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New reactive, halogen-free flame retardant system for epoxy resins

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Abstract

Compounds based on bromine are commonly used for flame retardant epoxy resins. However, in relation to forthcoming electronic waste regulations, the use of halogen containing additives will be banned in the future. For this reason, epoxy resin suppliers and processors are searching for halogen-free flame retardants which do not affect material properties or processing.

The article shows promising results achieved with a flame retardant system based upon an aminophenyl phosphate. The reactive, halogen-free compound can be used as a crosslinking agent for epoxy resins, replacing the common combination of dicyandiamide and TBBA.

Laminates made of aminophenyl phosphate crosslinked epoxy resin meet the UL 94 V-1 classification. They also meet requirements concerning water absorption, heat stability and high glass transition temperature.

Aminophenyl phosphates can be combined with conventional crosslinking systems and common phosphate flame retardants. Epoxy resins crosslinked with aminophenyl phosphates need no change of the processing technology.

Keywords: Aminophenyl phosphate; Halogen free; Reactive crosslinking/curing agent; Epoxy resin; Flame retardant; Laminates/electro laminates

1. Flame retardant epoxy resin for electro laminates

The worldwide consumption of epoxy resins in 2000 was about 1 mt. Important application fields of these resins are surface protection, electrical industry, composites and adhesives [1]. The demand for laminates for the electrical industry (printed circuit boards) is estimated as about 100,000 t/yr. Especially the laminates for the electrical industry have to meet a variety of mechanical and electrical requirements. They also have to be flame retardant. There is a multitude of detailed classified laminates existing [2].

Brominated reactive compounds, like tetrabromo bisphenol A (TBBA), are state of the art to achieve a sufficient flame retardance for glass fabric based laminates of the FR-4 class. With the commencement of the directive 2002/95/EG [3] the use of these well proven flame retardants will be prohibited from July 2006 on. From then there is a need to find an alternative, halogen-free flame retardant system which meets the demanding technical requirements for laminates.

2. Flame retardants for epoxy resins

Flame retardants for epoxy resins, especially laminates, should be halogen free, non-volatile, not hygroscopic, harmless and should show excellent thermal stability. The thermal stability of the resin under load must not be affected as well. The processing technology should be the same as is used for conventional TBBA-based resin which is crosslinked with dicyandiamide.

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Reactive flame retardants usually come close to these requirements. Aromatic structures impart sufficient thermal stability and together with a high functionality high glass transition temperatures can be achieved.

3. Aminophenyl phosphate

Aminophenyl phosphates are compounds, which come close to these requirements. They have been described already [4]. In practice it was shown that aminophenyl phosphates, which have been the basis of the patent application, had an insufficient functionality to meet the requirements. These products, which correspond approximately to bis-(3-aminophenyl)-phenyl phosphate, could not impart a sufficient crosslinking density and flame retardance. With synthesis methods which yield products, which correspond approximately to tris-(3-aminophenyl)-phosphate (TAPP), or contain a high amount of this compound, flame retardants have become available, which meet all requirements.

4. Synthesis of TAPP

The synthesis of TAPP is based on a transesterification of triphenyl phosphate with 3-aminophenol. The reaction yields incomplete replacement of the bound phenol by the 3-aminophenol. Beside the main product TAPP bis-(3-aminophenyl)-phenyl phosphate, traces of 3-aminophenyldiphenyl phosphate and oligo-3-aminophenyl phosphates are obtained. However, the product is nearly free of triphenyl phosphate, phenol and 3-aminophenol.

The by-products are as effective as TAPP concerning flame retardance and react with the epoxy resin in the same way. They marginally decrease the functionality of the pure TAPP.

5. Properties of TAPP

The reaction product TAPP is a white to brownish-beige solid. The following data have been measured for a product which contains 81.3% pure TAPP:

Melting point (°C): 154
Thermal stability, DSC in air (°C): 345
Thermal stability, DSC in N_2 (°C): 374
5% Weight loss, TGA (°C): 360
10% Weight loss, TGA (°C): 365

The product is insoluble in water. It is soluble, or fairly soluble in a variety of organic solvents according the following order: DMF > acetone > methyl ethyl ketone > methanol > toluene.

The following data are for the pure TAPP:

Molecular weight: 371
Phosphorus content (%): 8.3
Nitrogen content (%): 10.7

Both, the high phosphorus and nitrogen content have an synergistic impact on the flame retardant effect.

6. Processing of TAPP

Flame retardant epoxy resin based on TAPP can be processed in the same way as flame retardant epoxy resin based on TBBA, crosslinked with dicyandiamide. If TAPP is used as a reactive flame retardant then no additional curing agent is necessary. A typical formulation is shown in Table 1.

For better processing the epoxy resin is diluted with methyl ethyl ketone. TAPP, catalyst and, if required, further additives are dissolved or dispersed in the resin solution. For curing the formulation is put into an oven at 160 °C for 2 h. The glass transition temperature of this resin is 154 °C. The B-stage [5] is reached after about 210 s at 160 °C. The B-stage is an intermediate stage in the reaction of thermosetting resins in which the material swells when in contact with solvents and softens when heated, but may not entirely dissolve or fuse. The time to reach the B-stage gives an idea about the reactivity and processability of a resin formulation.

The DSC plots of the curing reactions of dicyandiamide and TAPP show rapid reaction beginning at about 100 °C with a peak at 140 °C for dicyandiamide. The reaction of TAPP is more moderate. It starts at about 120 °C and reaches a peak at 190 °C.

7. Combinations of TAPP with dicyandiamide and non-reactive phosphates

TAPP can be combined with other curing agents like dicyandiamide or 4,4-diamino diphenyl sulfone (DDS) without any problems. An addition of non-reactive

Table 1
Epoxy resin formulation based on TAPP (81.3% tris-(3-aminophenyl)-phosphate)

Components	Parts by weight
Epoxy resin (epoxy novolak, e.g. Ruetapox 0300)	100.0
Solvent (methyl ethyl ketone)	25.0
Catalyst (methyl imidazol)	0.2
TAPP (=crosslinker and flame retardant)	35.0

Table 2
Epoxy resin formulations based on TAPP (40% tris-(3-aminophenyl)-phosphate)

Component	Formulations											
	Dicyandiamid curing				TAPP curing				Combined curing			
	1	2	3	4	5	6	7	8	9	10	11	12
Epoxy novolak	100	100	100	100	100	100	100	100	100	100	100	100
Methyl ethyl ketone	25	25	25	25	25	25	25	25	25	25	25	25
Methyl imidazol (catalyst)	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Dicyandiamide	1.5	1.5	1.5	1.5					0.8	0.8	0.8	0.8
TAPP					50	50	50	50	25	25	25	25
XDP		10				10				10		
BDP			10				10				10	
DPK				10				10				10
Properties												
N-content, calculated (%)	1.2	1.1	1.1	1.1	2.8	2.6	2.6	2.6	2.2	2.0	2.0	2.0
P-content, calculated (%)	0	0.8	0.8	0.8	2.9	3.2	3.2	3.2	1.7	2.2	2.2	2.2
T_G (°C)	146	64	76	71	155	140	141	133	157	138	145	132
Weight loss, 300 °C (%)	3.2	2.6	5.7	3.4	3.1	3.2	2.8	5.0	3.6	3.3	3.4	4.0

phosphate flame retardants like resorcinol-bis-(dixylenyl phosphate) (XDP), bisphenol-A-bis-(diphenyl phosphate) (BDP) or diphenyl cresyl phosphate (DPK) is also possible. Surprisingly, the plasticising effect of these phosphate flame retardants is clearly weaker in a TAPP-based epoxy resin formulation compared to a formulation which has been crosslinked with dicyandiamide. The above-mentioned formulations and their properties (Table 2) are based on a TAPP product with the following composition:

Tris-(3-aminophenyl)-phosphate: 40%
Bis-(3-aminophenyl)-phenyl phosphate: 40%
3-Aminophenyldiphenyl phosphate: 11%
Oligo-3-aminophenyl phosphates and rest: 9%

By TAPP-based crosslinking high phosphorus and nitrogen contents of the resin can be achieved (formulations 5–8). A minimum concentration of 3% phosphorus in the epoxy resin is often postulated to impart sufficient flame retardance. Nitrogen is a synergist, which can improve the flame retardant effect of phosphorus compounds.

The glass transition temperature of a TAPP-crosslinked resin (formulation 5) is significantly higher compared to a dicyandiamide-crosslinked resin (formulation 1). Of special interest are the TAPP-based formulations which contain additionally a non-reactive phosphate flame retardant (formulations 6–8). The glass transition temperatures of these formulations remain high. The same phosphate flame retardants added to dicyandiamide-crosslinked resin (formulations 2–4), decrease the glass transition temperatures dramatically.

A high glass transition temperature can be achieved also by a combination of TAPP- and dicyandiamide-crosslinking (formulation 9). The plasticising effect of additive phosphate flame retardants is much weaker in a TAPP- and dicyandiamide-crosslinked resin (formulations 10–12) compared to a dicyandiamide-crosslinked resin (formulations 2–4).

All formulations can be crosslinked without any problems and show only little amounts of volatilities measured by TGA at 300 °C which marks the resins as thermal stable materials.

8. Properties of TAPP-based epoxy laminates

With the formulation of Table 1 a multi-layer laminate based on eight glass fabric prepregs with a thickness of 1.6 mm was made. The laminate meets easily class V-1 according to the vertical UL 94 fire test. Pressure cooker and soldering bath test can be passed without any damage. For these tests the laminates are exposed first to a saturated steam atmosphere at 116 °C for 20 min. Immediately after this treatment the laminates are dipped in a 280 °C hot soldering bath for 6 s. There have been no delaminations, bubbles or any other damage to the material.

9. Conclusion and outlook

Currently very expensive alternatives for TBBA in printed circuit boards are being introduced. They often do not meet the mechanical, electrical or economic requirements. TAPP is an alternative which shows promising results concerning mechanical properties, processability, thermal stability and flame retardance.

Especially the high glass transition temperatures and the possibility to combine TAPP with standard curing agents and additive phosphate flame retardants, which show in these combinations an excellent performance level, designate TAPP as an interesting flame retardant for epoxy resins.

Work is still in progress on an economic synthesis which yields the highest possible amount of pure tris-(3-aminophenyl)-phosphate. A high functionality generates high crosslinking density and glass transition temperature. Thereby the flame retardant effect is improved as well.

References

[1] Kunststoffe. 91 (2001) 10, S. 352.
[2] Becker GW, Braun D. Kunststoff-Handbuch, Bd. 10, S. 437. Carl Hanser Verlag München Wien; 1988.
[3] Official Journal of the European Union, L 37/19; 2003.
[4] DE-A-44 00 441, 1997.
[5] DIN 16916-02-C1, 1987.