

IMPROVED MATRIX MATERIALS FOR HIGH-PERFORMANCE CARBON FIBER COMPOSITES

AROMATIC THERMOSETTING COPOLYESTER

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Abstract

The use of new aromatic thermosetting copolyester (ATSP) is described and compared to the best available epoxies for high performance composites. In this paper, we demonstrate that ATSP oligomers display liquid crystalline behavior which was identified using optical microscopy with cross-polarizers. We also describe how ATSP tailored to have a liquid crystalline structure has reduced stresses at the fiber/matrix interface and better thermal fatigue resistance compared to epoxy.

Introduction

The automotive industry is moving towards fuel efficient, cost effective and reliable cars [1]. Composites fit into the picture because of their high strength to weight ratio and durability. Composites have become much more affordable because of recent advances in manufacturing technologies. For the near future, automotive materials need to meet specified performance properties like high thermal conductivity, chemical resistance, flame retardance, ease of manufacturing and high thermal stability. Replacement of metal parts with composites for 'under the hood' applications is a field ripe for development. 'Under the hood' applications can be divided into three general temperature zones: high temperatures including the engine block, ambient temperatures around the engine block and peripheral ambient temperatures [2]. ATSP, discussed in this paper can withstand temperatures in the vicinity of the combustion chamber which is much higher than the recommended usage temperatures of other high temperature engineering polymers (260 °C). Since composites are two-component systems, the interfacial Coefficient of Thermal Expansion (CTE) mismatch induces localized stress concentration, leading to formation of microcracks when cycled over a range of temperatures. The ATSP/ Carbon fiber composite can exhibit better thermal fatigue resistance for reasons that will be discussed in more detail in this paper.

Aromatic Thermosetting Copolyesters (ATSPs) are a relatively new family of thermosetting polyesters made

from relatively low cost precursors, including, p-hydroxybenzoic acid (pHBA), trimesic acid (TMA), hydroquinone (HQ), and isophthalic acid (IPA). These are melt-processed at 100-250 °C, depending on the molecular weight of the desired oligomeric system into a two-component acetoxy-terminated and carboxylic acid-terminated system. The oligomeric mixture is then cured at 250-330 °C to yield ATSP. The concerns with volatilization of the acetic acid byproduct to form voids are solved by preparing thin carbon fiber/ATSP lamina, which permits easy escape of acetic acid. These thin laminates can then be consolidated into thick section composites using Interchain Transesterification Reaction (ITR) which is discussed in the next paragraph. The novelty of this system lies in exploiting esterification reactions to yield a cross-linked all-aromatic product with excellent thermal, mechanical, and adhesion properties [3] [4]. ATSP is stable in air up to 350 °C and in nitrogen up to 425 °C whereas most thermally stable epoxies decompose at 170-190 °C in air or nitrogen. The moisture pickup of the resin is relatively low (0.3 wt%, as compared to 2.3% for epoxy), increasing the potential durability against physical ageing [3] [4] [5].

One of the salient features of this system is its ability to form adhesive bonds even after being cured. This is due to ITR at the interface between cured lamina as illustrated in Figure 1 [5] [6]. Thin laminates of ATSP can be consolidated even after curing, by heating under pressure at 300 °C, to prepare low-void advanced composite systems through ITR. This could enhance reparability of systems and also reduce problems of assembling large parts using mechanical fixtures. The possibility of recovery of an oligomer from the crosslinked product using the acetolysis reaction makes the technology environmentally friendly [7].

In summary, ATSP provides the potential for a greatly improved thermosetting polymer matrix for design of composites for use under highly aggressive conditions.

The literature includes some work on the orientational effect of carbon fibers on liquid crystalline melts [8] [9] [10]. For oriented polymers, it is well-known that the CTE in the direction of orientation is less than that in the

transverse direction [11] [12]. It is possible to generate liquid crystalline character in ATSP by controlling the monomer feed ratio. The liquid crystalline behavior seen in aromatic thermosetting systems has potential to help match the CTEs of ATSP and carbon fiber and provide better interfacial bonding to generate composites with high thermal fatigue resistance. This paper discusses liquid crystalline behavior of ATSP in the presence of carbon fiber and how it translates into better thermal fatigue resistance compared to epoxy composites.

Experimental Procedure

Oligomer Synthesis

The resin system is a two part oligomeric system (one consisting of carboxylic end groups [C2] and the other consisting of acetoxy end groups [A2]). 4-Acetoxybenzoic acid (ABA) and hydroquinone diacetate (HQDA) were prepared by the acetylation of pHBA and HQ (Sigma-Aldrich), respectively. C2 oligomers were synthesized by melt-condensation of TMA, ABA, IPA and HQDA (molar ratio 1:6:4:4 respectively) at 260 °C.

A2 oligomers were synthesized similarly with TMA, ABA, IPA and HQDA taken in the molar ratio 1:5:2:5. These ratios were used because it was reported that they would promote liquid crystalline character in the two oligomers. The synthesis procedure was closely followed to that given in [3].

Epon 828 resin and Epicure W curing agent were obtained from Hexion.

Composite manufacture

Unidirectional carbon fiber fabric Hex-3R wrap 103 (Hexcel) was used to produce both ATSP and epoxy composites for testing.

The ATSP composite was made by compression molding of the oligomer mixture (C2:A2 = 1.1:1) in a hot-press. The oligomer mixture (50 wt%) was dissolved in N-methyl-2-pyrrolidinone (NMP). The fibers were laid-up with the NMP solution and were sandwiched between platens, thermalimide sheet (Airtech), and non-porous PTFE coated fiberglass fabric (McMaster Carr). As illustrated in Figure 2, an 8 hour cure cycle was used for making the composite. A pressure of 1MPa (~150 psi) was applied after one hour at 270 °C during curing. Vacuum was applied to the hot-press chamber to facilitate removal of the acetic acid byproduct. These single ply cured lamina were cut into 5x5 cm squares that were subjected to an ITR cycle (4 hours at 340 °C) to give 4 ply [0/90/0/90] samples for thermal fatigue testing. Two adjacent faces of the composites were picked and polished

to facilitate microscopy. The surface plies were not used for testing due to difficulty to polish those regions. Figure 3 shows a schematic of the samples used and ply faces used for the study.

In the case of the epoxy composites, carbon fiber was impregnated with a mixture of Epon 828 and Epicure W (100:26.4 by weight). The cure cycle shown in Figure 4 was used to obtain 4 ply [0/90/0/90] epoxy composites.

Characterization

C2 and A2 oligomers were observed in a Reichert optical microscope equipped with a heating stage and cross-polarizers under 10x magnification. A small amount of the NMP solution was spread on a glass slide. The slide was heated at 205 °C on the heating stage to evaporate the solvent, leaving a thin polymeric film. A cover slip was placed on the slide then. The onset of liquid crystallinity marked by a characteristic birefringence pattern was observed against a dark background. The samples were viewed in transmission mode and pictures were taken using a digital camera (Canon Powershot G25). C2-A2 oligomers with carbon fibers were analyzed similarly.

Thermal fatigue testing was done by immersing the samples in liquid nitrogen (-196 °C) for 10 mins and heating it up in the oven at 80 °C for 10 mins. 20 such cycles were repeated both on ATSP and Epoxy samples. Mitutoyo Optical Microscope with 10x magnification was used to observe microcrack development in the composites.

Results and Discussion

Pictures taken by an optical microscope equipped with cross-polarizers indicated an onset of a melting liquid crystalline transition at around 160-170 °C. Figure 5 shows the birefringence pattern observed for C2-A2 oligomer mixture at around 160 °C. Higher intensity of birefringence at the surface of the carbon fibers suggests orientational behavior of the oligomers at the interface. After curing, C2-A2 oligomer mixture at 270 °C, in presence of carbon fiber, (Figure 6) shows birefringence suggesting the orientational behavior persists even after curing. C2 and A2 show this behavior due to higher persistence length and lesser branching (average functionality of 3) compared to other oligomers compositions (average functionality of 4). It is expected that the orientational effect of the resin would enhance the interfacial bonding at the interface of fibers and matrix.

Thermal fatigue tests suggest that ATSP has a better resistance to microcracking than epoxy. On an average, after 20 cycles, ATSP develops 15 cracks compared to 35

cracks for epoxy. Epoxy shows significant longitudinal microcracks as compared to ATSP which showed only transverse cracking, and a few smaller cracks not spanning the thickness of the lamina. Epoxy had a few cracks and voids even before the thermal fatigue testing. Some representative pictures are shown in Figure 7 and Figure 8.

Conclusions

We have demonstrated the liquid crystallinity of ATSP that enhances the thermal fatigue behavior in carbon fiber composites. Liquid crystalline ATSP orients in the direction of the carbon fiber, suggesting a better interfacial CTE match. Thermal fatigue tests (from -196 °C to 80 °C) were done on model 4 ply samples of ATSP and epoxy. ATSP shows better resistance to microcracking compared to epoxy composites. This is probably due to the liquid crystalline behavior leading to reduced stresses at the interface.

ATSP appears to be an important candidate for automotive composites because of the enhanced thermal fatigue resistance and other advantages listed earlier.

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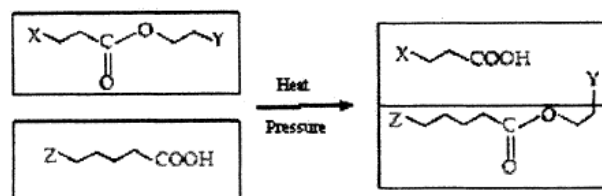


Figure 1. Interchain transesterification reactions leading to bonding [11].

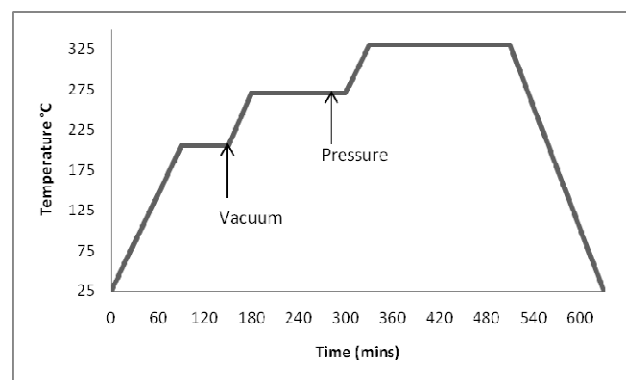


Figure 2. Cure cycle of ATSP. The point at which pressure and vacuum was applied is indicated by arrows.

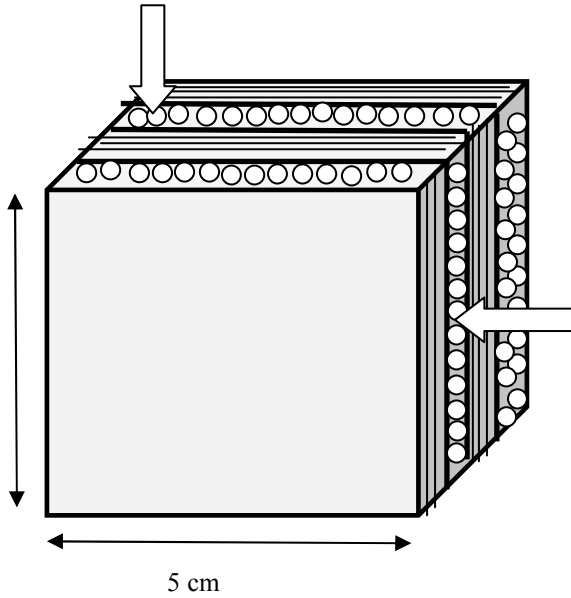


Figure 3. 4 ply [0/90/0/90] samples for thermal fatigue. The surface plies marked with arrows were used for studying microcracking by optical microscopy.

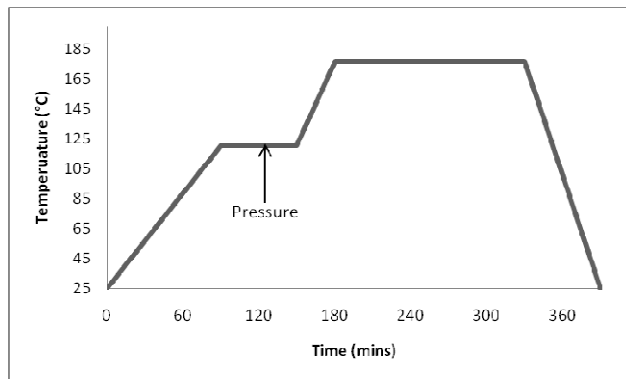


Figure 4. Cure cycle of Epoxy. The point at which pressure was applied is indicated by an arrow.

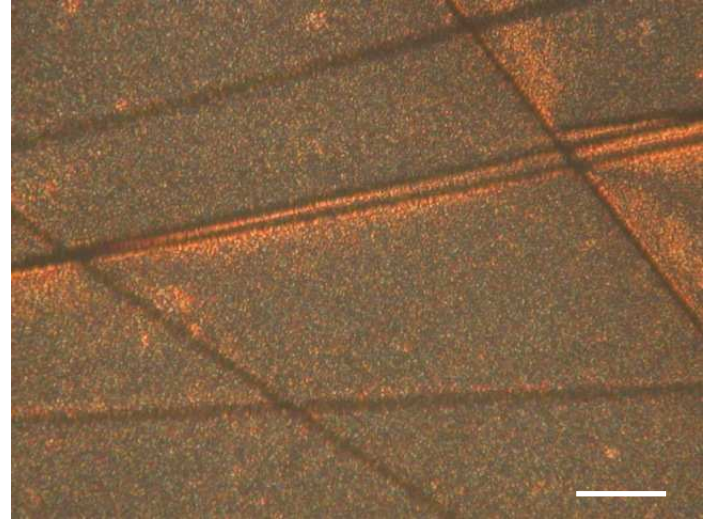


Figure 5. C2-A2 oligomer mixture observed in transmission optical microscope equipped with cross-polarizers while heating at 160-170 °C. Bar is 50 μm

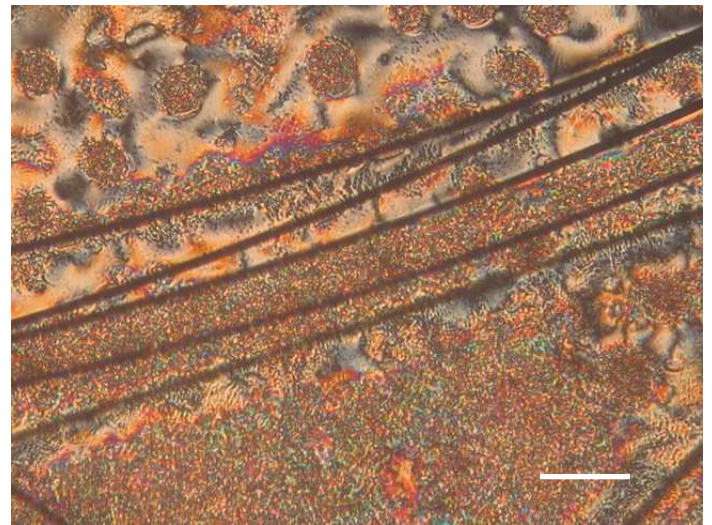


Figure 6. C2-A2 oligomer mixture with carbon fibers observed in transmission optical microscope equipped with cross-polars after curing around 275 °C. Bar is 50 μm .



Figure 7. Typical microcracking of Epoxy sample after 20 cycle. Bar is 50 μm .

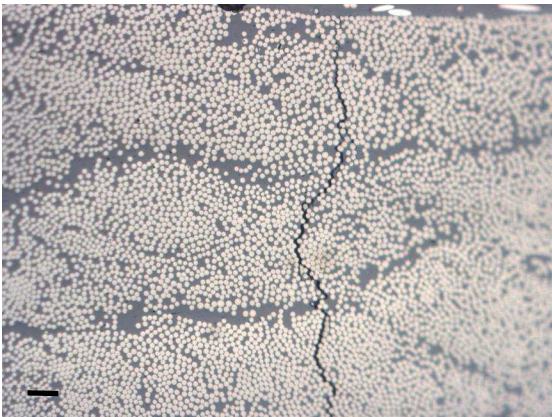


Figure 8. Typical microcracking of ATSP sample after 20 cycle. Bar is 50 μm .