

GREEN CHEMISTRY FOR PROTECTION OF HIGH TEMPERATURE (> 250°C) ELECTRONICS

Jochen Schuermans*

*ROARTIS BVBA, Genk, Belgium

Jochen.schuermans@roartis.com

Abstract— A new modified “green” thermoset resin was developed and evaluated as an alternative encapsulation packaging material in comparison to traditional higher temperature resistant resins such as epoxies, silicones, cyanate esters and polyimide resins. Where epoxies and silicones have shown to provide good reliability for applications up to 150 – 200°C, high temperature applications, often required other chemistries, such as cyanate ester or polyimides. However, cyanate ester and/or polyimide based resins have recently been affected by new European environmental legislation making their usability, and especially environmental and health acceptance, not viable for the medium and long term. In combination to these environmental concerns, the current significant growth of the market for high power and high temperature electronics, also in more “consumer-type” applications, imply the need for “green” chemistry, capable to respond to high temperature (> 250°C) requirements. This paper will describe new materials, based on hybrid chemistry, in line with current European chemical (SVHC-compliant) regulations, responding to the current and future harsh environment requirements. DSC analysis was done to demonstrate the newly developed green chemistry provides Tg values well over 250°C. The combination of a hybrid chemistry with optimized adhesion properties, high Tg and low coefficient of thermal expansion seem to provide mechanical features which can address the problem of mechanical fatigue of traditional epoxy solutions, which did historically not provide the solutions which often, non-environmental friendly solutions, based on poly-imides or cyanate esters could offer.

Keywords: >250°C electronics, encapsulation, nonylphenol-free, MHHPA-free, NMP-free, green chemistry, thermoset polymer resin,

Introduction

Encapsulation materials or underfill resins often form one of the final protection of electronic packages such as CSP's or BGA's on printed circuit boards. These protective resins are applied to protect the components from moisture, heat and environmental stresses such as thermal cycling mismatch.

For many decades, epoxy resins have been the mainstream solution for applications, where temperature resistance was required up to 150°C. For lower temperature applications, polyurethanes were also a viable alternative, where for temperatures up to 200°C or even 250°C silicone chemistry was used in general.

For applications exceeding 250°C, materials based on cyanate esters [1] or polyimides [2] were most often selected. To make these high temperature materials effective and/or applicable in liquid format, as well to realize thermoset properties, certain

additives are required, which are subject to the European SVHC list [3].

Ingredients such as nonylphenol (CAS 25154-52-3), hexahydromethylphthalic anhydride (CAS 25550-51-0) and/or 1-methyl-2-pyrrolidone (CAS 872-50-4), have been known as ingredients with CMR (carcinogenic, mutagenic, reprotoxic) properties, and hence identified for many years as subject for concern with regards to human health and environmental impact.

Applications in which such high temperature encapsulation technologies are required, include power electronics (f.e. IGBT's), terrestrial or deep-subsea oil-drilling applications, geothermal sensing, as well as space and defense electronics.

Results

Historically, cyanate ester, as well as polyimide based solutions appeared to provide the best technical fit, based on an optimum balance of high Tg, low CTE, low shrinkage and sufficient mechanical strength both at room temperature, as well as elevated temperature.

In this paper, a novel hybrid thermoset resin (HTR) chemistry is investigated, combining high temperature resistance (Tg > 250°C), low CTE (< 22 ppm/°K), and good mechanical strength (> 20 MPa)

Comparison between epoxy, silicone, cyanate ester, polyimide and HTR

Property	Epoxy	Silicone	Cyanate Ester	Polyimide	HTR
Thermal stability	150°C	220°C	300°C	400°C	300°C
Hardness	70 – 85 D	10 – 70 A	90 – 95 D	90 – 95 D	85 – 90 D
Tg	90 – 170°C	-55 - - 35°C	250 - 280°C	300 – 340°C	230 - 250°C

Test measurements to assess HTR resin in terms of mechanical properties, such as hardness and Tg, were determined by means of calibrated durometer and calibrated DSC (differential scanning calorimetry). Benchmark properties of epoxy, silicone and cyanate ester materials were evaluated by the same method,

whereas certain properties from polyimide materials were deducted from literature.

Figure 1 provides a comparison graph of various resins, analyzed by differential scanning calorimetry, indicating different glass transition temperatures (Tg's) for various type of epoxy and/or modified/hybrid resins.

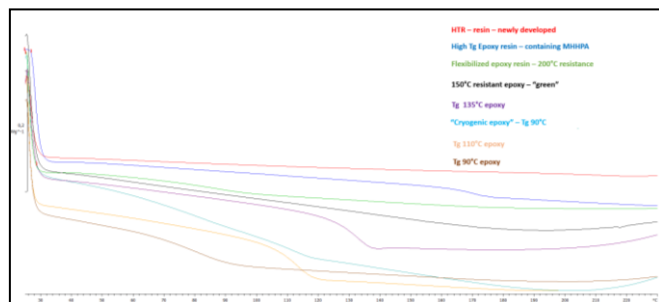


Figure 1: Tg comparison of various resins by Differential Scanning Calorimetry (DSC)

From figure 1 it can be seen that within the family of epoxy resins, a wide variety on glass transition temperatures can be realized. In the broader market, it's known that typically, most epoxy resins, are capable to withstand 150°C continuous operation temperatures, where certain specialty types, referenced in figure 1 as "High Tg epoxy resin", are capable to resist 175°C continuously.

Disadvantage of these grades however, is their use of MHPA as sole or combined curing agent, required, to achieve high Tg properties.

Also cyanate esters have known to achieve high Tg values, but typically require nonylphenol as co-curing additive. Lastly, polyimide materials, at least for liquid encapsulation processes, require specific solvent use to transfer them from a solid state into a liquid solution. In most cases, the solvent used contains NMP (i.e. 1-methyl-2-pyrrolidone).

As mentioned before, Europe's REACH regulation No. 1907/2006, as well as the following amendments 2019/1691 include a list of "Substances of Very High Concern" (SVHC), which provides an overview of ingredients which are expected to be banned from usage in the near future. This list contains the ingredients MHPA, Nonylphenol, as well as NMP, as mentioned above.

The HTR-resin, also referenced in figure 1, shows to provide a Tg value well above 230°C. For that reason, a DSC was performed up to 300°C, to have a more detailed determination of the glass transition temperature for the HTR-resin. The result is shown in Figure 2. The DSC analysis shows that the Tg value is about 268°C for this type of resin.

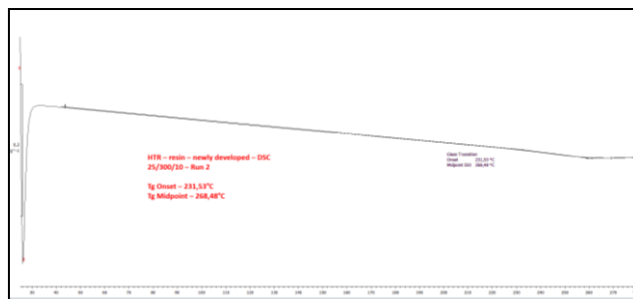


Figure 2: Tg determination HTR resin by Differential Scanning Calorimetry (25/300/10 - Run 2)

Important to note is the fact that the HTR resin is liquid at room temperature, and hence easily processable. Literature on other developments of high temperature resins [4], indicate that often such high temperature resins are only available in powder form, and hence are only applicable by special high temperature molding processes and/or special dispensing and processing equipment assuring high temperature dispensing, and in-application flowability. Although not impossible, these processing requirements bring significant additional process challenges for which these technologies are not readily adopted in often small to medium sized, high reliability electronic applications.

Adhesion tests were performed with different materials by means of dummy silicon dies (dimensions: 1 x 1 mm²) on glass substrates at room temperature, and measured with a 2 Kgf-gauge, as well as after pressure cooker testing (100°C – 2 bar – 2 weeks)

Property	Epoxy	Silicone	Cyanate Ester	Polyimide	HTR
Adhesion after cure (MPa)	>20	1	>20	6,6	>20
Adhesion after 2wks-100°C-2 bar	5,6	0	18,3	6,5	15,6

Table 1: Adhesion results of various resins at T0 and after 2 wks pressure cooker testing 100°C/2 bar

Although for many encapsulation applications, adhesion strength is not the main concern, evidenced by the broad use of low adhesion silicone chemistry in f.e. IGBT modules, it's becoming more and more relevant for applications where long term reliability is required, in combination with open, non-hermetic closed, devices. As an example, encapsulation of next generation IGBT modules, as well as local encapsulation such as underfill or edgefill solutions, require long term robust adhesion performance.

The results in table 1 show that especially moisture testing at elevated temperature, in combination with pressure is a harsh test with dramatic impact on certain chemistries. Where epoxy and silicone chemistry have a very significant decrease in adhesion strength when exposed to pressure-cooker testing, cyanate esters and polyimides seem to have much better

resistance, which is also documented in previous studies [5]. The newly developed HTR-resin, also provides good moisture resistance, although somewhat more in comparison to cyanate ester and polyimides.

Conclusions:

This work highlights the use of a newly developed “green” HTR thermoset resin for high temperature encapsulation applications, suitable for microelectronic packaging, and eliminating the use of certain hazardous substances, no longer allowed to be used in the near to longer term future with regards the European REACH regulation, and specifically the list of “Substances of Very High Concern”.

HTR-resin has been tested to last beyond temperatures of 250°C continuously and at elevated moisture and pressure testing.

Therefore, this chemistry seems to be a viable option for current and future high temperature electronic applications, such as power electronics, adverse environment drilling and sensing applications, electric vehicle electronics, etc.

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