COMPOSITE MANUFACTURING TECHNOLOGIES FOR NOVEL HIGH TEMPERATURE COMPOSITES

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Abstract

For high temperature aerospace applications, commercially available polymer systems do not fulfil all requirements, especially in terms of toxicity (BMIs), hygrothermal stability (cyanateesters) and thermo-oxidative stability (epoxies). Therefore, a novel resin was prepared based on cyanateester and epoxy, which is toughened with a high performance thermoplastic. Several processing routes for manufacturing of composites with this novel resin are investigated, including liquid composite moulding (LCM) and prepregging. Especially for LCM, the incorporation of the thermoplastic toughening agent is a challenge, as well as the high surface tension of the cyanate ester component. A solution was found with the Resin Tranfer Moulding (RTM) process and the application of a thin non-woven interlayer in the carbon fibre preform. It seems that the resulting composites with the new cyanateester/epoxy resin present significant advantages over the corresponding base components in terms of mechanical properties at higher temperatures.

1. Introduction

In future helicopters the enhanced engine performance in combination with certain flight maneuvers may induce an increased thermal load to the polymer composite structures, such as the tail boom. In the frame of a research project together with Airbus Helicopters and DLR, several technologies are investigated to improve the structure’s thermal resistance, e.g. by investigations into other polymer based composites that show improved high temperature resistance, which is the topic of this paper.

The main requirements for a new composite material include long-term thermal stability at high temperatures, sufficient fracture toughness and it should not contain any components that are toxic, mutagenic, carcinogenic, or pose any other threat to human health. Investigations into commercially available prepreg and infusion material systems are addressed by the other partners, whereas Airbus Group Innovations focuses on tailor-made new formulations of commercially available components that fulfil the above-mentioned requirements.

A market screening showed that a combination of novolac-based cyanateester and naphthalene based high-temperature epoxy show great potential in terms of (hygro)thermal stability and processing for composite structures [1]. In addition, a phosphor-based hardener was found that provides the resin with good flame retardation, which is of additional benefit to the final application. As both cyanateester and epoxy resins are relatively brittle, a significant amount of toughening agent needs to be added, which in this case is a high-performance amorphous thermoplastic that can be dissolved in the resin mixture. Full characterisation of the resin showed that all major requirements are fulfilled [to be published elsewhere], and the next step is to produce carbon fibre reinforced composite laminates with this resin system, which will be the topic of this paper.

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2. Preliminary Processing Investigations

Both liquid composite moulding (LCM) and prepregging routes are pursued for manufacturing of carbon fibre reinforced composite monolithic structures with the novel resin system described above.
For LCM processes, the main challenge is the incorporation of the toughening agent, which, when dissolved, increases the viscosity of the resin dramatically. Handlaminating and resin film infusion with the resin including the dissolved thermoplastic toughening agent provided good-quality laminates, but the aim is a more industrialised process that enables process control. Vacuum assisted processing (VAP) was therefore tried: the toughening agent was applied as powder binder to the carbon fibres while the cyanateester/epoxy/hardener mixture was drawn inside the fibres by means of applied vacuum. Unfortunately, a large portion of the fibres remained dry due to the high surface tension of the cyanateester component.

To overcome this effect, a higher injection pressure is required and therefore resin transfer moulding was performed in the following trials. Again, it was decided to place the thermoplastic toughening agent in the dry carbon fibre preform instead of in the resin, to prevent filtering of the thermoplastic by the carbon fabric. This filtering effect is caused by the injection temperature, which was just around the dissolution temperature of the thermoplastic in the resin causing only partial dissolution of the thermoplastic particles. Higher injection temperatures would initiate curing of the resin leaving a very narrow process window. Also, the viscosity of the resin is lower without the thermoplastic toughener, leading to a faster and more controllable process and ensuring full impregnation of the fibres.

First RTM trials were performed with 10 g/m² thermoplastic powder binder (particle size 200-300 µm diameter) between every layer of carbon fibre fabric to produce laminates with 2 and 4 mm thickness. These trials resulted in laminates with some porosity and poor (matrix-dominated) mechanical properties. Further inspection revealed that the carbon fibres showed large undulations caused by the large thermoplastic particles, see Fig. 1. The large size of the particles prevented them from being completely dissolved before curing of the resin started. An experimental grade finer powder is available, but due to a significant shipment delay this could not be tested yet.

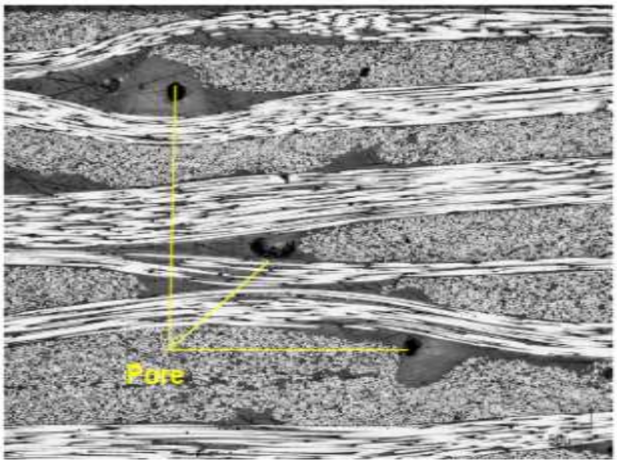

Figure 1. Micrograph of cross-section of CE/EP laminate manufactured by means of RTM and with thermoplastic powder as toughening interlayers.

Therefore, it was decided to investigate methods for incorporating the thermoplastic through different semi-finished products in the carbon fibre preform, either through a thin non-woven interlayer for the

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LCM route, or through the application of a fine thermoplastic powder to a thin UD reinforcement for prepregging.

For prepregging a high viscosity is desired, meaning that it could be beneficial to incorporate the thermoplastic in the resin for resin filming trials. However as earlier mentioned, the dissolution temperature of the thermoplastic (~135°C) lies close to the curing initiation temperature (~150°C), which leaves only a small processing time for resin filming and impregnation. Therefore, two types of trials will be performed; one with thermoplastic in the resin and one with the thermoplastic already placed on the reinforcing fibres. For the latter, a finer grained thermoplastic powder was used (~30-50 µm) to prevent large undulations of the UD prepreg tapes. The 200 mm wide carbon fibre spread tows were prepared using equipment at Airbus Group Innovations in Ottobrunn. The resin filming and prepreg impregnation trials will be performed at Neue Materialien Bayreuth GmbH later in 2016. Therefore, the focus of this paper lies on the results obtained with RTM, including mechanical testing, ageing and physical characterisation, which will be evaluated below.

2. Experimental

2.1. Materials

A novolac-based cyanateester (Lonza, CH) was mixed in a proprietary ratio with a naphthalene based high-temperature epoxy (DIC, J). DOPO-modified salicilic hardener (DIC, J) was used for curing the thermoset system. A polyetherimide (Ultem® 1000P, Sabic, US) powder with diameter 200-300 µm was used as toughening agent and binder. An experimental grade melt-spun non-woven veil with 8g/m² based on polyetherimide (PEI) was received from Kuraray (J). As reinforcement, a 5HS carbon fibre fabric was used (Hexply® G0939 from Hexcel, F). As reference matrix, Hexply® M18/1 resin film was used (Hexcel, F).

2.2. Specimen Preparation

The resin was prepared by mixing the cyanateester (CE), epoxy (EP) and the hardener (H) with a dissolver at 80°C. Afterwards, the resin was heated to 90°C and was degassed under vacuum. The carbon fibres were cut to dimensions 650 x 350 mm². 9 layers were used for a laminate of 2 mm thickness and 16 layers for a 4 mm thick laminate. The 2 mm laminate had a unidirectional lay-up, whereas the 4 mm laminate was quasi-isotropic. The veils were placed in between every layer and on top and bottom of the dry carbon fibre stack.

The carbon fibre preforms were placed in a tool for RTM, which was in turn placed in a hot press set to 125°C. The injection went from the outside towards the centre of the preform where the vacuum connection was placed. The processing parameters were as follows: the injection pressure was 5bars while the resin was heated to 120°C. For the 2mm and 4mm laminates an injection time of 2, and 5 minutes, respectively, was required. The laminates were cured by heating the press to 150°C with 2K/min, dwell for 1.5hrs, heating to 175°C with 2K/min and leave it to cure for another 3hrs before cooling to room temperature. The laminates were exposed to a free-standing post-cure in an air-circulating oven at 250°C for 2.5hrs.

The resulting laminates were scanned for their inner quality by means of C-scanning and when satisfactory, specimens according to test standards (see below) were cut out for testing by means of water-jet cutting. The specimens for ageing were placed in an air circulating oven at the prescribed temperature (see below).

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For the thermo-oxidation ageing tests, ILSS composite specimens were cut to size of 20 x 10 x 2 mm^3. In addition, reference composite specimens based on an epoxy matrix were cured according to the manufacturers' recommended cure cycle and prepared for comparison.

2.3. Test Set-Up

The tests that were performed on the composites are presented in Table 1.

Table 1. Test Matrix for composites.

Test	**Test Standard**	**Test Parameters**	**Specimen dimensions [l x w x t in mm^3]**	**Conditioning**
Physical chemical				
DMTA	DIN 65583	RT - Peak tanδ+50°C; 3K/min; 1Hz; 0.1% strain	50 x 10 x 2	Dry for 24 h at 80°C < 10mbar
DSC – degree of cure	AITM 3-0008	5K/min, RT - 400°C	15 g	Dry for 24 h at 80°C < 10mbar
Moisture absorption	EN2378	Distilled water 70°C, 14 days	ILSS specimens	Dry for 24 h at 80°C < 10mbar
Mechanical				
ILSS	DIN EN 2563	23°C; 50% rh	20 x 10 x 2	Dry for 24 h at 80°C < 10mbar
ILSS h/w	DIN EN 2563	h/w 75°C		Distilled water 70°C, 14 days
ILSS hot	DIN EN 2563	135°C, 160°C		Dry for 24 h at 80°C < 10mbar
ILSS very hot	DIN EN 2563	180°C, 200°C, 250°C		Dry for 24 h at 80°C < 10mbar
ILSS after ageing	DIN EN 2563	23°C; 50% rh		250°C; 10h, 100h, 200h, 500h, 1000h; 200°C; 10h, 100h, 500h, 1000h
Compression strength Celanese	DIN EN ISO 14126 A	23°C; 50% rh	100 x 10 x 2	
Compr. strength Celanese hot	DIN EN ISO 14126 A	135°C, 160°C		
Compr. strength Celanese very hot	DIN EN ISO 14126 A	180°C, 200°C, 250°C		
CAI	AITM 1-0010	23°C; 50% rh	150 x 100 x 4	30J impact

Interlaminar shear strength (ILSS) and compression tests were performed with Zwick universal testing machines for the testing temperatures RT to 135°C. Mechanical testing above those temperatures was performed by the University of Bayreuth. A Hilger USPC 3040 C-Scanning device with Hillgus® software was used to test the quality of the laminates for residual compression strength after impact (CAI) testing in a non-destructive manner. In addition, this equipment was used to assess the damage

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area after impact of the specimens. This impact was performed for the CAI tests using a Myrenne Impact tower with an impactor of 15.75mm diameter and 2.49kg weight. The tests were also conducted on a Zwick 1494 test (500kN) machine.

Dynamical mechanical thermal analysis (DMTA) was performed with an Advanced Rheometric Expansion System (ARES) from Rheometric Scientific. A TA Instruments DSC Q-2000 was used to determine the degree of cure. The mass loss after thermo-oxidation specimens was measured using a Sartorius scale after the specimens were allowed to cool down in a dessicator. Microscopy was performed using a Keyence VH-Z 100R.

4. Experimental Results

Below a micrograph of the 2mm laminates' cross-section is shown.

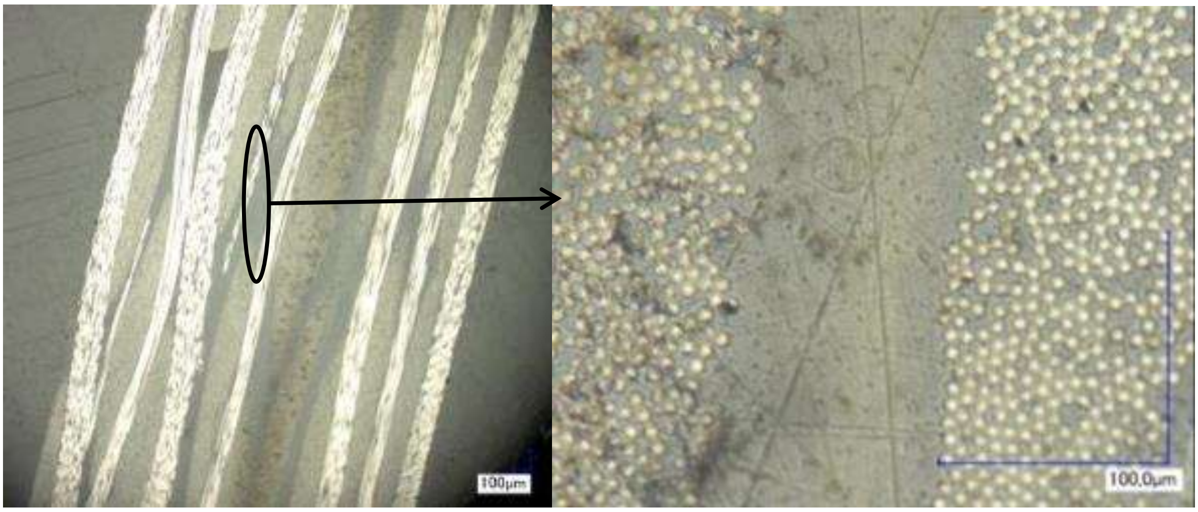

Figure 2. Micrographs of cross-section of carbon fibre reinforced CE/EP and thermoplastic veils as interlayer manufactured with RTM.

Fig. 2 shows that a high-quality laminate was obtained with no porosity nor significant undulations. The thermoplastic is clearly visible in the matrix after dissolution in the uncured resin followed by reaction-induced phase separation, which can be explained by the visible micelles structure.

4.1 Mechanical properties

The results from the ILSS tests are displayed in Fig. 3 where a comparison is made with a reference prepreg material (values taken from [2]. The CF reinforced CE/EP composite shows no significant decrease in ILSS compared to room temperature when tested at higher temperatures up to 135°C, nor when aged for prolonged times at 200°C. The significant decrease when aged at 250°C can be related to thermo-oxidative ageing, which will be discussed later. The hot/wet specimens tested at 135°C shows a decrease of ~20%. Compared to the reference epoxy-based composite, the ILSS values at room temperature and under regular hot/wet conditions are lower for the CE/EP based composite, but at higher temperatures, the CE/EP is superior. The same holds for the compression strength results, see Fig. 4.

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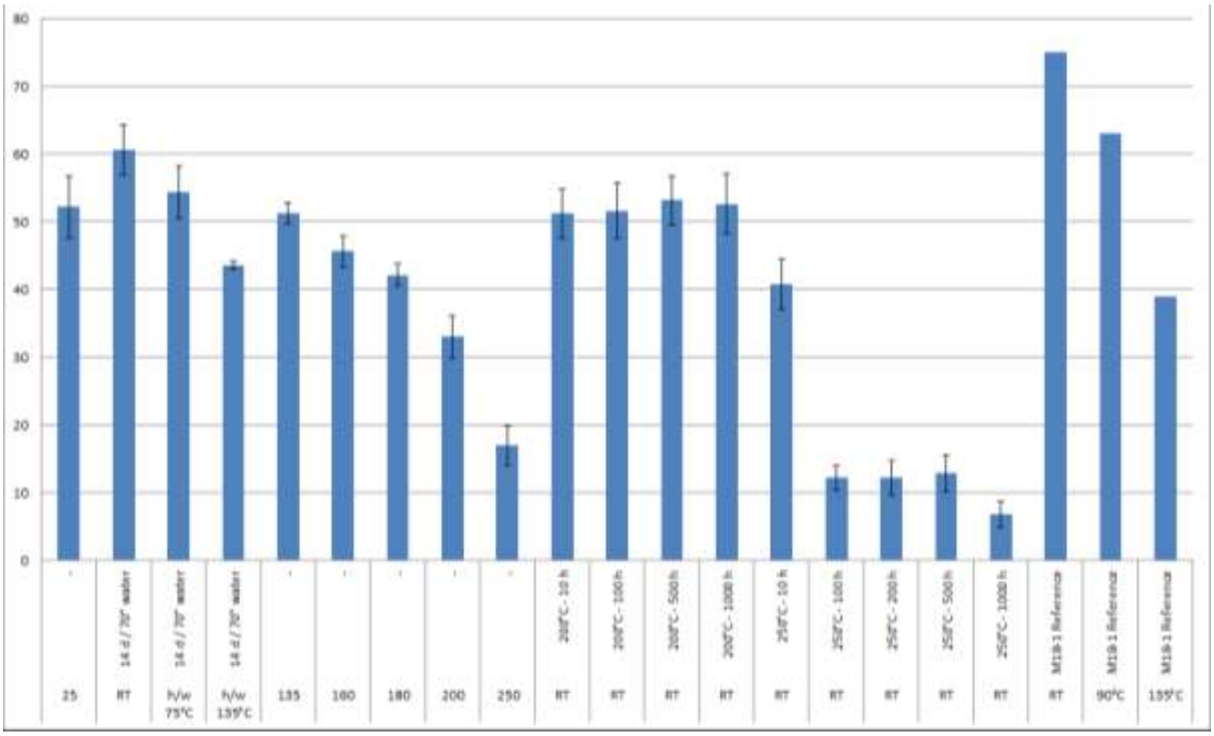

Figure 3. ILSS results for CE/EP composites and reference composite, values in MPa.

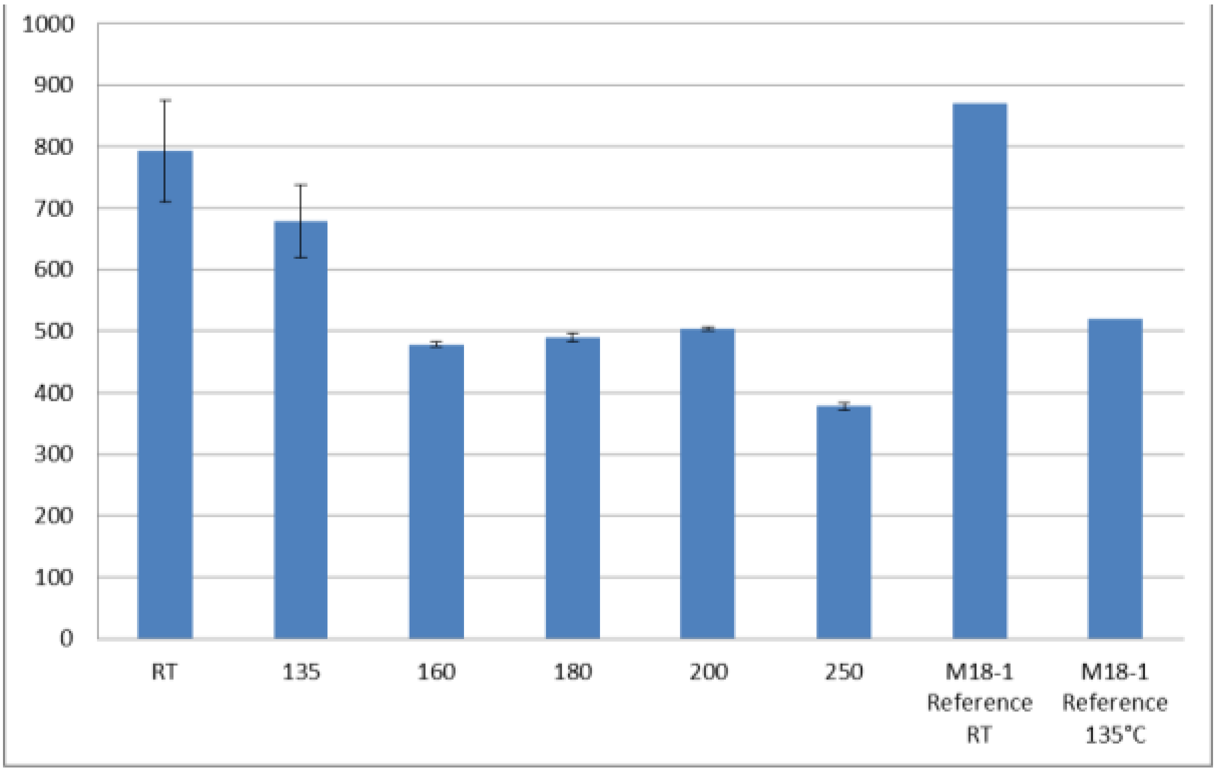

Figure 4. Compression strength (Celanese) of the CE/EP based composites (in MPa). Values for reference material were taken from [2].

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A slight decrease in compression strength (~5-6%) of the novel composite can be observed when tested at 135°C compared to room temperature, though this decrease is much less as for the reference material (~40%), even though the value at room temperature is a bit higher for the reference. At higher temperatures, the compressive strength seems to remain relatively constant up to 200°C. The same was found for the compressive modulus (not shown here).

The residual compressive strength after impact (CAI) of 30J was found to be 166 MPa for the CF reinforced CE/EP, whereas this is 210 MPa as reported for the reference material (by the material supplier). This difference may be explained by a higher amount of phase separated toughener in the reference prepreg material and more dense cross-linked (hence more brittle) CE/EP resin in the novel composite material.

4.2. Physical-chemical Properties

The glass transition temperature as determined with DMTA was 279°C (max tanδ) or 249°C ($T_{g,onset}$), which is well above the required service temperature. The degree of cure was established using DSC to be ~ 98%. The mass loss over time of the composite ILSS specimens during the thermo-oxidation tests is displayed in the following figure.

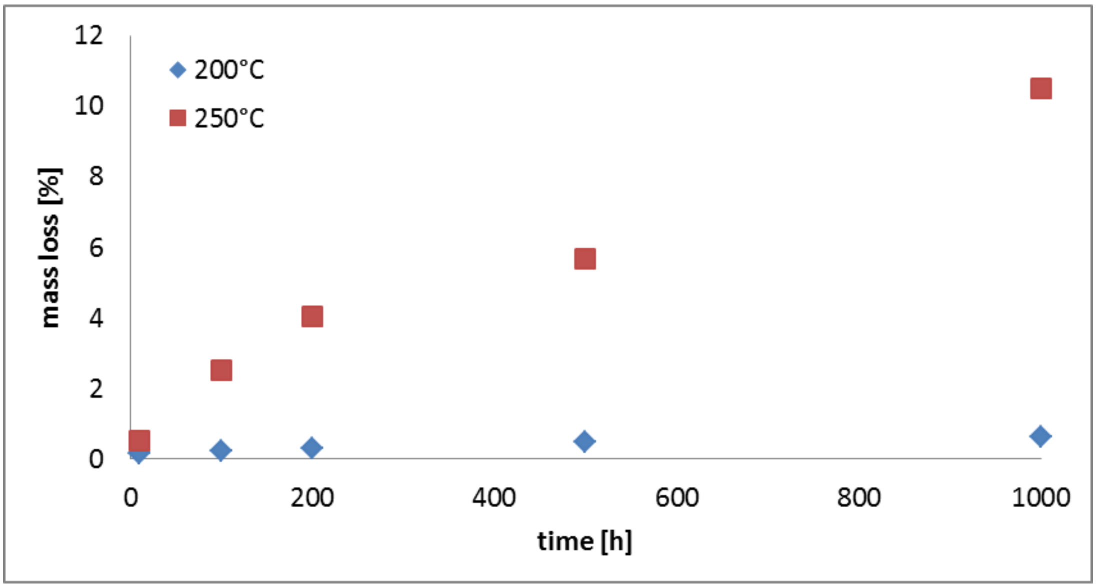

Figure 5. Mass loss over time of CF reinforced CE/EP at 200°C.

The mass loss of the novel composite is maximum 0.62 wt% after 1000 hrs in a thermo-oxidative environment at 200°C. At 250°C, a significant mass loss can be observed, which can be related to thermo-oxidative degradation of the matrix. This is reflected by the ILSS results as presented above. For reference, a comparison is made with a reference epoxy matrix and cyanate ester resin, displayed in the following figures.

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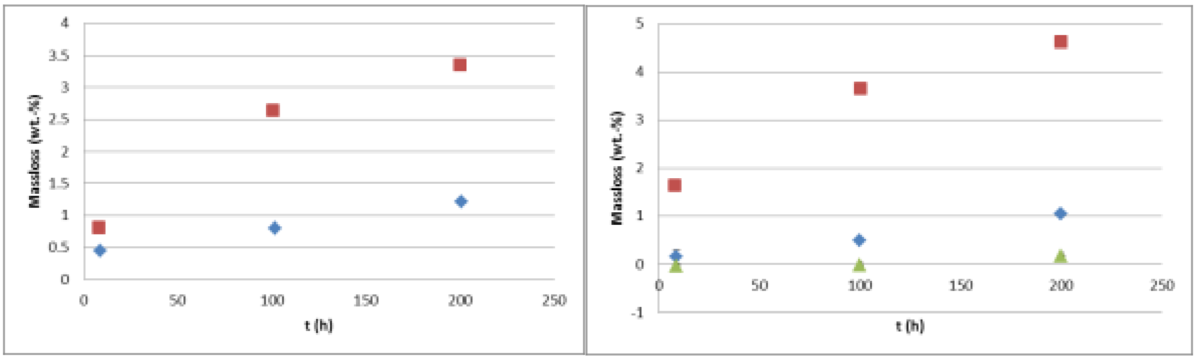

Figure 6. Mass loss over time of CE/EP (diamonds) and epoxy reference (squares) resins at 210°C (left) and cyanateester (triangles) resins at 220°C (right).

The mass loss of the pure CE/EP mixture is significantly lower than the EP reference material upon thermo-oxidative ageing at 210°C and 220°C and amounts up to maximum 1.2wt% after 200 hrs, while the epoxy reference material loses ~5wt% after 200 hrs at 220°C. The virgin cyanateester resin reference shows only little degradation at 220°C and seems also stable at 250°C (results not shown here). Therefore, the latter resin seems more suitable for a thermo-oxidative environment. However, the cyanateester resin is very brittle, rendering it unsuitable for applications in aerospace structures and is prone to hygro-thermal degradation, as will be shown in a future publication.

5. Conclusions

An epoxy-modified cyanateester (CE/EP) resin was developed for high temperature aerospace applications. A successful manufacturing process for the production of carbon fibre reinforced composites based on this resin was established based on resin transfer moulding. The most important factor was the incorporation of the toughener as a non-woven veil in the carbon fibre preform. Even though the mechanical properties are less than the reference epoxy based composite (values taken from suuplier) at room temperature, the epoxy-modified cyanateester proved superior at higher temperatures (>135°C) with more constant properties over temperature. In addition, the thermo-oxidative stability of the resin is improved compared to the epoxy reference composite. Therefore, the CE/EP resin seems to be a suitable composite resin for temperatures where epoxies fail. Future work will include investigations into the development of a prepreg based on this particular resin system.

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