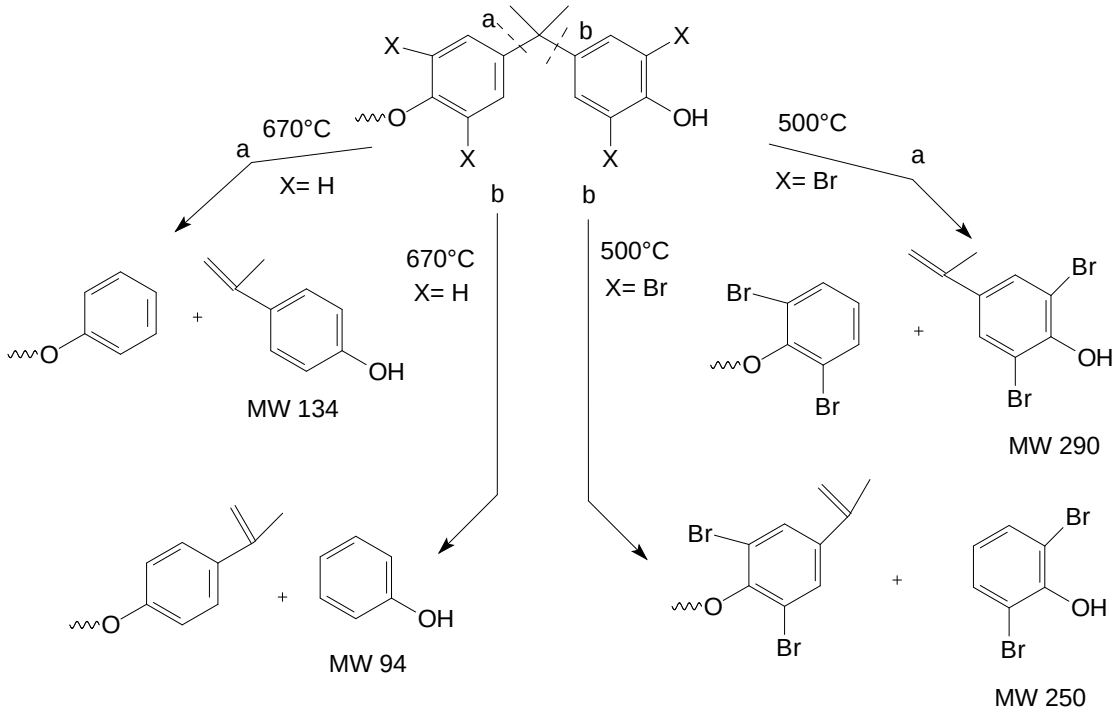
Acetone evolved at 500°C could derive from degradation of MW652 (II or III) and of MW340 (II or III), (scheme 5) supporting the rearrangement of DGEBA and DGETBBA to keton form.

It is interesting to note that debromination of DGETBBA results in simultaneous appearance of tribromobisphenol A and brominated aliphatics (bromoacetone in particular) indicative of a displacement of Br from the aromatic structures to the aliphatic ones. At this temperature radicals are able to abstract Br from the aromatic substrate, according to scheme 6. Notably *ortho* and *para* Br from the bisphenol will be preferably removed, due to the intrinsic thermal lability of this bond [18-21]. R° radicals contribute to the formation of the charred residue in agreement to IR finding of Fig. 8.



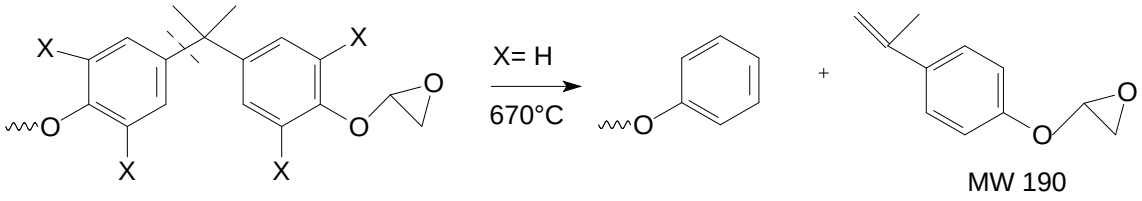
Scheme 6

In concert to the formation of brominated aliphatics, scission of isopropyl bridge in BER-PHT and DGETBBA occurs: facile scission at the *ortho - para* position comes about, due to the intrinsic instability in phenols of substituents in these positions [18-21] (scheme 7, X= Br right branches)



Scheme 7

Pyrolysis at higher temperatures leads to extensive fragmentation of the systems: pyrolysis of ER-PHT at 670°C (Fig. 11, upper pyrogram), in addition to the products already formed at lower temperatures, turns out into propene (MW 42) acetaldehyde (MW 44), considerable amount of phenol (MW 94), methyl(ethenyl)phenol (MW 134) and product MW 190 which indicates breaking of the isopropyl bridge of bisphenol A (scheme 7, X= H left branches). A possible mechanism of formation of this compound is reported in scheme 8.



Scheme 8

PY-GC/MS of BER-PHT at 590°C is reported in fig 11, lower pyrograms, with an enlarged portion of the products eluted earlier: propene (MW 42), acetaldehyde (MW 44), acrolein, propen-1-ol, acetone, bromomethane (MW 94 (I)) HBr (MW 80) bromopropene (MW 120) bromoacetone (MW 136). Phenol (MW 94 (II)), PHT (MW 148), Bromophenol (MW 170) bisphenol A (MW 228), Dibromobisphenol A (MW 384), Tribromobisphenol A (Mw 462), TBBA (MW 540), MW 228, MW 284 (II), Mw 596 (II) and a minor amount of 340 (I and II) and MW652 (III) comes out at larger retention times. At 590°C, differently from lower temperatures, HBr is evolved and dehydrobromination occurs because at this temperature bromine radicals are able to abstract H from the surrounding structures.

Conclusion

From fast pyrolysis experiments, the following reactions can be considered to occur in epoxy ester resins:

- Pyrolysis of the ester bond, reforming the reactives epoxides and PHT, occurring presumably from 386° C either on brominated or not brominated systems.
- Rearrangement of the oxirane ring into a more stable functional group. This reaction competes with volatilization and deglycidylation. At 386-423°C volatilization prevails over rearrangement with compounds enough volatile such as DGEBA.
- Loss of the glycidyl end groups forming a phenolic OH and acrolein. This reaction is reasonably fast at 423 °C however where sufficiently light molecules (such as DGEBA) are formed by pyrolysis, evaporation and rearrangement prevail over deglycidylation.

Tacking in account the different thermal regime in fast pyrolysis (immediate heating for few seconds) and in dynamic TGA (progressive heating for tenth of minutes) these reactions are possibly responsible of the overlapping trend up to 340°C in dynamic TGA of both systems, Facile evaporation of DGEBA contribute to the main step of weight loss in ER-PHT at 418 °C.

- Debromination of TBBA units and formation of brominated aliphatic taking place in PY-GC/MS at 500°C. This reaction also favors charring.
- Scission of the isopropyl bridge of bisphenol A occurring at 500°C in brominated systems and at higher temperature in not brominated ones.

These reactions are possibly responsible of the steeply step of weight loss located, in TGA, at 380 °C in BER-PHT and of successive charring .

- HBr formation (in brominated systems) at about 600°C

Epoxy ester resins are thermally more stable than epoxies cured with aliphatic amines and more or less stable as those cured by aromatic amines. However they present some differences in thermal degradation because the thermally weaker structure in amine cured epoxies is C-N, and in epoxy ester is the ester functionality. In all cases however brominated units reduces thermal stability in comparison to analogues unbrominated [11-12].

The most valuable products of pyrolysis of brominated epoxies esters are pyrolysis oil and

gases. Pyrolysis oil, if directly used as fuel, must be free from toxics and toxics precursor, in alternative chemicals recovery can be performed. Amongst gases, recovery of hydrogen bromide has the most interesting economical revenue.
Therefore advantageous pyrolytic recycling must maximize the amount of pyrolysis oil avoiding as much as possible the formation of brominated phenols, precursor of dioxins [21].
The key-factor in thermal weakness of brominated epoxy ester can be imputed to the intrinsic lability of the *ortho*-bromine in TBBA units.
Low pyrolysis temperature and fast removal of decomposition products could account for recovery of DGEBA, TBBA and phthalic anhydride. Debromination at moderate temperature produces brominated aliphatic and contemporary favors charring, reducing the amount of oil.
At higher temperatures scission of the isopropyl bridge in BER-PHT leads to brominated phenols, HBr is formed at even higher temperature at which brominated phenols are also evolved.

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Caption to the figures

Fig. 1 upper line: TIC chromatogram from acetone solution of DGEBA (left) and DGETBBA(right); bottom line: TIC chromatogram from 386°C PY-GC/MS of DGEBA (left) and DGETBBA (right)

Fig 2. MS spectra of selected compound from pyrolysis of epoxy ester resins which were not identified by current spectral Wiley and NBS MS libraries. Q= quintuplet Qr= quadruplet T= triplet; r.t.= retention time in GC slow heating program

Fig. 3 DSC thermograms of ER-PHT curing. dashed line: first heating; solid line: second heating

Fig. 4. DSC of crosslinked ER-PHT(Upper) and BER-PHT (bottom)

Fig. 5 IR of PHT, DGEBA, DGETBBA and of crosslinked BER-PHT

Fig. 6 IR of the mixture DGEBA-PHT and of crosslinked ER-PHT

Fig. 7 TGA of epoxy systems ER-PHT and BER-PHT (upper); TGA of neat epoxy monomers DGEBA and DGETBBA (bottom)

Fig. 8. Evolution of the solid residue of ER-PHT (upper) and of BER-PHT (Bottom) during heating. ATR spectra on powdered residues

Fig 9 PY-GC/MS of ER-PHT (upper left) and DGEBA (upper right) BER-PHT (bottom left) and DGETBBA (bottom right) at 423°C. TIC chromatograms; figures on the peaks refer to the molecular weight of the corresponding compound. (Bromine is considered 79 amu)

Fig. 10. PY-GC/MS of ER-PHT (upper left) and DGEBA (upper right) BER-PHT (bottom left) and DGETBBA (bottom right) at 500°C. TIC chromatograms. Peaks are marked by using by the molecular weight of the corresponding products (Bromine is considered 79 amu)

Fig. 11. PY-GC/MS of ER-PHT (upper left) at 670°C and of BER-PHT (bottom left) and DGETBBA (bottom right) at 590°C. TIC chromatograms. Peaks are marked by using by the molecular weight of the corresponding products (Bromine is considered 79 amu)

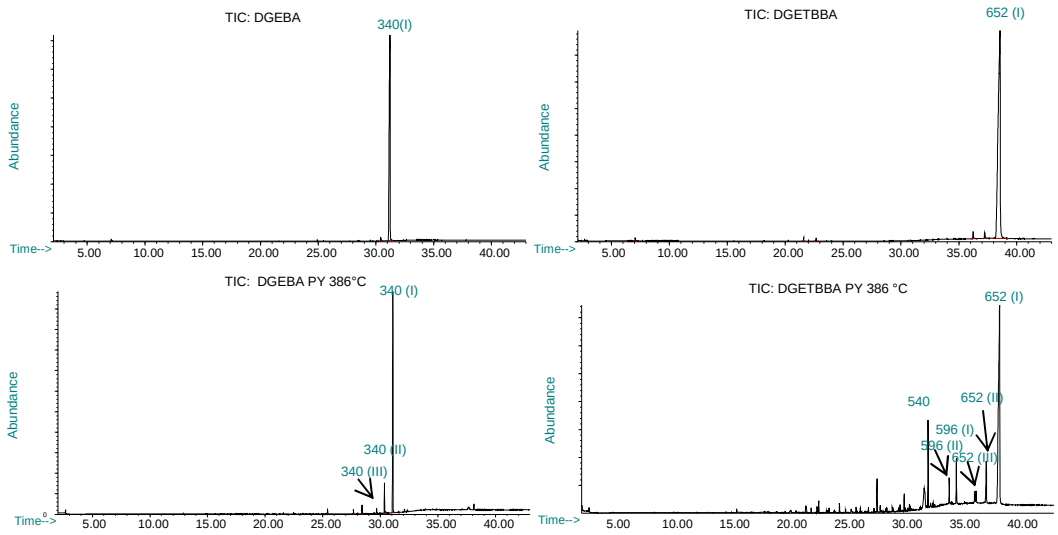
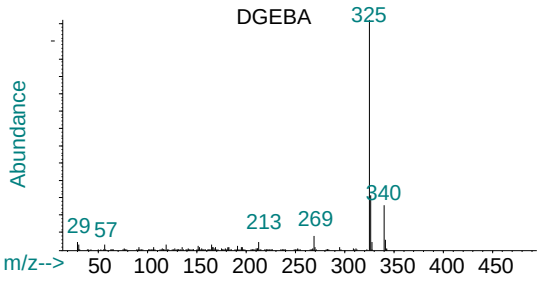
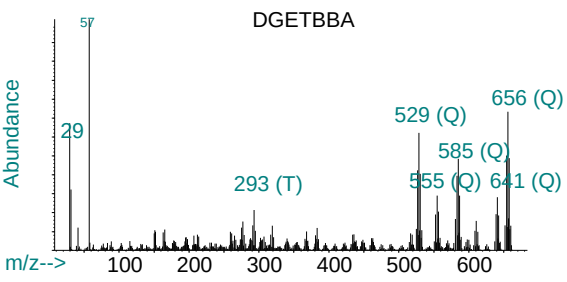
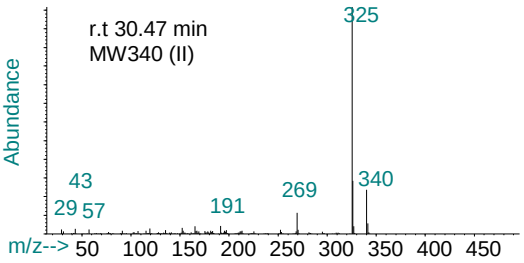
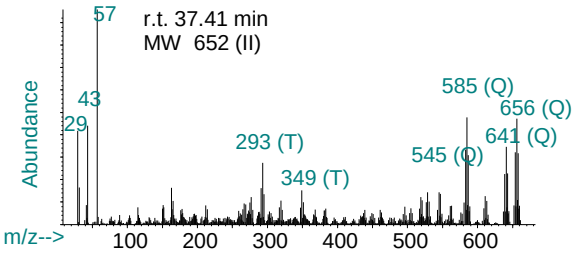


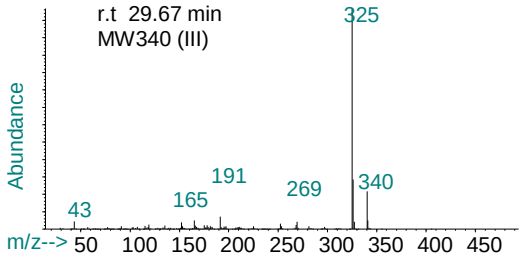
Fig. 1 upper line: TIC chromatogram from acetone solution of DGEBA (left) and DGETBBA(right); bottom line: TIC chromatogram from 386°C PY-GC/MS of DGEBA (left) and DGETBBA (right)


DGEBA
325
Abundance
29
57
213
269
340
m/z-->
50 100 150 200 250 300 350 400 450


DGETBBA
57
Abundance
29
293 (T)
529 (Q)
585 (Q)
555 (Q)
641 (Q)
656 (Q)
m/z-->
100 200 300 400 500 600


r.t 30.47 min
MW340 (II)
325
Abundance
43
29
57
191
269
340
m/z-->
50 100 150 200 250 300 350 400 450


r.t. 37.41 min
MW 652 (II)
57
Abundance
43
29
293 (T)
349 (T)
545 (Q)
585 (Q)
641 (Q)
656 (Q)
m/z-->
100 200 300 400 500 600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MW340 (III)
325
Abundance
43
165
191
269
340
m/z-->
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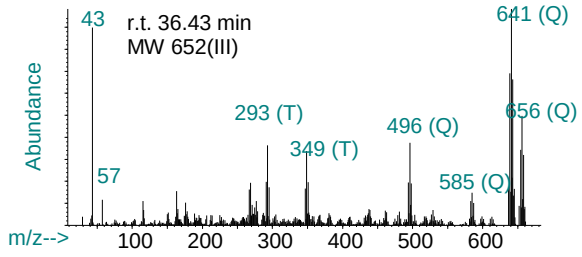
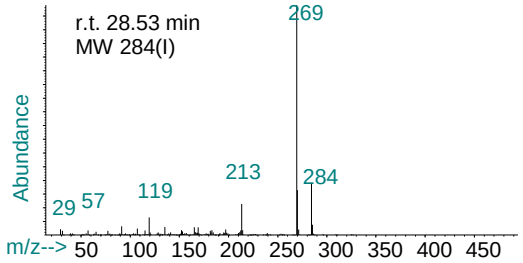

r.t. 36.43 min
MW 652(III)
43
Abundance
57
293 (T)
349 (T)
496 (Q)
585 (Q)
641 (Q)
656 (Q)
m/z-->
100 200 300 400 500 600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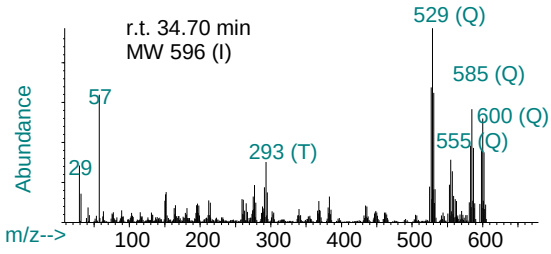
MW 284(I)
269
Abundance
29
57
119
213
284
m/z-->
50 100 150 200 250 300 350 400 450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Abundance
57
29
293 (T)
555 (Q)
585 (Q)
600 (Q)
m/z-->
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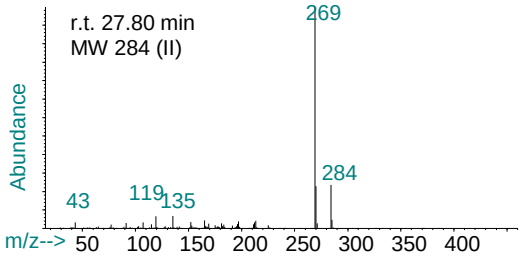
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269
Abundance
43
119
135
284
m/z-->
50 100 150 200 250 300 350 400

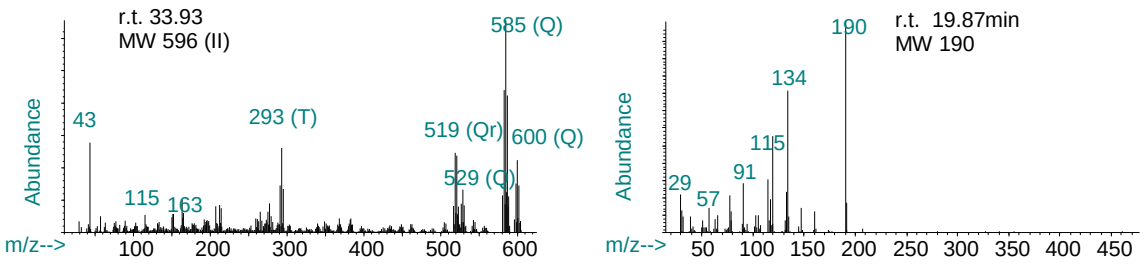


Fig 2. MS spectra of selected compound from pyrolysis of epoxy ester resins which were not identified by current spectral Wiley and NBS MS libraries. Q= quintuplet Qr= quadruplet T= triplet D= doublet; r.t.= retention time in GC slow heating program

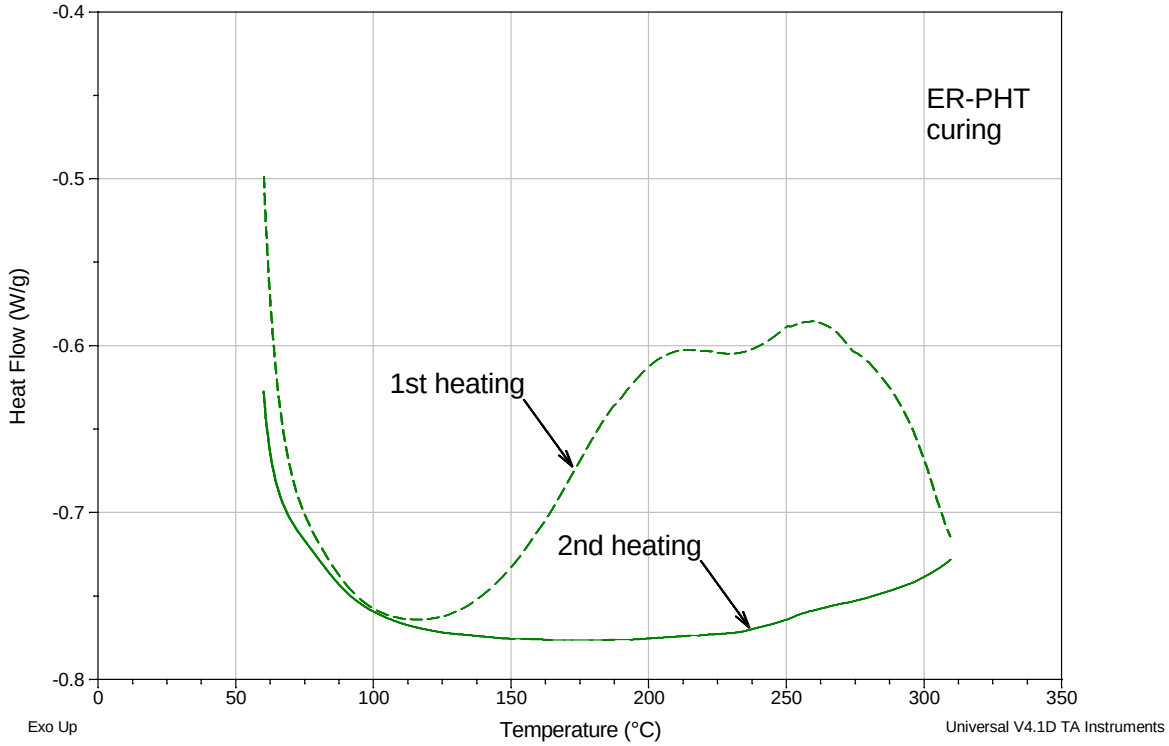


Fig. 3 DSC thermograms of ER-PHT curing. dashed line: first heating; solid line: second heating

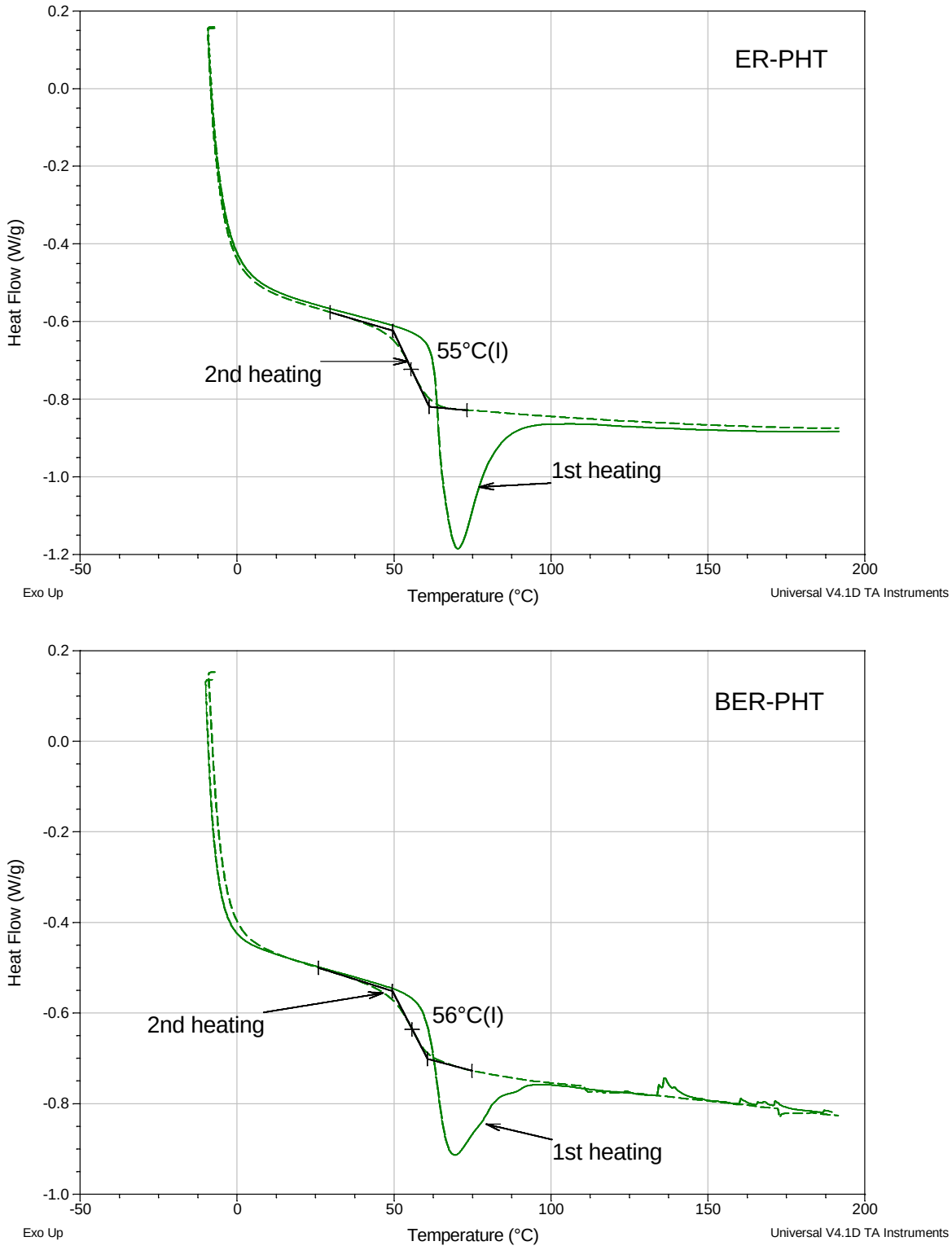


Fig. 4. DSC of crosslinked ER-PHT(Upper) and BER-PHT (bottom)

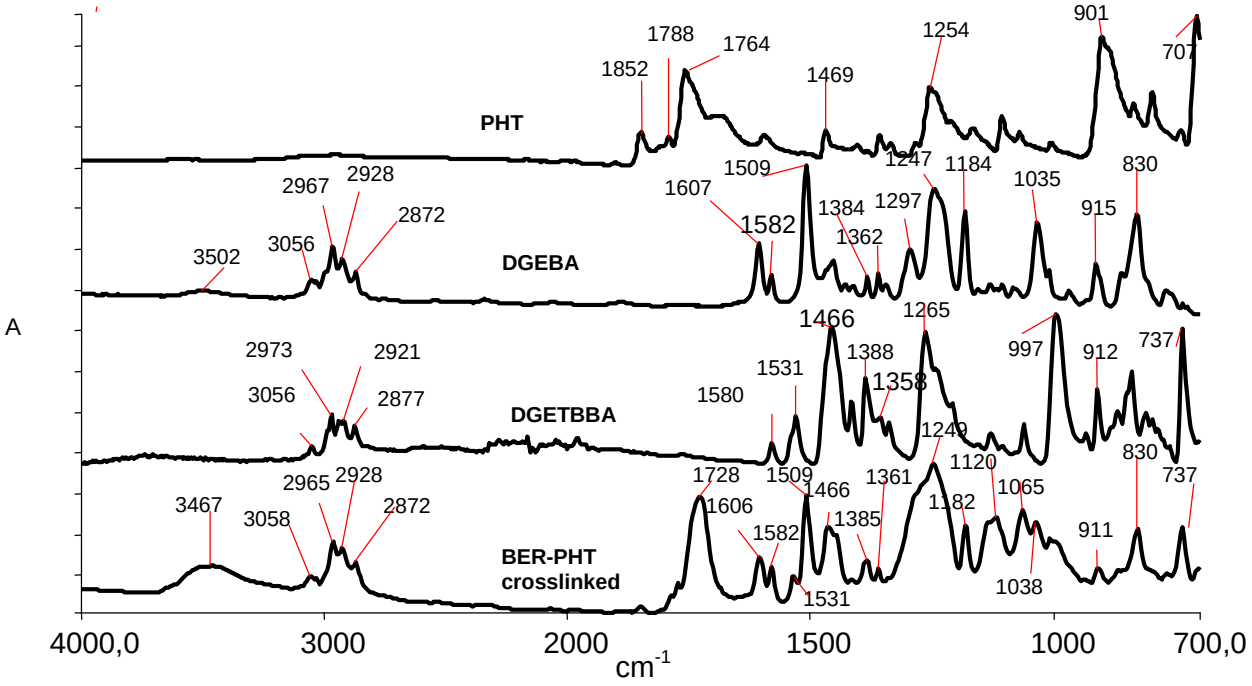


Fig. 5 IR of PHT, DGEBA, DGETBBA and of crosslinkedBER-PHT

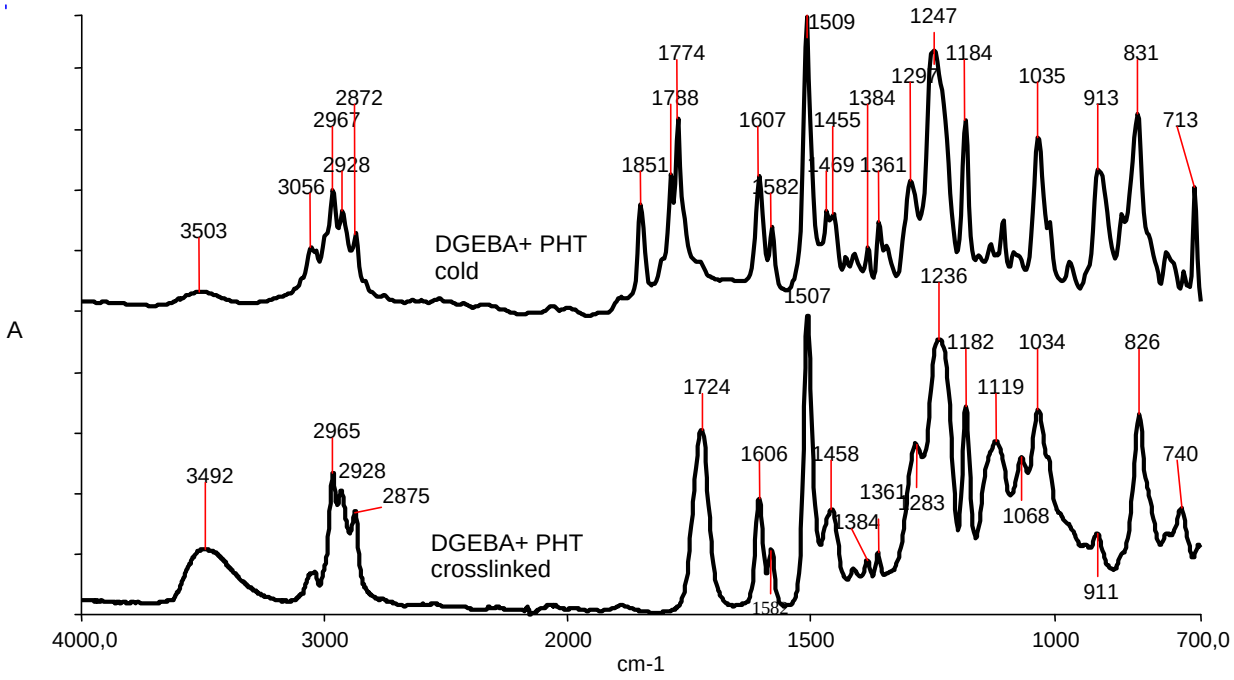


Fig. 6 IR of the mixture DGEBA-PHT and of crosslinked ER-PHT

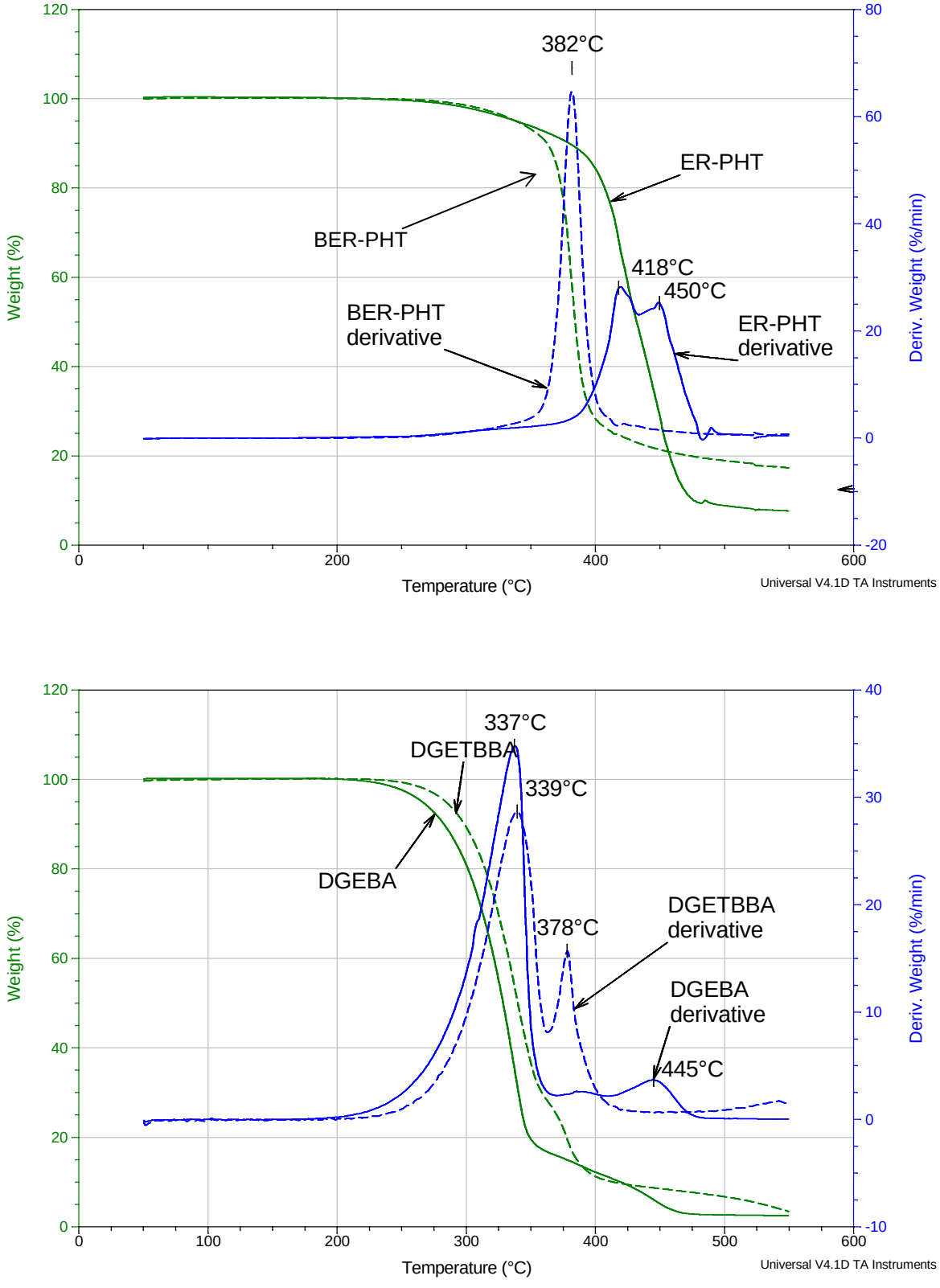


Fig. 7 TGA of epoxy systems ER-PHT and BER-PHT (upper); TGA of neat epoxy monomers DGEBA and DGETBBA (bottom)

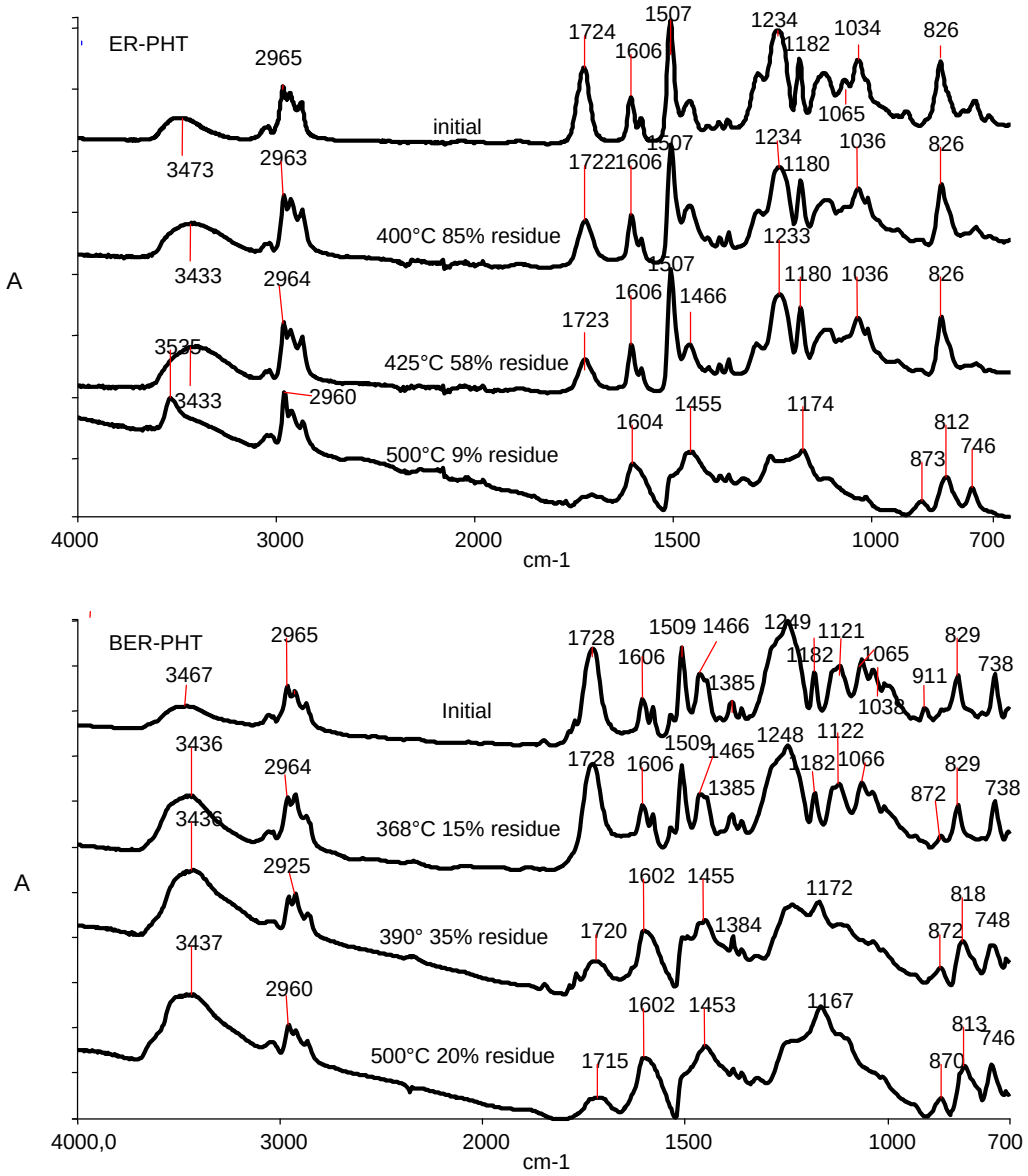


Fig. 8. Evolution of the solid residue of ER-PHT (upper) and of BER-PHT (Bottom) during heating. ATR spectra on powdered residues

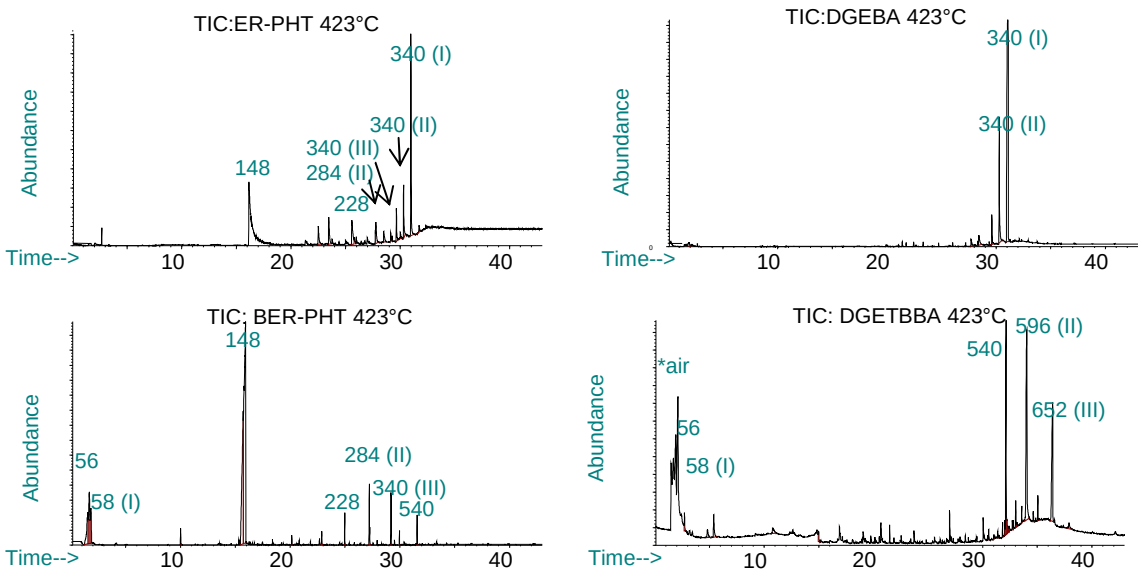


Fig 9 PY-GC/MS of ER-PHT (upper left) and DGEBA (upper right) BER-PHT (bottom left) and DGETBBA (bottom right) at 423°C. TIC chromatograms; figures on the peaks refer to the molecular weight of the corresponding compound.

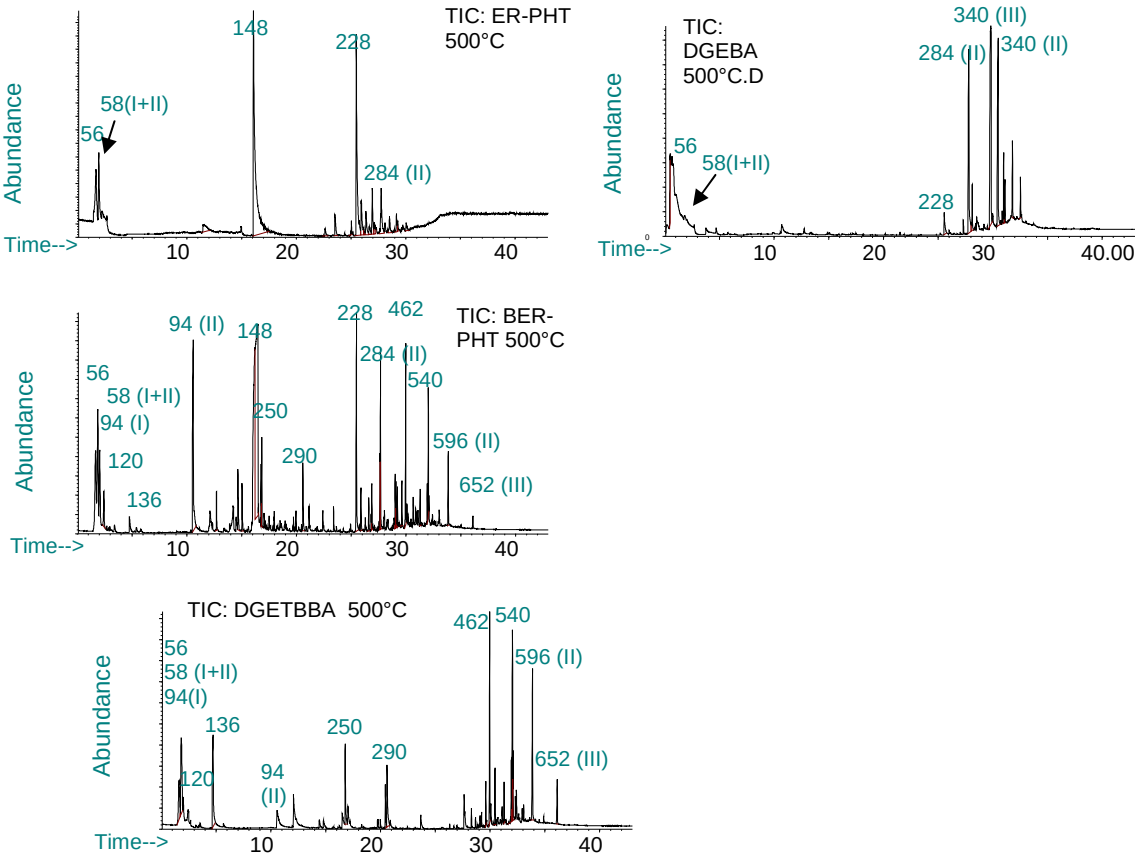


Fig. 10. PY-GC/MS of ER-PHT (upper left) and DGEBA (upper right) BER-PHT (bottom left) and DGETBBA (bottom right) at 500°C. TIC chromatograms. Peaks are marked by using by the molecular weight of the corresponding products (Bromine is considered 79 amu)

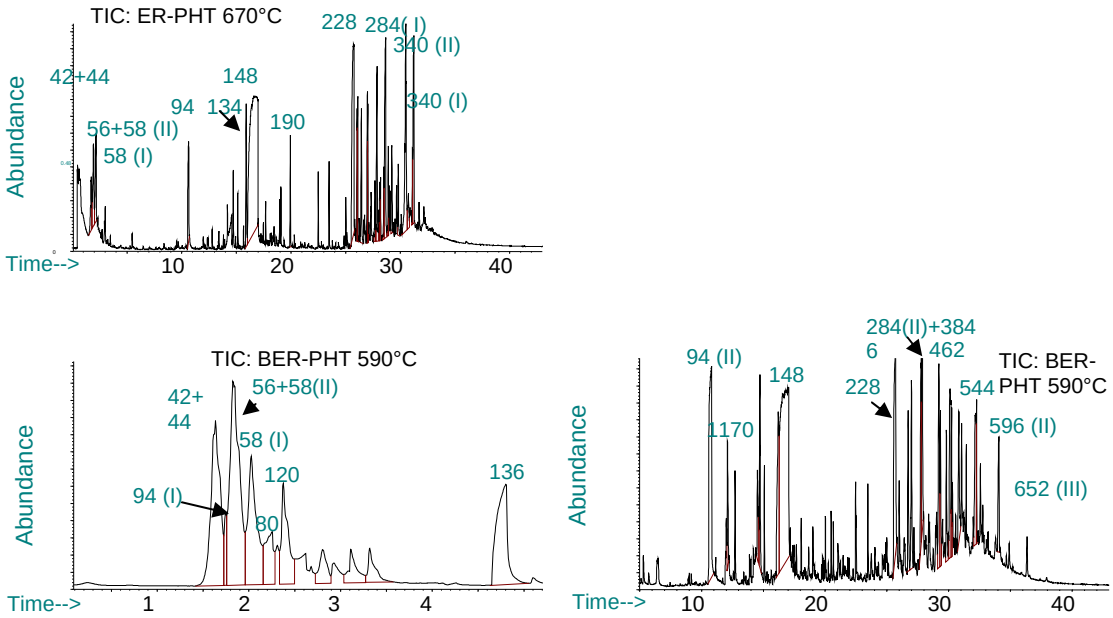
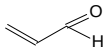
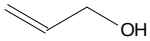
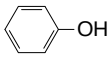
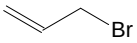
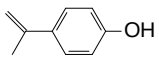
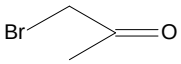
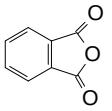
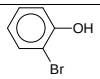
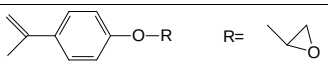
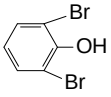
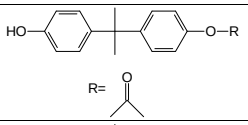
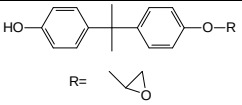
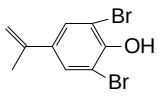
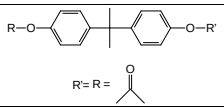
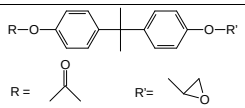
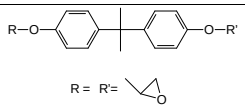
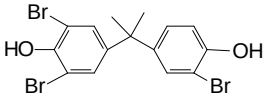
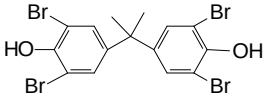
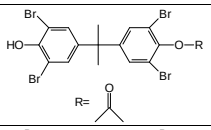
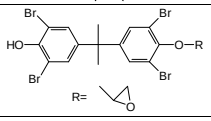
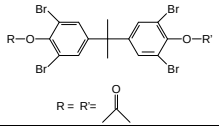
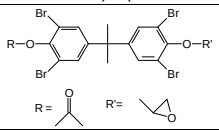


Fig. 11. PY-GC/MS of ER-PHT (upper left) at 670°C and of BER-PHT (bottom left) and DGETBBA (bottom right) at 5900°C. TIC chromatograms. Peaks are marked by using by the molecular weight of the corresponding products (Bromine is considered 79 amu)

Table 1 Main degradation products in the Py-GC/MS at 386, 423, 500, 590, 670°C of ER-PHT, DGEBA, DGETBBA, BER-PHT. Products listed in order of increasing MW (Br =79 amu)

MW	Ret. Time (min)	Compounds	Molecular Structure	MS attribution; Ref.
94	1.74	94 (I) Bromomethane		Wiley and NBS MS library
56	1.87	Acrolein		Wiley and NBS MS library
58	1.90	58 (II) Aceton		Wiley and NBS MS library
58	2.07	58 (I) Propen-1-ol		Wiley and NBS MS library
94	10.82	94 (II) Phenol		Wiley and NBS MS library
120	2.38	bromopropene		Wiley and NBS MS library
134	15.91	(methyl ethenyl) phenol		Wiley and NBS MS library
136	4.81	Bromoacetone		SDBS spectral database [15] and [16]
148	16.46	PHT		Wiley and NBS MS library
170	12.10	2-bromophenol		Wiley and NBS MS library
190	19.87	isopropenylphenyl glycidyl ether		Wiley (ref 30028) MS library and this work
228	25.53	Bisphenol A (BPA)		Wiley and NBS MS library
250	16.92	2,6-dibromophenol		Wiley and NBS MS library
284	27.80	284(II)		This work
	28.53	284(I)		
290	20.60	dibromo(methyl ethenyl) phenol		[17]
340	29.67	340(III)		This work

MW	Ret. Time (min)	Compounds	Molecular Structure	MS attribution; Ref.
	30.47	340(II)		
	31.20	DGEBA (340 (I))		Wiley (ref. 134714) and NBS (ref 48164) MS library, this work
462	29.97	Tribromobisphenol A		Blaszo [16]
540	32.05	TBBA		Wiley and NBS MS library
596	33.93	596(II)		This work
	34.70	596(I)		
652	36.43	652(III)		This work
	37.41	652(II)		
652	38.59	DGETBBA (652 (I))