THERMOPLASTIC COMPOSITES FOR AEROSPACE APPLICATIONS, DEVELOPMENTS TOWARDS HIGH-TEMPERATURE MATERIALS

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Abstract

Thermoplastic composites find an increasing use in aerospace applications. In order to extent this technology to areas with increased service temperatures, new organic resin systems are screened for use in carbon fiber reinforced composites. In this paper we will introduce a new high-temperature liquid crystal polymer (LCT) and present the rheology and after cure neat resin properties. In addition, preliminary results on composite materials will be discussed.

1. Introduction

Thermoplastic composites are gaining importance in various structural light-weight applications due to their combination of specific mechanical properties and ease of processing, ie. thermoforming, thermoplastic welding. Applications include automotive, oil&gas, civil infrastructure and aerospace.

Exemplary applications in the later field are the fixed wing leading edge on the A380, manufactured by Fokker Aerostructures, made from TenCate CETEX® glass fabric reinforced PPS. Another typical example include clips to join the fuselage, frames and stringers in the A350. The amount of these clips adds up to a few thousand parts per aircraft. These clips are manufactured from TenCate CETEX® carbon fabric reinforced PPS, and selected for reasons of mechanical performance and the ability to produce a large amount of these materials. These and other typical examples are depicted in Figure 1.

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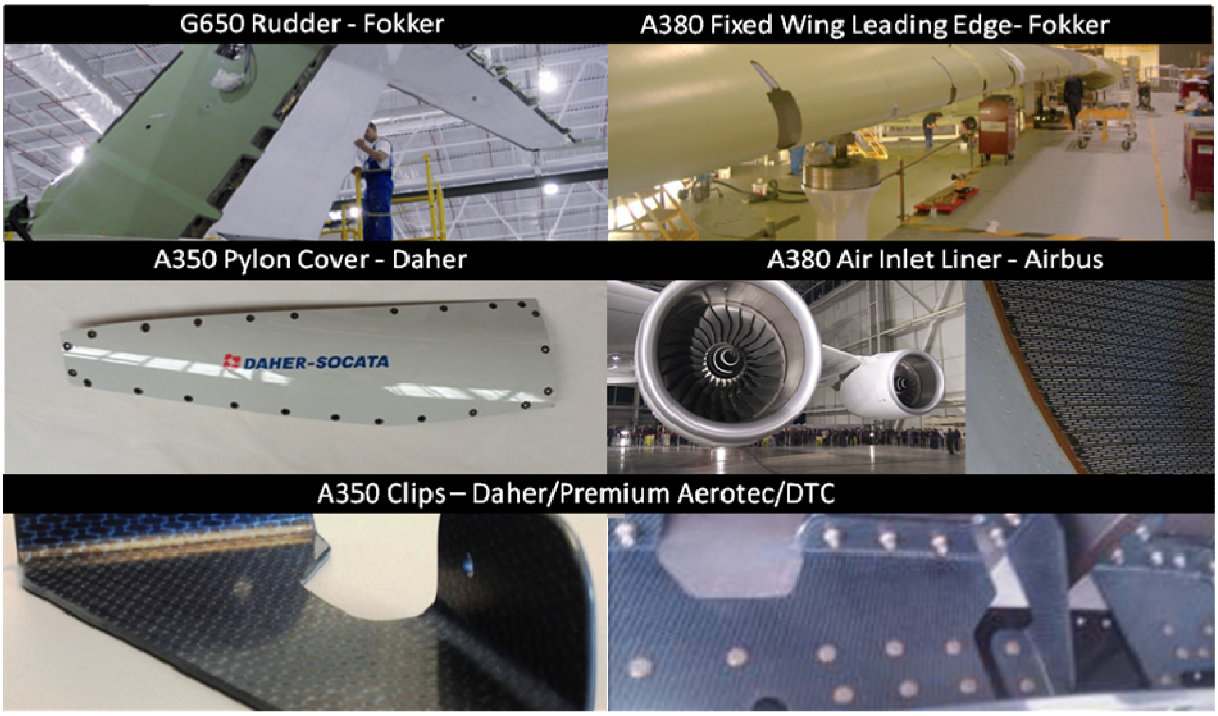


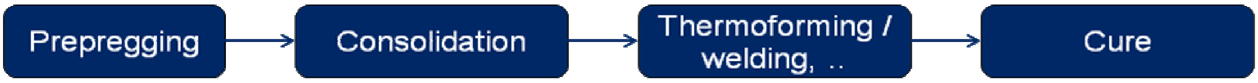
Figure 1. Typical examples of TenCate CETEX® aerospace applications.

The Range of Aerospace grade CETEX® materials include matrix systems such as poly(phenylene sulfide) (PPS), poly(aryl ether ketones) (PAEK copolymers) such as poly(ether ketone ketone) (PEKK) and poly(ether ether ketone) (PEEK), and poly(ether imide) (PEI); all reinforced with carbon or glass fibers. These materials are used for their combination of (thermo-)mechanical performance, inherent good fire, smoke and toxicity properties and inherent chemical resistance to a wide variety of fluids.

Within this range PAEK polymers feature the highest thermo-mechanical properties for structural applications. With a T_g of around 150 °C, the majority of aircraft applications can be covered. However, some new applications within the aerospace or space segment require increased thermos-mechanical properties. These can be for example applications which are closer to the engine. For these applications, nowadays typically thermoset matrix systems such as bismaleimide (BMI) or cyanate esters (CE) are used.

This study presents part of a screening for thermoplastic composites with an increased service temperature, with the aim to be able to provide materials which are on par with BMI and CE, with an improved processability. For this technology liquid crystalline materials show good potential.

The general processing route of this material could be as follows, first the material would be prepregged and subsequently consolidated. These materials can be further processed by thermoforming and welding. The final shape will be subsequently cured to obtain the final properties.



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Liquid crystalline polymers – Background & Properties

A liquid crystal polymer (LCP) can be described as a material with the characteristics of both the liquid (l) and the solid (s) state. A certain degree of orientational and/or positional order is maintained by the molecules while they diffuse through the melt, this phenomenon manifests itself in the formation of domains of aligned molecules.[1] The ordered nature and close molecular packing of liquid crystal polymers result in high strength, high stiffness, excellent solvent resistance, low gas permeability, low water absorption as well as a low coefficient of thermal expansion. These properties make LCPs suitable for structural applications, such as high-performance fibres, barrier films, high-precision mouldings in electronics and high-performance mouldings in sports goods, electro-optical displays and surgical devices.[2] The final use temperature of LCPs, however, is still limited by their low T_g (~140 ºC) and low storage modulus (E') at elevated temperatures.[3] A thermosetting LCP version, on the other hand, can provide outstanding mechanical and thermal properties, such as high E' above T_g, low mould shrinkage, low coefficient of thermal expansion, high solvent resistance and good adhesion. [4] Processing techniques such as tape laying, resin film infusion and resin transfer moulding are possible when low molecular weight reactive oligomeric LC precursors are used. Structural composites for aerospace, automotive and wind turbines would be obvious applications to consider.[5] Over the last 10 years, a variety of all-aromatic thermotropic reactive oligomers terminated with latent reactive end-groups have been explored. The reactive oligomers can be processed like any other thermoplastic polymer but after a successive high temperature thermal post treatment step the reactive oligomers react to form a nematic network structure or liquid crystal thermoset (LCT). [6, 7] By using this approach, the processing characteristics of a thermotropic LCP are combined with the mechanical performance of a cured thermoset.[3] With the reactive oligomer approach the processability is improved as the presence of end-groups decreases the molecular weight, and as a consequence the melt viscosity and melting temperature are reduced.[3] The end-groups must be compatible with mesophase formation and the processing temperature of the oligomers. A variety of end-groups with different curing temperatures is available but, with respect to processing temperatures typically used for processing thermoplastic polymers, the choice of end-groups is very limited. Cyanate, benzocyclobutene, maleimide and ethynyl, for instance, are not suitable because their curing temperature is too low. Nadimide end-groups produce toxic volatiles during curing, and biphenylene end-groups result in brittle networks.[8] Best results so far have been obtained with phenylethynyl functionalities. In the 90's, scientists at NASA Langley Research Center developed phenylethynyl-terminated imide (PETI) oligomers in support of NASA's high-speed civil transport program. The best combination of processing and after cure properties were obtained with PETI-5, a crosslinkable polyetherimide oligomer with an exceptional long duration performance (>10.000 h.) in combination with excellent (thermo)mechanical properties, e.g. a T_g of 270 °C and E'(25 °C) of 3.0 GPa.[9] Phenylethynyl end-groups have been successfully applied in the PETI series due to a combination of properties: stability under harsh synthesis conditions, excellent shelf life, no volatiles upon curing and excellent after cure thermo-mechanical performance.[8] For the reason mentioned above, phenylethynyl end-groups are used in the design of LCTs. Over the years, researchers at TU-Delft have have explored one of the most rigid LCT formulation known to date, which is based on 4-hydroxybenzoic acid (HBA), terephthalic acid (TA) and 4,4'-biphenol (BP) and this has resulted in LCTs with heat deflection temperatures in excess of 375 ºC.[9] Incorporation of the reactive phenylethynyl end-groups allows us to control the molecular weight (M_n) of the oligomers and hence the melting range, melt viscosity and the final after-cure thermo-mechanical properties. One of the challenges associated with using rigid backbone chemistries based on the above mentioned backbone formulation is that the melting temperature ($T_{K\text{-}N}$) is typically close to or above the decomposition temperature, making processing very challenging. In order to lower the $T_{K\text{-}N}$ to acceptable levels we introduced a non-linear co-monomer, i.e. 2,6-naphthalenedicarboxylic acid (NDA).[10] The reactive oligomer used for this study is based on HBA, BP, TA and NDA, with the following monomer ratio: HBA(60%)/BP(20%)/TA(15%)/NDA(5%). To produce a reactive thermoplastic oligomer with a low melting point and low melt viscosity, an oligomer with a number average molecular weight of 5,000 g/mol was synthesized. This reactive oligomer was labelled 5N5K, and the molecular structure is shown in Figure 2.

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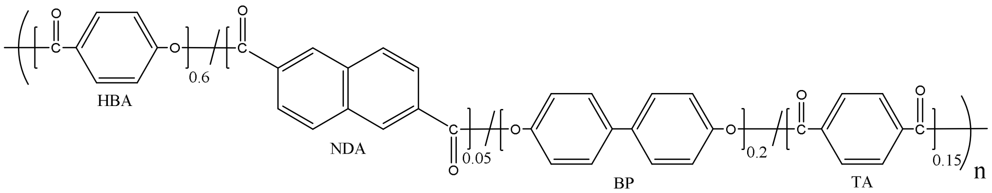

Figure 2. HBA/BP/TA(15)-NDA(5) oligomer backbone, labbelled 5N5K. Note: The reactive phenylethynyl end-groups are not shown but are positioned at the chain termini.

2. Results

Thermo-mechanical characterization oligomer and cured thermoset

The thermal stability of the cured oligomer was investigated with thermogravimetric analysis (TGA) after the samples were cured at 370 °C for 60 minutes under a nitrogen atmosphere. After cure, 4 samples were measured from room temperature to 600 °C with heating rates of 2.5, 5, 10 and 20 °C/min, respectively, under a nitrogen atmosphere. With this procedure it was possible to determine the decomposition temperatures (T_d, temperature at which a 5% weight loss occurs) at different heating rates, as shown in Figure 3A. High values of T_d are reported and are in the range of 478–522 °C and, as expected, the faster the heating rate, the higher the T_d.

The melt transitions, i.e. the crystal-to-nematic transition ($T_{K\text{-}N}$) of the oligomer, was studied with differential scanning calorimetry (DSC). The sample was analysed using a heating rate of 20 °C/min under nitrogen atmosphere from 50 to 350 °C. The glass transition temperature (T_g) of the oligomer could not be detected with this instrument, whereas the $T_{K\text{-}N}$ transition is clearly visible at 300 °C (Figure 3B).

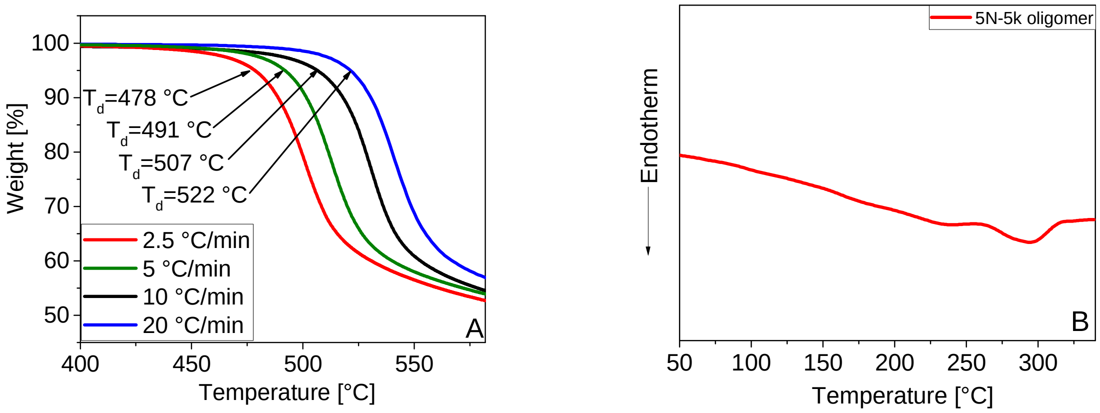

Figure 3. A. TGA curves of the cured oligomers 5N5K, measured at different heating rates in nitrogen atmosphere. **B**. DSC curve of the 5N5K oligomer, measured at a heating rate of 20 °C/min in nitrogen atmosphere.

Dynamic Mechanical Thermal Analysis (DMTA) was performed to determine the glass transition temperature and storage modulus (E’) as function of temperature of the cured film. Experiments were conducted using a thin film (0.25 mm) in the temperature range of 20 °C to 475 °C. Using similar experimental conditions we analyzed two well-known commercially available high-performance thermoplastic polymers, PPS and PEKK, and the results are summarized in Figure 4A. The T_g value of the 5N5K cured oligomer is 270 °C, while we identified the glass transition teperatures of PPS and PEKK at 110 and 150 °C, respectively. All DMTA tests were performed applying a load of 1.2 N that was maintained throughout the experiment until the polymer started to strain as function of temperature. Figure 4B shows the strain vs temperature behavior of 5N5K, PPS and PEKK films. For the two thermoplastic samples the strain increases drastically in the vicinity of the T_g, whereas the cured 5N5K LCT does not strain up to 300 °C.

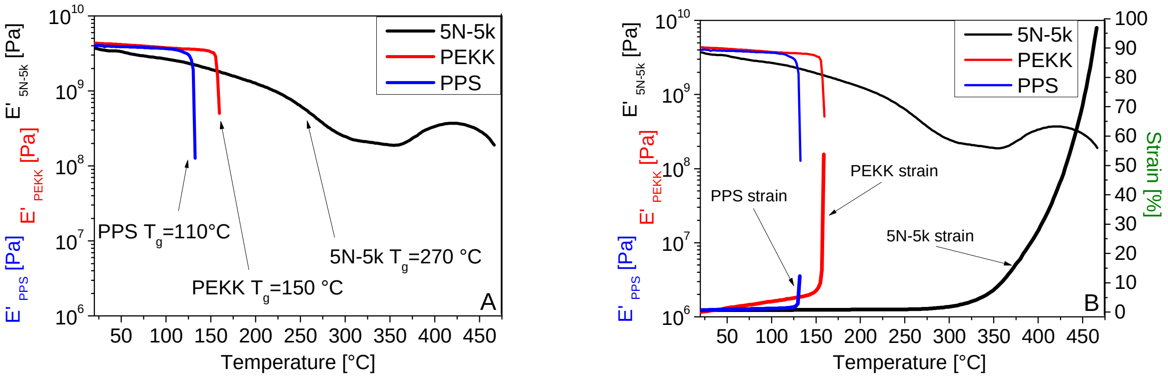

Figure 4. A. Storage moduli of the cured oligomer film 5N5K (black), PPS (blue) and PEKK (red). All measurements were conducted at a frequency of 1 Hz, a heating at 2 °C/min, in nitrogen atmosphere **B**. Storage moduli and strain vs temperature behavior of cured oligomer film 5N5K (black), PPS (blue) and PEKK (red).

In addition to the after cure performance, we evaluated the oligomer melt viscosity and curing behaviour using a parallel-plate rheometer. Pellets of 20 mm diameter and approximately 0.5 mm thick were prepared by compression molding and investigated under a nitrogen atmosphere using 5 rad/sec and at 1% strain. The temperature was increased to 370 °C using a heating rate of 5 °C/min. The pellets were then held at 370 °C for 60 minutes to enable the oligomers to fully cure. As visible in Figure 5, the experiment shows the melt viscosity as function of temperature and time: the viscosity drops at the melting temperature ($T_{K\text{-}N}$) and then, when the cure temperature is reached, the viscosity increases due to chain-extension and crosslinking. The minimum viscosity for this oligomer is 10 Pa·s at 295 °C. In Table 1 we have listed the main results of the thermal and thermo-mechanical characterization of the oligomer and the cured thermoset.

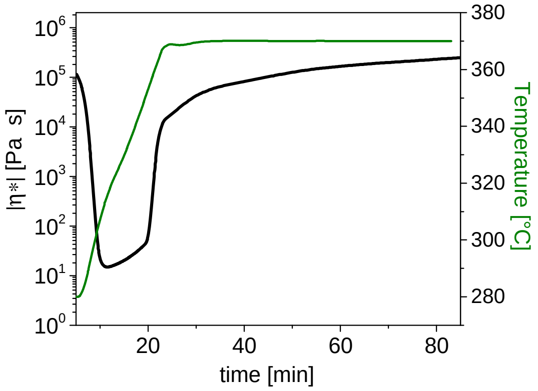

Figure 5. Complex melt viscosity of the 5N5K oligomer. Heating rate of 5 °C/min, 5 rad/s, strain 1%, nitrogen atmosphere.

Table 1. Thermal and thermo-mechanical properties of 5N-5k oligomer and cured thermoset.

Polymer	$T_{d\text{-}10\ °C/min}$ [°C]	$T_{K\text{-}N}$ [°C]	T_g [°C]	Min |η*| [Pa·s]	$E'_{25\ °C}$ [GPa]	$E'_{100\ °C}$ [GPa]	$E'_{200\ °C}$ [GPa]	$E'_{300\ °C}$ [GPa]
5N5K	507	300	270	10	6.5	2.8	1.3	0.25

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Carbon fiber reinforced LCTs

With the LCT described in previous section (5N5K), carbon fiber reinforced materials were made for screening on a composite level. The shear thinning behavior, typical for liquid crystalline polymers, require an adapted setup for press consolidation. Figure 6 shows a laminate with an optimized consolidation cycle. Although, adaptation of the processing cycle has significantly improved, still some porosity is present in the laminates.

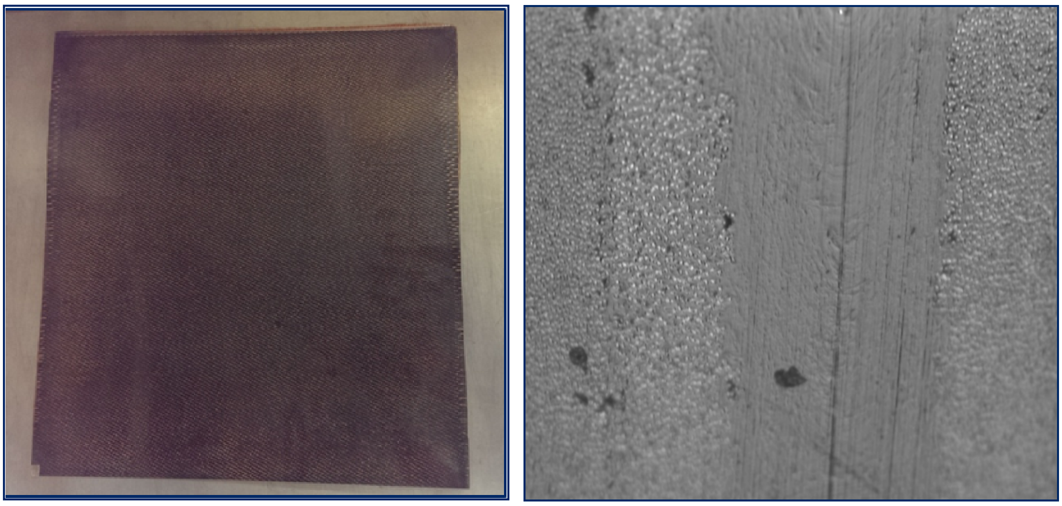

Figure 6. Laminate consolidation of C/LCT materials. **A**: Consolidated Laminate. **B**: Cross section micrograph of consolidated laminate

As a measure of consolidation and fiber/matrix interface quality in-plane shear tests were performed. Results shown in Figure 7 indicate a positive trend and show that interface quality as well as consolidation quality play an important role. Further adaptations to improve these properties are ongoing.

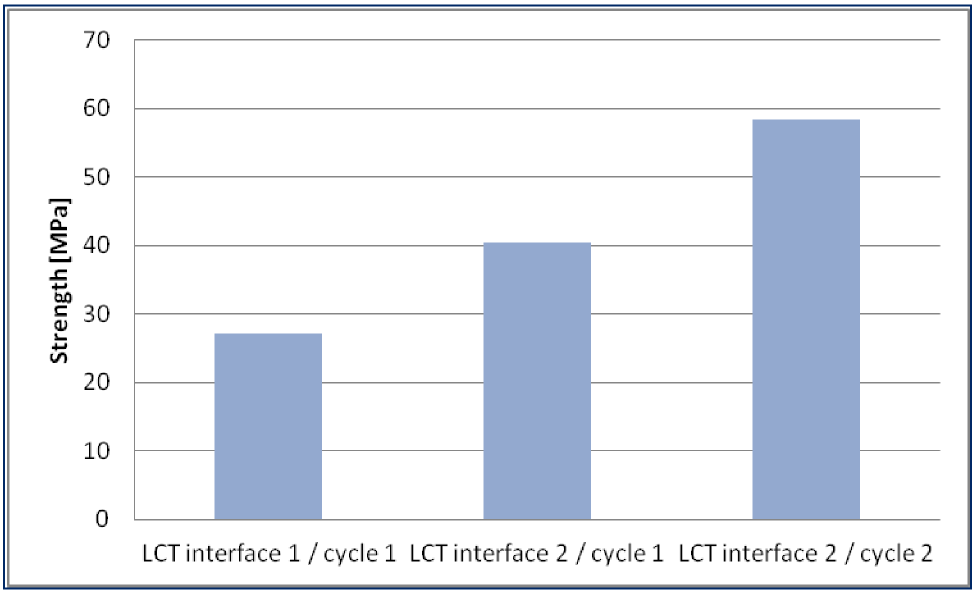

Figure 7. Typical In-plane shear values of obtained Carbon fiber reinforced LCTs.

The processing behavior of carbon fiber reinforced 5N5K LCT was validated by, amongst others, stampforming trials. Results show that the consolidated materials can indeed be stampformed prior to final cure.

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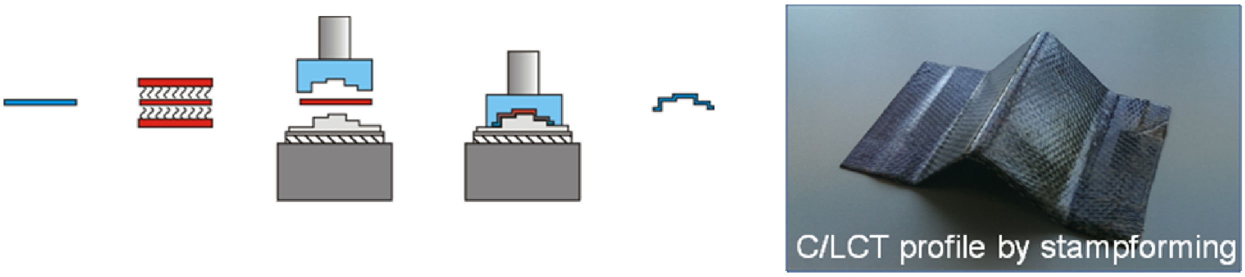

Figure 7. **A.** Principle of Stampforming. **B**. Example of processing a simple carbon fiber reinforced LCT profile.

3. Conclusion

Liquid crystalline thermosets are a relatively new class of high-performance polymers, which have been designed for an optimal combination of thermo-mechanical properties and processability. In this study 5N5K LCT was screened for use in composite applications for aerospace applications. Results show that the consolidation quality and interface quality could be improved. Adaptions to further improve the thermo-mechanical properties are planned, to fully exploit the potential of this new class of polymers.

4. Acknowledgements

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