HIGH TEMPERATURE AND FLAME RETARDANT CYANATE ESTER RESINS FOR AEROSPACE APPLICATIONS

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ABSTRACT

Currently, there is considerable pressure on aerospace manufacturers to build more and more technologically advanced aircraft with lower weight at reasonable costs while maintaining the highest standards of safety. Future requirements to improve structural performance, high-temperature capability and durability can be achieved by the next generation of high temperature resistant, polymer based composites.

Lonza Primaset™ cyanate esters (CE) are high temperature resistant thermoset resins with glass transition temperatures up to 400 °C and comparable processability to epoxy resin systems. Cyanate esters and other high T_g resins, while possessing high strength, can be brittle due to their highly crosslinked structure. Lonza offers toughened systems of cyanate esters which provide greatly improved toughness without sacrificing strength. All cyanate esters exhibit low dielectric values at elevated frequencies as well as low moisture absorption.

There is a large increase of polymeric material in aerospace applications. Recently FAA set new safety standards for flame, heat release and smoke generation in the areas of aircraft interiors (ref. 1). Cyanate ester thermoset resins alone or combined with epoxy resins can effectively meet these challenges. They can show improved surface finish, superior mechanical strength, and comparable or superior heat release rate compared to the phenolic resins currently used. A new phosphorus-containing cyanate ester has been developed, which acts as flame retardant, achieves UL94V-0 results when combined with epoxy resins and cyanate esters.

KEYWORD: cyanate ester, high temperature, aerospace resins, flame retardant, composites.

SUMMARY

Nowadays the constant needs for materials with higher temperature resistance and flame retardancy frequently reveal the limits of traditional resin materials such as vinyl esters, polyurethanes, epoxy and phenolic resins which are well-known and established in the marketplace. Cyanate ester thermoset resins alone or combined with epoxy resins can effectively meet these challenges.

1. INTRODUCTION

In the last decades composite materials have been increasingly applied in commercial aircraft, replacing aluminium in different primary and secondary structures in order to reach desired levels of cost efficiency, performance and light-weighting. In commercial aircraft the current state-of-the-art in lightweight structures is demonstrated by the Boeing 787, which makes widespread use of structural composites and even has a fully-composite fuselage. In military aircraft, helicopters and generally in aviation the use of whole airframes and support structures has already been successfully adopted (ref. 2).

Composite materials should be designed to withstand extreme environments such as high and low service temperatures, fire, corrosive and extreme loadings. Each of these conditions can affect the durability of a composite, but the combination of more than one can have dramatic effects. There are also considerable concerns regarding fire safety due to the flammable nature of the organic matrix in a composite material.

1.1 Cyanate esters

Cyanate esters (CE) provide attractive physical, electrical, thermal and processing properties and have been commercialized since the late 1970s. Different grades of CE are available as liquid, semisolid or high melting point solid and they present a good solubility using low boiling point solvents such as acetone, MEK and dichloromethane. The curing process can be performed with and without the use of a catalyst. Cure catalysts such as carboxylate and chelate complexes of transition metal ions are used. For example for Primaset™ PT resins a relatively long cure cycle at a high cure temperature close to the DSC exotherm and followed by a post-cure are suggested in order to achieve high glass transition T_g value. One potential effect to take in consideration during cure of CE is the relatively high exothermic heat of reaction. However, the exothermic temperature rise can be controlled by adjusting the catalyst concentration or setting an appropriate curing cycle. The outstanding glass transition temperature properties of Lonza Primaset™ CE is in the range of 260 °C up to 400 °C, which clearly exceeds the well-known Novolac aerospace epoxy resins with a maximum glass transition temperature of 250 °C. The CE monomers and prepolymers exhibit a very low total volatile content upon curing, e.g. a Primaset™ PT resin produces a maximum volatile content of 0.5% (ref. 3). This feature is important in vacuum-assisted processing.

Also CE exhibit handling properties similar to epoxy or polyurethane. This processing ability allowed adopting these resins in composite processing methods such as prepregs, resin transfer moulding, filament winding, pultrusion and compression molding (ref. 4).

Furthermore, all CE are likewise attractive in terms of flammability properties. Primaset™ PT-30 resin, for example, is a fire resistant and high char yield thermoset (≈65% char yield) with high decomposition temperature, a very good toxicity profile and lower peak heat release with respect to phenolic resin. This resin offers a considerable potential as replacement for phenol formaldehyde systems in aircraft cabin and high speed train interiors (ref. 5). Recently a new phosphorus containing CE flame retardant has been developed, Primaset™ FR-300, which has the advantage to be halogen free and can achieve a UL94V-0 rating when combined with epoxy resins and/or conventional cyanate esters.

The mechanical properties of CE resins are in between epoxies and bismaleimides (BMI) resin systems. While possessing high strength, they can be brittle due to their highly crosslinked structure. Lonza offers toughened systems of cyanate esters which provide greatly improved toughness without sacrificing strength. Examples of toughened Primaset™ systems are Primaset™ BA-3000, PTC-2500 and DT-7000.

There is a wide range of current and possible future applications for cyanate esters, which are described below. Cyanate esters have been used in composite satellite antennae and missile components for aircraft products from Boeing, Raytheon, Sunstrand and others. For example, in missile applications, the current material temperature resistance requirements range from 260 °C to 371 °C – which are expected to become even more stringent for the development of the next material generation.

Typically cyanate esters exhibit rather low moisture absorption when compared to BMI and commercial epoxy resins. For example, the methylated commercial monomer Primaset™ METHYLCy was found to retain 83% of its flexural modulus at 150 °C after immersion in boiling water. This compares with only 53% for a commercial multifunctional aerospace epoxy, giving this cyanate ester a distinct advantage in advanced structural composite matrices (ref. 6).

2. EXPERIMENTAL

2.1 Sample Preparation

The specimens were prepared using a new development casting molding, which allows obtaining excellent surface finish. The plate dimensions were 150 × 100 mm^2 with 1.67 mm thickness. Release All® 45 from Airtech was used as release agent and was applied in the mold the night before the curing process. Four types of formulation were made: a. Primaset™ PT-30 pure resin for DMA testing, b. Formulations containing Primaset™ FR-300 flame retardant in epoxies (MY0510 and Epikote™ 828) for UL-94V Flammability test, c. Formulations containing Primaset™ FR-300 flame retardant in Primaset™ PT-15 for UL-94V Flammability test, d. Formulation containing the commercial hardener 4,4'-diaminodiphenylsulfone (DDS) in Epoxies (MY0510 and Epikote™ 828) for UL-94V Flammability test. All the compounds were mixed at 120 °C for about 60 minutes except the one containing DDS, which was mixed at 130 °C for 60 minutes, maintaining the temperature constant until complete homogenization was reached. Then the mixtures were poured in the casting mold and degassed to remove air bubbles using a vacuum oven at a temperature of 120 °C between 30 up to 60 minutes. Afterwards the specimens were inserted in the oven where the following cure cycles have been applied depending on the mixture:

- For cyanate esters and blends thereof: 1 h @ 150 °C + 3 h @ 200 °C + 1 h @ 260 °C

- For epoxy/amine blends: 4 h @ 130 °C + 4 h @ 160 °C + 4 h @ 190 °C

The temperature settings had been controlled with a thermocouple inside the sample material to make sure the specimen had the correct temperature; all indicated temperatures represent mass temperatures.

After curing the plates were cut out with strips of 35 × 13 mm^2 with 1.67 mm thickness in order to perform a DMA test in bending mode and five specimens of 125 × 13 mm^2 with 1.67 mm thickness for the UL94V test.

2.2 Dynamic mechanical analysis (DMA) Set-up

A DMA (Q800, TA Instrument) was used with a single cantilever probe. Samples were heated from 30 to 450 °C in an air atmosphere, while applying 20 µm deformation at varying frequencies of 0.1, 1 and 10 Hz.

2.3 Fire Tests

For distinguishing the flammability and burning behavior of flame retarded specimens the Underwriter Laboratories' UL 94 (Standard for tests for flammability of plastic materials for parts in devices and appliances) has been used as a comparative assessment. The procedure consists of subjecting a set of five specimens of identical composition and geometry to a standard test flame for two 10 s flame applications.

Table 1: Material Classifications of Burning Characteristics of Solid Plastics in Vertical Position.

Criteria Conditions	V-0	V-1	V-2
After-flame time for each individual specimen, t_1 or t_2	≤ 10 s	≤ 30 s	≤ 30 s
Total after-flame time for any condition ($t_1 + t_2$ for the five specimens)	≤ 50 s	≤ 250 s	≤ 250 s
After-flame plus afterglow time for each individual specimen after the second time flame application ($t_2 + t_3$)	≤ 30 s	≤ 60 s	≤ 60 s
After-flame of any specimen up to the holding clamp	No	No	No
Cotton indicator ignited by flaming drops	No	Yes	Yes

The after-flame is recorded after the first flame application, and the after-flame and afterglow times are recorded after the second flame application. Information is also recorded on whether or not flaming material drips from the specimen and total flame time for a particular specimen set. The burner was positioned to an angle to 45° towards the wide side of the specimen and a blue flame was adjusted to be 20 ± 2 mm high. The formulated specimens are evaluated following the classification system shown in Table 1.

3. RESULTS AND DISCUSSION

3.1 Primaset™ PT-30 DMA

Primaset™ PT-30 was analyzed by Dynamic mechanical analysis (DMA) at the conditions mentioned in Section 2.2. As the material is heated, the storage modulus (E') decreased step-wise by several orders of magnitude (Figure 1); this large change means that the glass transition can be measured with great sensitivity. The loss modulus (E'') is usually associated with the viscosity or toughness of the material. The ratio of the loss to the storage modulus is the tan delta and it is often called damping. It is a measure of the energy dissipation of a material (ref. 7).

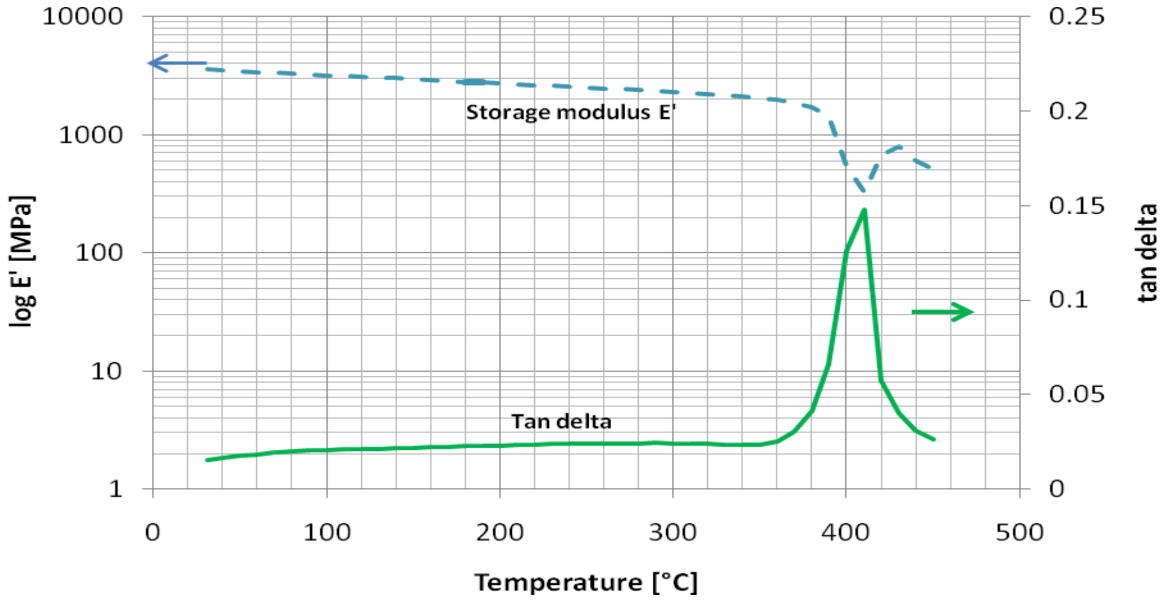


Figure 1: Storage Modulus E' and damping by DMA (single cantilever, 10 Hz, 10 K/min under air) for Primaset™ PT-30.

The relaxation processes are frequency dependent and it can be observed that the glass transition shifts from 379 °C up 384 °C varying the frequency from 0.1 to 1 Hz considering the onset of decreased E' modulus. The T_g evaluated by the damping behavior is about 400 °C. The E' storage modulus was measured at 30 °C and a value between 3.40 and 3.57 GPa was assessed depending on the frequency rates. The technical data are listed in Table 2.

Table 2: T_g and storage modulus E' of Primaset™ PT-30 by dynamic mechanical analysis at various frequencies.

Frequency	0.1 Hz	1 Hz	10 Hz
T_g evaluated at onset of decreased modulus (E'), [°C]	379	384	385
T_g evaluated at peak value tan delta, [°C]	400	400	401
Storage Modulus (E') at 30 °C , [GPa]	3.40	3.49	3.57

3.2 Flammability Behavior of Primaset FR-300.

A flame retardant test was carried out according to the UL94V testing procedures. The flammability behaviors of various blends using a CE flame retardant Primaset™ FR-300 were studied and the UL-94V results are summarized in the figures below. Two types of epoxies (Huntsman MY0510 and Hexion Epikote™ 828) were compared to Primaset™ FR-300 as shown in Figure 2 and 3. Superior performance of Primaset™ FR-300 could be observed when added to the multifunctional epoxy resin MY0510 (which is one of the most commonly used epoxies in aerospace applications) compared to the bisphenol A based epoxy Epikote™ 828.

To achieve a UL94-V1 classification, 20% in weight of Primaset™ FR-300 is sufficient in the epoxy MY0510 and 30% in weight of Primaset™ FR-300 is instead needed for Epikote 828 to obtain the same rating. To qualify for the superior classification UL94-V-0, 25% of Primaset™ FR-300 is necessary in the MY0510. In additional trials the performance of Primaset™ FR-300 was assessed when being added to an unmodified cyanate ester PT resin. In this case only 10% in weight of FR-300 is needed to achieve the UL94V-0 as shown in Figure 4.

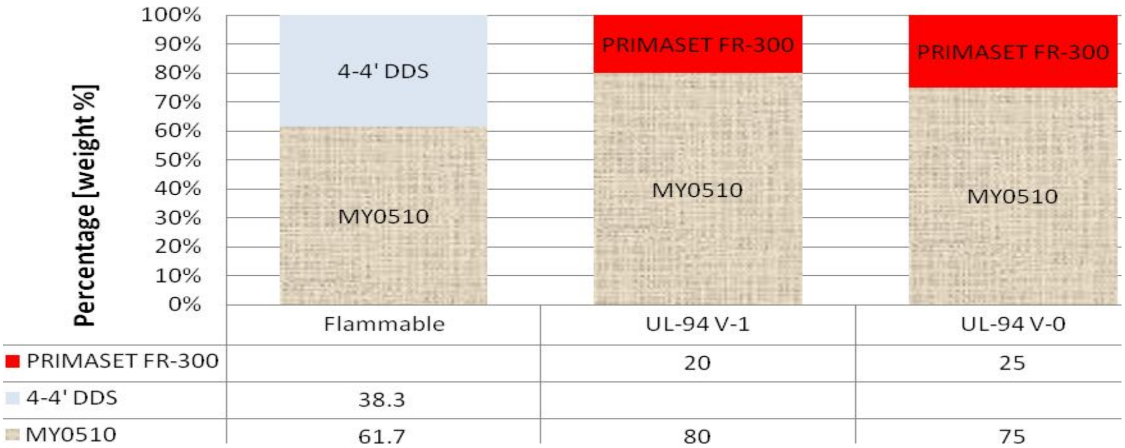


Figure 2: UL-94V flammability results for MY0510-Primaset™/FR-300 and MY0510/DDS mixtures.

As described in Table 1, for each set of five specimens, the total combustion time must not exceed 50 seconds (UL-94V-0) or 250 seconds (UL-94V-1 and UL-94V-2) respectively. No dripping of flame particle must fall from the specimen during the test (UL-94V-0 and UL-94 V-1). The materials tested adding Primaset™ FR-300 showed no dripping of flame over the cotton. The total combustion time was 50 seconds for the MY0510 containing 25% FR-300 and for MY0510 with 20% FR-300 only was 70 seconds instead. In case of the formulation with Epikote™ 828 containing 30% FR-300, the total flame time was 173 seconds. Finally for the formulation of Primaset™ PT-15 containing 10% of FR-300, the total flame time was 16 seconds.

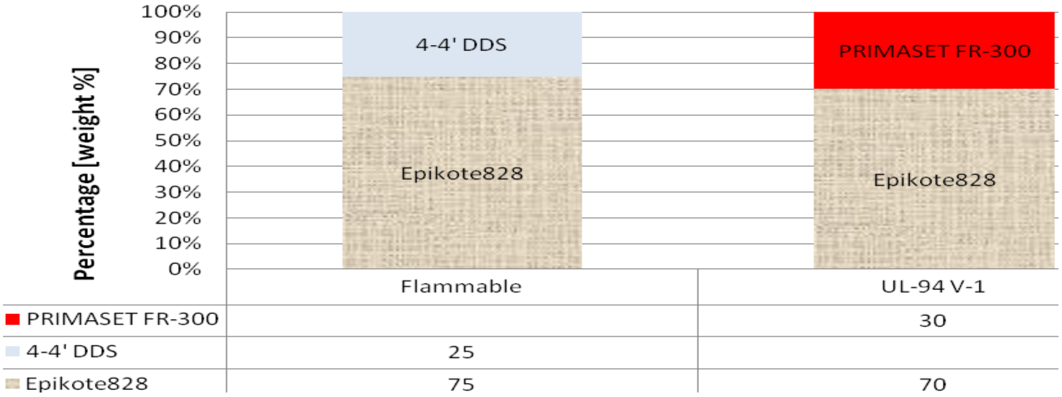
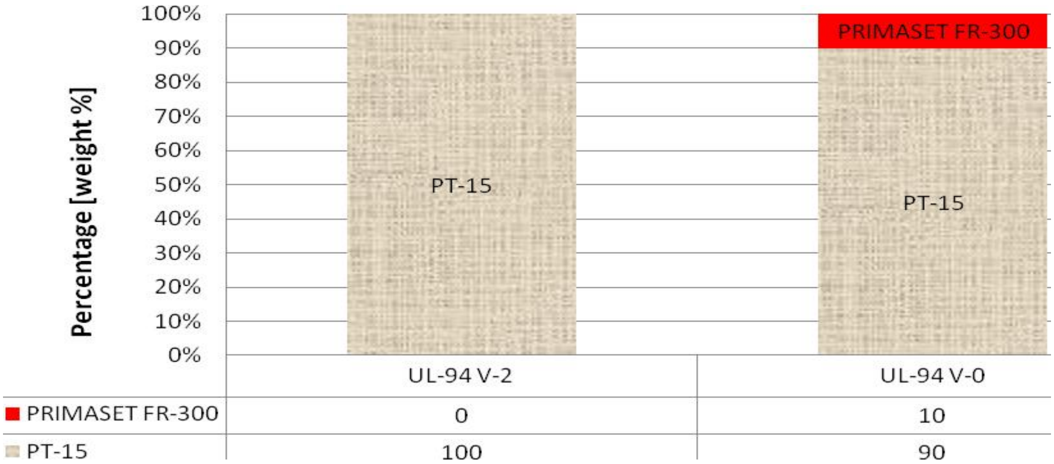


Figure 3: UL-94V flammability results for Epikote™ 828-Primaset™ FR-300 and Epikote-DDS mixtures.



	UL-94 V-2	UL-94 V-0
🟥 PRIMASET FR-300	0	10
▨ PT-15	100	90

Figure 4: UL-94V flammability results for Primaset™ PT-15/Primaset™ FR-300 and PT-15 formulations.

A comparison was carried out with two epoxies systems containing the hardener DDS (1:1 stoichiometric equivalent ratio to the epoxide). The equivalent ratio of the mixtures Epoxies-DDS is converted in weight percentage to compare with FR-300-Epoxies mixtures as indicated in Figures 2 and 3. These mixtures were classified highly flammable in the UL-94V flame test. Only one flame impingement could be applied as the fire did not cease and consequentially the material was completely consumed after the flame test. No char formation occurred.

The char yield was significant for all the formulations containing Primaset™ FR-300 which is due to the phosphorus content. The char formations at the polymer lower the flammability by acting as a barrier to inhibit gaseous product from diffusion to the flame and to protect the polymer surface from the heating flux. Also the crosslinking can increase the char formation and this is another feature of phosphorus-containing compounds. The incorporation of Primaset™ FR-300 resulted provided a UL94V-0 and UL94V-1 flame retardancy classification without the need for halogenated additives. As it is well-known halogenated compound are very effective flame retardant, however they present several disadvantages such as the potential to corrode metal components, and the toxicity of the halogen halide formed during burning which has been recently considered in some parts of the world (ref. 8)

4. CONCLUSIONS

Primaset™ cyanate ester resins present outstanding thermal properties with glass transition temperature in the range of 260 °C up to 400 °C. Cyanate esters are the material of choice, where high temperature resistance is a key performance for composite light weight constructions. It has been shown that composite materials requiring high temperature resistance and improved flame retardancy can be efficiently manufactured by the combination of traditional and modified cyanate esters such as Primaset™ FR-300.

An alternative for providing fire resistance to epoxy resins has been discussed: the flame retardancy of epoxy resins can be improved by the use of a modified cyanate esters, while reducing the undesired health concerns related to halogenated compounds as well as improving processing and final mechanical properties by substituting mineral based flame retardants.

Beyond the above mentioned property improvements cyanate esters and modified versions thereof are another step forward, where low moisture absorption, improved toughness and excellent dielectric properties of a composite are of importance.

5. ACKNOWLEDGEMENT

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