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High-performance composites based on all-aromatic liquid crystal thermosets

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ABSTRACT

In this study, a new high-performance liquid crystal ester-based thermoset for composite applications was investigated. All-aromatic liquid crystalline thermosets (LCTs) are a promising class of polymers that offer a unique combination of properties such as solvent resistivity, high modulus, high strength, low coefficient of thermal expansion and high after cure glass-transition temperatures ($T_g \geqslant 150\,°C$). Fully cured LCTs offer superior thermo-mechanical properties over high-performance thermoplastic polymers such as PPS, PEEK and PEI. For this study we used a 9000 g mol^{-1} ester-based LCT based on cheap and readily available monomers, *i.e.* 4-hydroxybenzoic acid (H), isophthalic acid (I) and hydroquinone (Q), abbreviated by us as HIQ-9. Composite panels prepared from T300 carbon fiber (5-harness satin weave) showed in-plane shear strength of 154 MPa and an in-plane shear modulus of 3.7 GPa. The tensile strength and modulus were measured to be 696 MPa and 57 GPa, respectively. A *post-mortem* inspection showed that the interfacial strength was excellent and no delamination was observed in the test specimen. Preliminary results show that LCT-based composites exhibit a better combination of (thermo) mechanical properties over PPS and PEI-based composites.

1. Introduction

The demand for light-weight structures in the aerospace and automobile industry has increased considerably over the years. Due to their high specific strength and stiffness, fiber-reinforced composites have become an important class of structural materials. Fiber-reinforced composites based on thermoplastic polymer matrixes are now in use for more than twenty years. A special class of fiber-reinforced thermoplastic composites is based on all-aromatic semi-crystalline polymers such as PPS, PEEK and PEI. They offer several desirable properties such as unlimited shelf life, low manufacturing costs and can be used in all but aggressive chemical environments [1–4]. Despite these properties they also have several short comings. Due to the semi-crystalline nature of these polymers the thermal history has a pronounced effect on the degree of crystallinity, which consequently has an effect on the overall mechanical properties of the final composite [5]. The microstructure, or the morphology of semi-crystalline thermoplastic composites, is highly dependent on the applied processing parameters [6]. In thick laminates, for example, the outer layers will cool at a much faster rate while the layers at the center of the composite will cool at a lower rate. This results in thermal stresses at the fiber resin interface, which again weakens the final composite structure [7]. Another point of concern is the low glass-transition temperature (T_g) of most all-aromatic commercial thermoplastics. Carbon fiber based composites based on PPS ($T_g = 85\,°C$) loose 60% of their flexural strength at 140 °C while the in-plane shear strength decreases already at 45 °C, which is far below T_g. A similar effect was also observed for PEEK-based composites [8]. Amorphous high T_g poly(ether imide)s (PEIs) and thermosetting PEIs, on the other hand, offer advantages for high temperature applications but their use is limited due to high cost and processability issues [9].

In order to provide a useful alternative we are currently exploring all-aromatic liquid crystal thermosets, which can be processed as thermoplastic polymers and cured into so-called liquid crystal networks or liquid crystal thermosets (LCTs) [10–12]. An important advantage is that our LCT concept could be useful for the production of thick composites structures because in fully cured LCTs the molecules are closely packed, which is a consequence of liquid crystallinity, but lack crystallinity, which we anticipate, will result in lower thermal stresses in the final composite structure. LCTs combine both the advantages of thermoplastic liquid crystalline polymers as well as that of thermosetting polymers. The advantages include improved processability, high glass-transition temperatures, excellent thermal stability, high strength and stiffness, outstanding interfacial properties and low shrinkage after curing. Herein we will present the properties of composites based on T300 carbon fibers (5HS) and a 9000 g mol^{-1} reactive random co-polymer based on 4-hydroxybenzoic acid, isophthalic acid and hydroquinone, labeled by us as HIQ-9. Thermal, mechanical and interfacial properties were investigated and will be discussed.

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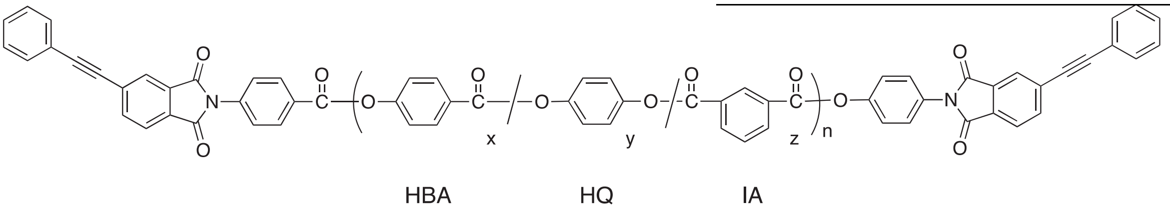
2. Experimental methods

2.1. Materials

Carbon fabric T300 (5 HS) with areal density of 280 g m^{-2} and thickness of 0.35 mm was provided by Ten Cate Composites and the LCT precursor HIQ-9 was synthesized in our laboratory. The synthetic details can be found elsewhere [13]. The reactive liquid crystal oligomer used for this study has a maximum after cure T_g of 190 °C, which depends on the applied temperature–time (*T*–*t*) cure profile. The structure of the reactive HIQ-9 oligomer is shown below.



2.2. Composite manufacturing

Laminates (6-plies, 40 × 40 cm) were prepared using a simple resin film infusion process. A 5-harness satin weave T300 Carbon fabric was selected and the reactive oligomer was distributed evenly between the individual layers. The resin–fiber content at this point was 40/60 (40 wt.% resin and 60 wt.% fiber). The whole assembly was placed in a Joos press and heated to 350 °C at a heating rate of 9 °C min^{-1} and at a pressure of 2 bar. At 350 °C, the pressure was increased to 10 bar and the composite was kept at this temperature and pressure for 15 min, followed by increasing the temperature to 370 °C and a pressure of 10 bar for 30 min. The complete curing cycle will be discussed in more detail in Section 3. To study the effect of curing on thermal and mechanical properties neat resin thin films were also cured at different temperatures *i.e.* 340, 370 and 400 °C.

2.3. Analysis

A Leica DMLM optical microscope equipped with a hot stage was used to investigate the oligomer melt behavior. A powder sample was investigated between two glass slides and heated to 450 °C. Optical microscopy was also used to investigate the void content in the fully cured T-300/HIQ-9 composite specimen. A Perkin-Elmer Sapphire differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA) were used to investigate the thermal properties of the reactive oligomers and their fully cured thermosets. The heating and cooling rates used were 20 °C min^{-1} for DSC and 10 °C min^{-1} for TGA experiments. All DSC experiments were performed under a nitrogen atmosphere whereas all TGA experiments were conducted in the presence of nitrogen or air. LCT samples were cured at 370 °C for 45 min. in a nitrogen atmosphere and cooled to room temperature before measurement. The dynamic mechanical analysis (DMTA) was performed using a PerkinElmer Diamond dynamic mechanical thermal analyzer (DMTA) under a nitrogen atmosphere and at a heating rate of 2 °C min^{-1}. The tensile and in-plane shear tests were performed on a Zwick 250 kN machine according to ASTM standards (Tensile D 3039, In-plane shear D3518 and Flexural D7264). The flexural tests were performed on a Zwick 20 kN machine. Five specimens were used for each test. A Jeol JSM-7500F, high-resolution scanning electron microscopy (HRSEM) was used to study the composite fracture surfaces after failure. A Midas 3 × 1.5 m single through-transmission ultrasonic transmission scanner with a probe diameter of 10 mm and a natural focusing transducer was used to inspect the defects in the laminates and density variations at a frequency of 10 MHz.

3. Results and discussion

3.1. Thermal and thermo-mechanical properties of HIQ-9

In order to investigate the thermal behavior of the reactive HIQ-9 oligomer we used a differential scanning calorimeter (DSC). The samples were heated to 370 °C at a heating rate of 20 °C min^{-1} and isothermally cured at this temperature to allow chain extension/crosslinking to take place via the reactive end-groups. After a 45 min. hold the sample was quenched and cooled to room temperature, followed by reheating from room temperature to 400 °C. In the first heating cycle a melt transition (T_{K-N}) was observed. In the second heating cycle no melt transitions were detected, which is a strong indication that the resulting polymer was fully crosslinked. The DSC heating traces of the HIQ-9 oligomer, before and after cure, are shown in Fig. 1. Thermo gravimetric analysis (TGA) was used to investigate the thermal stability and decomposition temperatures. A heating rate of 10 °C min^{-1} was used for these measurements. The thermal stability was evaluated in terms of 5% weight loss ($T_d^{5\%}$) both in air and nitrogen. HIQ-9 showed excellent thermal stabilities (>400 °C) both in air and nitrogen. The storage modulus (E') and glass-transition temperatures were measured using dynamic mechanical thermal analysis (DMTA) in the temperature range of −100 to 500 °C at 1 Hz. The fully cured thermosets exhibit high glass-transition temperatures and show excellent moduli at elevated temperatures. With the reactive oligomer approach, we achieved a significant improvement in the glass-transition temperature as compared to commer-

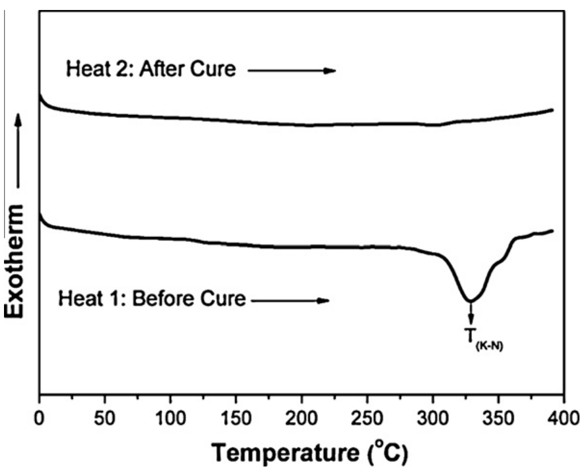


Fig. 1. DSC thermogram of the HIQ-9 oligomer measured at a heating rate of 20 °C min^{-1} under a nitrogen atmosphere. The lower curve represent the first heating cycle, showing a melting endotherm (T_{K-N}). The upper curve represent the second heat after curing and is consistent with a nematic thermoset.