

Solvolysis of Flame Retarded Circuit Boards

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1. Introduction

Due to the expansion of German legislation concerning municipal and industrial waste, recycling has to be extended to include even the products of the electronic industry⁽¹⁾. Waste from obsolete electronic products, „scrap of electronics“, is estimated in amounts of 1.5 to 2.0 million tons for 1996. Scrap of electronics consists of a great variety of different materials and substances.

Although scrap of electronics is already used as a raw material resource for metals, the flame retarded plastics from electronics are especially problematic during recycling. More than 200.000 tons of flame retarded plastics were used in the electronics industry in Europe, of which about 150.000 tons contained brominated additives as flame retardants⁽²⁾. The most common additives over the last decades have been polybrominated diphenylethers (PBDE) and brominated bisphenols (tetrabromobisphenol-A, TBBA)⁽⁴⁾.

Conclusive evidence was provided, that these brominated plastics are a source of brominated dioxins and furans, either from contaminants in the flame retardants or generated due to thermal stress (extruder, incineration, pyrolysis, etc.)⁽⁵⁻⁹⁾. Hence, these materials are often regarded as „non-recyclable“.

We are introducing a method of removing brominated epoxide resins from scrap of electronics by solvolysis, to enable the integration of materials containing brominated plastics into recycling activities⁽³⁾.

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2. Experimental

FR4-material (glass fibre reinforced epoxide resin, amine cured bisphenol-A, reactive flame retardant tetrabromobisphenol-A) representing printed circuit boards, was chopped to pieces (< 500 µm), suspended in different organic solvents and treated in a 250 ml autoclave at temperatures of 260° to 320°C for 1 to 12 hours in a nitrogen atmosphere (50 - 110 bar, depending on temperature and solvent). After filtration, the organic phase was directly analysed by GC/MS. The residue was investigated by thermogravimetry, CHN-Analysis and XRF-spectroscopy (quantification of bromine).

For GC/MS, a FISON GC 8060 coupled with a low resolution mass spectrometer TRIO 1000 FISON (scan mode) was used. The identification of the compounds was achieved by mass spectrometry. For quantification external standards were used (bisphenol-A, mono-, di-, tri- and tetrabromobisphenol-A).

3. Results and Discussion

Under the reaction conditions all three solvents provided a significant decomposition of the resin, mainly at temperatures higher than 300°C. Using ethanol resulted in a greater than 95% decomposition of the resin, as determined by thermogravimetry. This corresponds with an almost quantitative removal of the hydrocarbons from the FR4 matrix, leaving almost carbon- and bromine free glass fibres (Table 1, Figure 1).

Table 1: Bromine and carbon content in educt material (FR4) and after solvolysis (Ethanol, 320°C, 12 hours).

| | Bromine (weight %) | Carbon (weight %) |
|--------------------------|--------------------|-------------------|
| Educt FR4-material | 11.2 | > 45 |
| Residue after solvolysis | 0.14 | 3.2 |

The polymeric hydrocarbons were partially cracked and transferred into the organic solvent, most effectively with polar solvents like ethyl acetate or ethanol. After removing the solvent, the fragments of the resin could be isolated as a viscous substance consisting mainly of oligomers of the former resin.

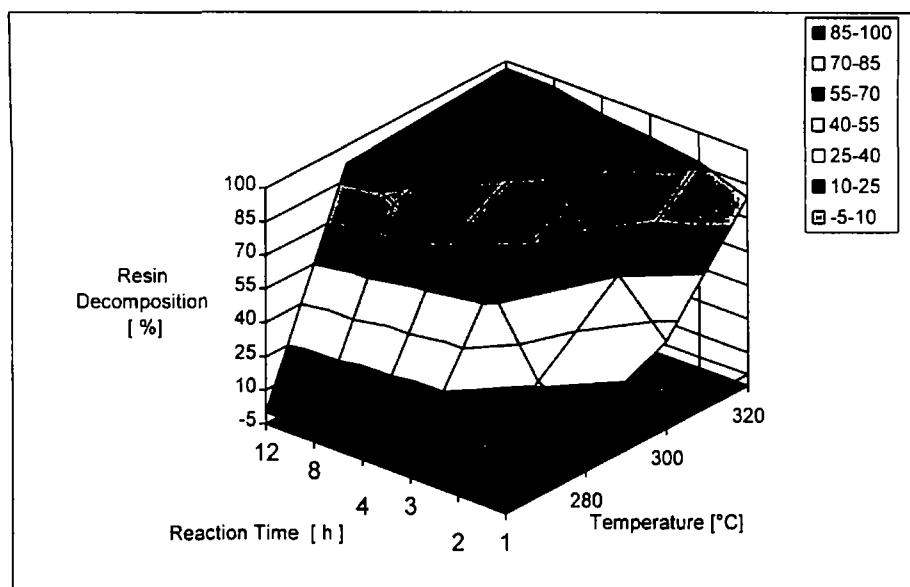


Figure 1: Decomposition of the epoxide resin (determined as carbon content in the residues after reaction related to the educt FR4-material, solvent = ethanol)

GC/MS proved the presence of low concentrations of monomeric bisphenol-A and brominated derivatives. Figure 2 shows the total amount of monomers (bisphenol-A and mono-, di-, tri-, tetrabromobisphenol-A), related to the total amount of resin. Less than 50% of the resin is converted into monomers.

A wide range of debromination and bromine exchange reactions occur under the conditions of the solvolysis depending upon the temperature and the duration of the solvolysis. The concentration of tetrabromobisphenol-A is reduced while the concentration of bisphenol-A and the mono- and di-halogenated homologues is being increased. Qualitatively TBBA is extracted from the resin and debrominated.

The applied reaction conditions and solvents are not useable for a selective cleavage of the resins but give a wide variety of products. Due to the observed dehalogenation, it can be assumed that no 2,3,7,8-brominated dioxins and furans and higher brominated homologues⁽¹³⁾ are formed during the decomposition of the resin. This will have to be proved by further investigations.

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The proposed reaction might be profitable with the purpose of removing inert hydrocarbons like epoxide resins from complex matrices.

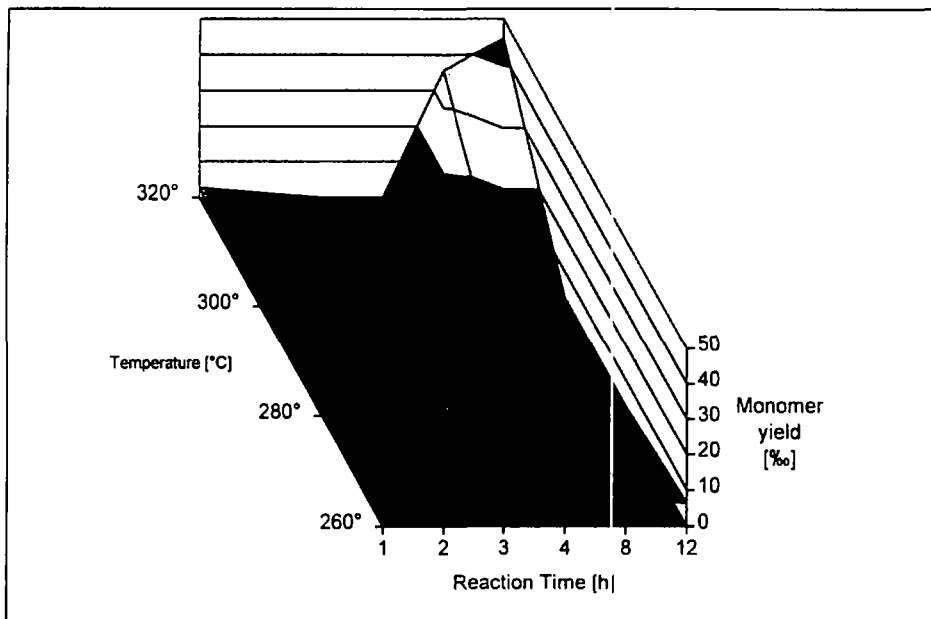


Figure 2: Monomer yield (related to the amount of educt epoxide resin, solvent =ethylacetate)

4. Literature

- 1) Act for Promoting Closed Substance Cycle Waste Management (Kreislaufwirtschaft) and Ensuring Environmentally Compatible Waste Disposal (Kreislaufwirtschafts- und Abfallgesetz - KrW-/AbfG), 27.09.1994, BGBl. III 2129-27-2.
- 2) Information material APME (Association of Plastics Manufacturer in Europe), Brüssel, 1994.
- 3) J. Langhojer (1996): Hochdrucksolvolyse von duroplastischen Werkstoffen Diplomarbeit, Institut für Anorganische Chemie, Universität Erlangen-Nürnberg.
- 4) R. Gächter, H. Müller (1993): Plastics Additives Handbook, Carl Hauser Verlag, München 1993.
- 5) K. S. Brenner, H. Knies (1990): Organohalogen Compounds 2, 319.
- 6) R. Dumler (1989): Brandversuche zur Bildung von bromierten Dibenzofuranen und -dioxinen aus flammgeschützten Kunststoffen, Dissertation, Bayreuth.

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- 7) H. Thoma, G. Hauschultz, E. Knorr, O. Hutziner (1987): *Chemosphere* 16, No. 1, pp. 277-285,
- 8) Umweltbundesamt Berlin, Presseinformation Nr. 3/93, Bromierte Flammschutzmittel in Kunststoffserzeugnissen, 08.02.1993
- 9) W. Lorenz, M. Bahadir (1993): *Chemosphere* 26, No. 12, pp. 2221-2229.
- 10) D. L. McAllister, S. J. Mazac, R. Gorisch, M. Freiberg, Y. Tondeur (1991): *Chemosphere* 20, No. 10-12, pp.1537-1541.
- 11) J. Thies, M. Neupert, W. Pump (1990): *Chemosphere* 20, No. 10-12, pp. 1921-1928.
- 12) G. Bertilli, L. Costa, S. Fenza, E. Marchetti, G. Camino, R. Locatelli (1988): *Polymer Degradation and Stability*, 20, 296-314.
- 13) Ordinance on banned chemicals (Chemikalien Verbotsverordnung), BGBl.I, S. 1493, 6. Juli 1994.