

Determination of unreacted TBBPA in different production stages of printed circuit boards

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Background and objectives

TBBPA is used in FR-4 printed circuit boards as a reactive flame retardant. TBBPA is chemically reacted with the epoxy resin to form a brominated and flame retarded thermoset polymer. The purpose of the study was to assess if unreacted TBBPA is left as a residue after the reaction in the final product. In order to make this evaluation, samples of the main production stages of printed circuit boards from different manufacturers (A, B, C) were analyzed for unreacted TBBPA; laminates and prepregs. In addition, the report includes also data produced by an external and independent laboratory, using a different method, for samples provided by an additional manufacturer (D).

Definitions:

- Prepregs: stands for "pre-impregnated" composite fibers where epoxy, as the based resin, is only partially cured to allow easy handling; this is called B-Stage. The impregnated "glass cloth" layers are later on assembled into laminates.
- Laminates : Laminates can be copper coated on both sides (copper clad laminates - CCL) or not (unclad laminates)

Experimental

(i) ICL-IP procedure

The following samples were delivered to ICL-IP: a CCL-F4 type from manufacturer A, three unclad laminates from manufacturer B and five pre-impregnated composite fibers (prepregs) from manufacturer C. These samples were prepared for extractions using the following procedures:

- The CCL-F4 was cut into pieces of approximately 1 cm². The copper coating was removed from the pieces by treatment with HNO₃, followed by washing with water and drying in an oven. Subsequently, the sample was milled in liquid nitrogen (cryo-milled). Two portions of the CCL sample (ca. 6 g each) were prepared.
- The three unclad laminates (ca. 2.5 g each) were cut into pieces of approximately 1 cm².
- The prepregs were milled in liquid nitrogen. Approximately 5-6 g of the grounded prepregs were used for the extraction.

All prepared samples (CCL, unclad laminates and prepregs) were extracted in 2-propanol (isopropanol) for 6 -7 hours by warm Soxhlet with an automated Büchi B-811. Using this technique, the solvent that is distilled at 82.6 °C into the extraction chamber is also heated below its boiling point. Consequently, the sample is in permanent contact with the hot solvent, which improves and speeds the analyte extraction from the matrix. A blank was prepared and analyzed under the same conditions as the samples.

A non-validated GC-MS method was used in order to quantify the unreacted TBBPA in the isopropanol extracts.

(ii) Analytische Laboratorien procedure

Unclad laminate and prepreg samples were provided by manufacturer D. The laminates (ca.10 g) were cut with a diamond blade into small pieces. The saw dust was collected and used as a fine powder for the analysis of TBBPA.

The samples (fine powder) were extracted with isopropanol at a ratio of 1:5 sample: solvent, by stirring with a magnetic stirrer at room temperature for 2 hours.

After the stirring, the eluate was separated by filtration and concentrated by evaporation to a final volume of 2 ml. The eluate was analyzed by GC.

Results

The results of the analyses obtained by ICL-IP and Analytische Laboratorien are shown in Table 1.

ICL analyses:

The identification of the TBBPA in the extracts was done by comparing the spectrum of 5 µg/ml standard TBBPA to those of the samples. Concentrations of free TBBPA were calculated based on the volumes of the isopropanol extracts and the weights of the samples. The following results were obtained:

- The CCL (manufacturer A) contained less than 20 ppm of TBBPA.
- The unclad laminates (manufacturer B) contained less than 20 ppm of TBBPA.
- The prepreps (manufacturer C) contained less than 20 ppm of TBBPA.

Analytische Laboratrien analyses:

- Manufacturer D's laminates and prepreps both contained less than 10 ppm TBBPA

Conclusions

The results of the analyses obtained by ICL-IP and Analytische Laboratorien are shown in Table 1. All samples contained unreacted TBBPA at levels of less than the detection limits of either 10 or 20 ppm. Therefore, the unreacted residues levels can be considered as very low, indicating that the presence of TBBPA as an individual compound is negligible in the laminates.

Table 1: Concentrations of unreacted TBBPA

Sample	Origin	Reported by	Method	TBBPA, ppm
CCL	Manufacturer A	ICL-IP	GC-MS	< 20
Unclad Laminates	Manufacturer B	ICL-IP	GC-MS	< 20
Prepregs	Manufacturer C	ICL-IP	GC-MS	< 20
Unclad Laminates	Manufacturer D	Analytische Laboratorien	GC-FID	< 10
Prepregs	Manufacturer D	Analytische Laboratorien	GC-FID	< 10