

NOVEL LIQUID CRYSTAL THERMOSET RESINS FOR CRYOGENIC FUEL TANK APPLICATIONS

Theo.J. Dingemans^{*}, Sybrand van der Zwaag^{*}, Alwin Knijnenberg^{*},
Erik S. Weiser^{**}, Brian J. Jensen^{**}

^{*}Delft University of Technology, Faculty of Aerospace Engineering
Kluyverweg 1, 2629 HS Delft, The Netherlands

^{**}NASA Langley Research Center, Mail Stop 226, Hampton, VA 23681-2199, USA

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Abstract

In support of NASA's Next Generation Launch Technology (NGLT) we have developed a liquid crystal thermoset resin, which can be used as a matrix resin for carbon reinforced cryogenic fuel tanks. This resin is suitable for pultrusion, RTM and RFI composite processing and exhibits outstanding barrier properties, high thermal stability and excellent adhesive properties. After processing the composites are thermally cured, which results in a wholly aromatic liquid crystal network or thermoset.

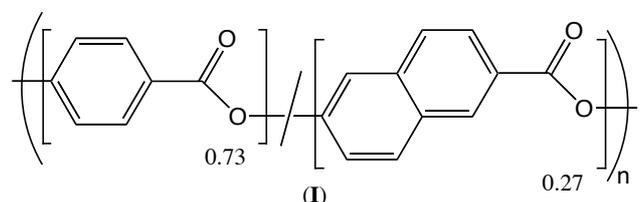
1 Introduction

One of the major challenges for NASA's next generation reusable launch vehicle (RLV) program is the design of a cryogenic lightweight composite liquid hydrogen (LH₂) fuel tank. Potential resin systems need to exhibit a low coefficient of thermal expansion (CTE), good mechanical strength, and excellent barrier properties at cryogenic temperatures under load. In addition, the resin needs to be suitable for a variety of processing techniques such as resin transfer molding (RTM), resin film infusion (RFI), pultrusion, and advanced TOW placement (ATP).

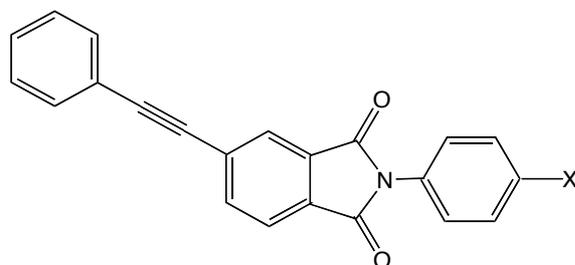
To meet these requirements, we have designed a new family of wholly aromatic liquid crystalline (LC) resins with a wide range of processing capabilities. Thermotropic liquid crystal polymers (LCPs) are a well-known class of engineering plastics with excellent physical properties, high mechanical strength in the direction of orientation, outstanding barrier

properties, and low viscosity during processing. Although most commercial available LCPs are synthesized from aromatic monomers, they exhibit low glass-transition temperatures (T_g) and low moduli (E') at elevated temperatures. One potential solution to this problem is the design of densely cross-linked anisotropic networks. Ortiz and co-workers[1] demonstrated this concept in a variety of epoxy-based LC resins. Both nematic and smectic networks showed an increase in moduli at elevated temperature, however, a decrease in T_g upon increased molecular ordering was observed. Several groups researched thermotropic systems and these materials appeared more promising. Low-molecular weight mesogenic structures, end-capped with different reactive functionalities displayed high T_g's and high rubbery moduli.[2-4] This approach, however, gave materials with small processing windows and poor mesophase behavior.

Herein, we will present the chemistry and properties of a new family wholly aromatic high-performance LC thermoset materials, which are suitable as matrix resins for fiber reinforced composites.[5, 6] The resins are designed around the VectraTM (I) concept, where the 4-hydroxy-benzoic acid (HBA)/6-hydroxy-2-naphthoic acid (HNA) polymer back-bone is end-capped with thermally crosslinkable phenylethynyl units.



The end-groups (**II**) are chosen such that the phenylethynyl unit remains dormant throughout the melt condensation process –where the maximum temperature during polymerization can be close to 310 °C.



(**II**) where X= -OH or -COOH

The advantage of this approach is two-fold. The obtained oligomers have low melt temperatures and viscosities, and the oligomers can be crosslinked to form high-molecular weight thermosets in a second, high-temperature, step. These resins can be made using conventional, environmentally benign, one-pot melt-condensation techniques.

2. Results and Discussion

The HBA and HNA monomers (in a 73/27 mol ratio) were successfully polymerized in the presence of cross-linkable phenylethyl units (**II**). In order to investigate the effects of molecular weight on properties such as viscosity, T_g , and cured mechanical properties, we synthesized four ester oligomers in different molecular weights (MW), *i.e.* 1000, 5000, 9000, and 13000 g/mol. We found that all oligomers melt into nematic phases and do not exhibit isotropization temperatures ($T_{N-I} > T_{dec}$).

Mesophase Behavior: The phase behavior of the oligomers was confirmed using hot-stage polarizing microscopy and temperature dependant small angle X-ray Diffraction (SAXS). The texture of the 1000 g/mol ester oligomer is shown in Figure 1. This material melts at 236 °C and does not have an isotropization temperature. The texture and melt behavior remain virtually unchanged below 310 °C but at higher temperatures crosslinking takes place, which becomes apparent by the rapid

increase in viscosity. In most cases crosslinking is complete after one hour at 370 °C and an immobilized nematic texture remains.

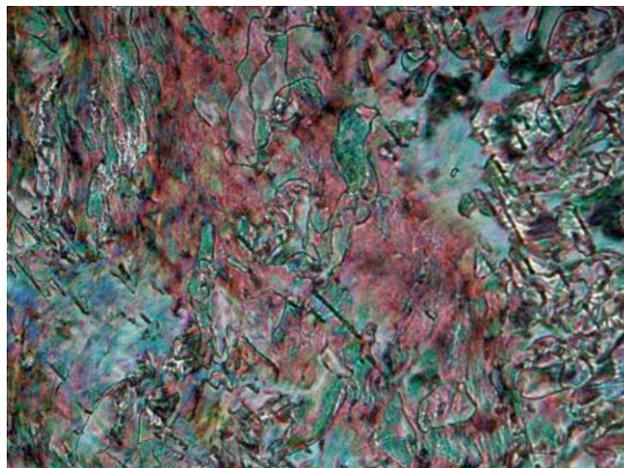


Fig 1. Nematic Schlieren texture of the 1000 g/mol LC oligomer at 290 °C; crossed polars and 20X.

Melt Behavior: Depending on the oligomer MW, the oligomers display a wide range of melt viscosities. LCPs are known for their shear thinning effect[7], and the advantages of this effect become immediately evident in Figure 2.

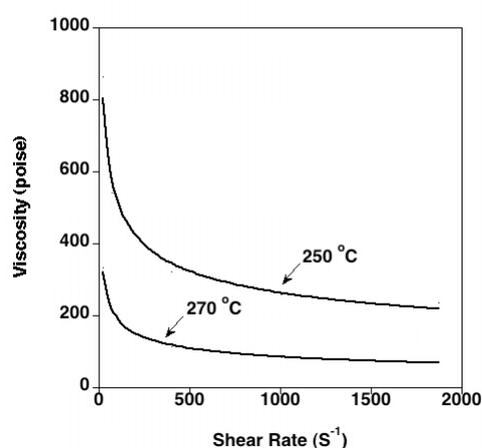


Fig. 2. Viscosity as a function of shear rate at 250 °C and 270 °C for a 9000 g/mol LC oligomer.

Figure 2 shows how the melt viscosity varies as a function of shear rate at a given

temperature. All isotropic polymer melts show an initial drop in viscosity when the shear is increased, however, not as dramatically as observed for LCPs. Depending on the applied shear rate, the viscosity during processing at, for example 250 °C, can be selected anywhere between 200 and 800 poise.

Figure 3 shows the viscosity dependence as a function of cure temperature at a fixed shear-rate ($100 \text{ rad}\cdot\text{s}^{-1}$).

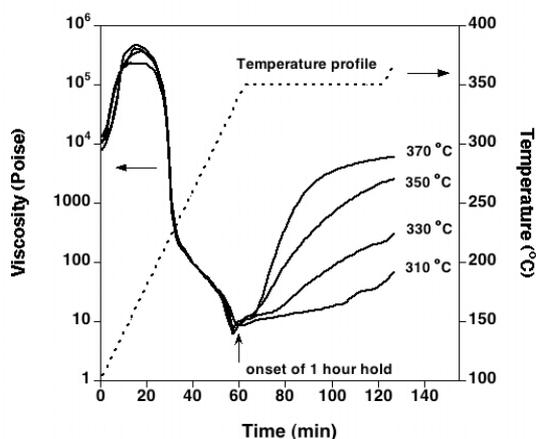


Fig. 3. Viscosity as a function of temperature and hold time (1 h.) of a 9000 g/mol oligomer.

Below 300 °C virtually no cross-linking takes place, while above that temperature cross-linking proceeds slowly at 310 °C and fast at 370 °C. When the temperature is kept around 300 °C, a viscosity of 10 poise can be maintained for at least 1 hour, which makes this resin suitable for the production of large structures using Resin Transfer Molding (RTM) techniques.

Thermal Properties: All oligomers and their cured products were investigated using Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA) at heating rates of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$. The uncured oligomers show glass-transition temperatures (T_g) of 110 °C, and depending on the MW, melting points (T_m) of 236 °C for the 1000 g/mol oligomer, and 296 °C for the 13000 g/mol oligomer. The cured resins exhibit no T_g or T_m transitions observable by DSC. Cured samples showed excellent thermal stabilities in both air and

nitrogen, *i.e.* 5% weight-loss points were measured at 490 °C or higher.

Neat Film and Composite Properties: In order to study neat film and composite properties, we prepared quasi isotropic $20 \times 20 \times 0.05 \text{ cm}$ cured films by melt pressing the 9000 g/mol oligomer for one hour at 375 °C. Strong, flexible films were obtained, which exhibit a room temperature modulus of 3.1 GPa and an elongation at break of 2.8%.

A 6 ply T650 (5H satin weave) carbon composite was fabricated using vacuum assisted RFI, followed by a one-hour cure at 375 °C. Mechanical analysis of the composite showed a room temperature modulus of 74.1 GPa and a flexural strength of 552 MPa. A Scanning Electron Microscope (SEM) cross-section analysis, Figure 4, shows an area of good fiber wet-out.

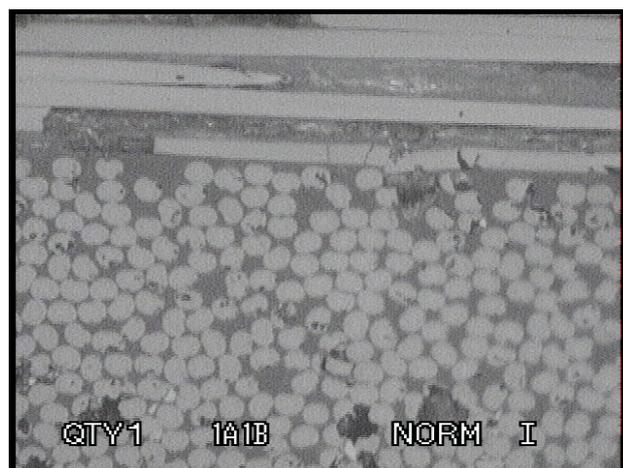


Fig. 4. SEM picture (50 x) of a 6 ply T650 (5H satin weave) carbon composite.

At this point the processing cycle has not been optimized and it is expected that we are able to improve on the flexural strength.

Adhesive Properties: We have performed lap-shear experiments to determine the adhesive characteristics of a LC thermoset resin. A glass scrim cloth was melt impregnated with the 9000 gram/mol LC oligomer and used as the adhesive layer between two titanium (Ti, 6Al-4V) strips. The total area of overlap was 0.5 inch^2 and three different lap-shear sets were prepared at three different bond pressures. The

room temperature lap-shear results are summarized in Table 1.

Bond Pressure (kPa)	Area of overlap (inch ²)	Mean shear strength (MPa)
105	0.5	20
350	0.5	22
700	0.5	24

Table 1. Mean shear strengths measured for a cured 9000 g/mol oligomer on titanium (T, 6Al-4V) at room temperature.

The lap-shear values shown in Table 1 are excellent and these experiments strongly suggest that LC thermosets can be used for adhesive applications as well. Also, we found that all lap-shear test specimen failed on one side of the glass scrim cloth, which suggests that the lap-shear values can even be improved considerably.

Barrier Properties: For fuel tank applications one needs to carefully select a polymer system, which is compatible with the stored fuel. LCPs are well known for their outstanding barrier properties towards many harsh solvents, including Skydrol. In order to obtain information on the barrier properties of LC thermosets we tested a fully cured 9000 g/mol oligomer film using a standardized Helium (He) leak test. The film, with a thickness of 0.01 mm, was mounted between two flanges and pressurized at one side using He(g) at 25 psi. A manometer was used to detect any He(g) transport through the film. No He(g) transport could be detected through the film for 24 hours, and after this time a steady leak rate was measured of 1.04×10^{-10} mol.s⁻¹.

3. Conclusions

We have presented a new family of LC thermosets with excellent thermal, mechanical and barrier properties. For the first time it has been demonstrated that LC resins can be used as composite matrixes. Mechanical studies of un-oriented cured films and composites gave values

very similar to typical aerospace epoxy resins. Although cryogenic composite testing with H₂(l) is still in progress, our results so far suggest that LC thermoset resins are excellent candidates for the fabrication of carbon-reinforced fuel tanks.

4. Experimental Section

All oligomers were synthesized according to known literature procedures [5]. Thermal analysis experiments were performed using a PerkinElmer Sapphire DSC and a PerkinElmer Diamond TG/DTA. For all experiments, heating rates of 10 °C.min⁻¹ were used. The mechanical properties of neat films and composites were determined using a Sintech 2W according to ASTM D-690 and ASTM D-790-7. The melt behavior of the oligomers was investigated using a Kayness capillary rheometer in scanning shear mode and the cure behavior was measured using an Ares melt rheometer in a parallel plate configuration at 100 rad.s⁻¹. Lap-shear experiments were performed conform ASTM D-1002 using a United SFM-10 apparatus. Helium leak rates were measured using a standard gas transmission cell according ASTM D 1434-82.

Note: *This invention has been licensed exclusively to TICONA LLC, 90 Morris Avenue, Summit NJ 07901, USA*

References:

- [1] Ortiz C, Kim R, Rodighiero E, Ober C, Kramer E, *Macromolecules*, 31, pp 4074, 1998.
- [2] Hoyt A, Benicewicz B, *J. Polym. Sci. Part A: Polym. Chem.*, 28, pp 3403, 1990.
- [3] Mormann W, Kuckertz C, *Macromol. Chem. Phys.*, 199, pp 845, 1998.
- [4] Melissaris A, Litt M, *Macromolecules*, 26, pp 6734, 1993.
- [5] Dingemans T, Weiser E, StClair T, *US Patent Application*, 09/757,398, 2001.
- [6] Dingemans T, Weiser E, StClair T, *Reinforced Plastics*, 47(1) pp 17, 2003.
- [7] Acierno D, LaMantia F.-P. *Processing and Properties of Liquid Crystalline Polymers and LCP Based Blends*. 1st edition, ChemTec Publishing, 1993.