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Characterization of Fourth-Generation High-Temperature Discontinuous Fiber Molding Compounds

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Abstract: Thermal, physical, and mechanical properties of discontinuous fiber molding compounds incorporating fourth-generation high temperature matrices and T650-35 carbon fiber were characterized as a function of matrix chemistry. These new, lower cost structural materials provide an alternative to traditional wet lay-up prepreg materials with out-of-autoclave processability, no volatile evolution during cure, and no toxicity. Measured maximum properties include a glass transition temperature of 456°C, flexural strength of 376 MPa, compression strength up to 236 MPa, compression modulus up to 30 GPa, and short beam shear strength of ~50 MPa.

Keywords: Composites; High-temperature materials; Polyimides; Poly(imide siloxanes)

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INTRODUCTION

Both reinforcing fibers and matrix resins are very important in producing fiber composites with excellent thermal and mechanical properties. Addition cure polyimide matrix composites are being targeted for use in commercial aerospace, power generation, and offshore drilling applications requiring structural performance and durability in high-temperature oxidative environments.^[1-13]

Thermoset polyimides have excellent mechanical properties, low relative permittivity, high breakdown voltage, low losses over a wide frequency range, wear resistance, good solvent resistance, low thermal expansion, and excellent thermo-oxidative stability. Compared to condensation cure polyimides, thermoset polyimides have the advantageous ability to be processed into relatively thick, void-free composite laminates.

In thermoset polyimide composite processing, solvent removal and imidization (cyclodehydration to imide) is completed prior to the application of pressure, allowing cross-linking to occur at higher temperatures without the evolution of volatiles. Existing state of the art organic matrix composites are, however, limited in use by temperature and environmental durability because of the inherent fundamental limitations of organic chemistry.

Similar to polyimides, polysiloxanes possess unique properties, including performance tailorability and good thermal stability. The viscoelastic cold flow behavior of polysiloxanes however, renders them unusable as high-temperature structural composite matrix materials. Significant research in recent years has focused on improving processing and performance of condensation type polyimides through incorporation of inorganic (predominantly dimethylsiloxane) moieties into the polyimide backbone and sol-gel routes to provide interconnected polyimide/silica hybrid systems.^[14,15] Incorporation of flexible siloxane segments significantly enhances flexibility in the polyimide backbone, can improve thermomechanical performance, improves transparency, reduces the dielectric constant, improves adhesion, provides for molecular design flexibility, and improves melt flow characteristics.

We have referred to advanced high-temperature polymer and organic-inorganic polymer technology as *fourth-generation* high-temperature materials as the state of polyimide technology has evolved from condensation-type thermoplastic polyimides in the 1950s, thermosetting norbornene terminated polyimides such as PMR-15 in the 1970s, vinyl and acetylene terminated polyimides in the 1980s and 1990s, to novel organic and organic-inorganic hybrid chemistries of today.^[1-4,12]

This work seeks to characterize the thermal, physical, and mechanical performance of a specific class of fourth-generation materials

in early-stage commercial development: high-temperature fiber molding compounds. These low-cost discontinuous fiber and textile reinforced materials offer significant advantages to traditional polyimide prepreg materials as they are processed out of autoclave, compression molded under moderate temperatures and pressures into complex shapes, free of volatiles and toxic components, have an infinite shelf life, and exhibit excellent high-temperature strength and thermo-oxidative stability.

EXPERIMENTAL SECTION

Materials

Fourth-generation high-temperature molding compounds of various chemistries were manufactured by Performance Polymer Solutions Inc. (Centerville, Ohio, USA), using a proprietary manufacturing process that rapidly yields solvent- and volatile-free thermosetting molding compounds of discontinuous fibers or textiles. In this work, 13 mm discontinuous fiber tow (T650-35, 6K tow, Cytec Carbon Fibers) was used as the molding compound reinforcement. Multiple test panels of three developmental matrix materials, A, H, and AC, varying primarily in cross-link density (Table I), were fabricated by filling a 413 cm² steel mold with fiber molding compound (Figure 1) and compression molding under 150–1000 psi pressure (Figure 2). The cure temperature was 343°C for 4h followed by a 371°C/6h post-cure under nitrogen atmosphere. Test specimens were sectioned using a diamond-blade wet saw.

Physical Characterization

Mass density, fiber volume fraction, and void content were determined using ASTM D3171 (Procedure B)/D792 standard. Composite panels were subjected to through transmission C-scan for quality analysis.

Table I. Matrix of materials characterized in this work

| Panel code | Matrix | Fiber | Fiber length |
|------------|--------|---------|--------------|
| AC-070725 | AC | T650-35 | 13 mm |
| AC-070728 | AC | T650-35 | 13 mm |
| A-080826 | A | T650-35 | 13 mm |
| H-080122 | H | T650-35 | 13 mm |
| H-080117 | H | T650-35 | 13 mm |



Figure 1. Mold filling with fiber molding compound.

Thermal Characterization

Dynamic mechanical analysis (DMA) was performed using a Perkin-Elmer DMA 7. The spectra were obtained in three-point bending mode at a frequency of 1 Hz and heating rate of 5°C/min to 500°C.



Figure 2. Molding compound plate after post-cure.

Glass transition temperature was determined from the onset of the storage modulus versus temperature curve. The thermal oxidative stability of the materials was analyzed by thermogravimetric analysis (TGA) using a TA Instruments model TA-SDT Q600 at a heating rate of 10°C/min up to 1000°C in air.

Mechanical Characterization

The compression, flexural, and short-beam shear properties have been measured as per the ASTM D695, ASTM D7264, and ASTM D2344 standards, respectively, using an Instron 4204 electromechanical testing machine. The flexural properties were measured using a 900 N load cell and the compression properties using 44 kN capacity load cell. All data were collected every 0.5 s at a displacement rate of 1.27 mm/min. Procedure B of ASTM D7264 was used to carry out the four-point flexural test. The specimens for the four-point flexural test had a span of 94 mm. A span of five times the thickness was employed for the short beam shear test.

RESULTS

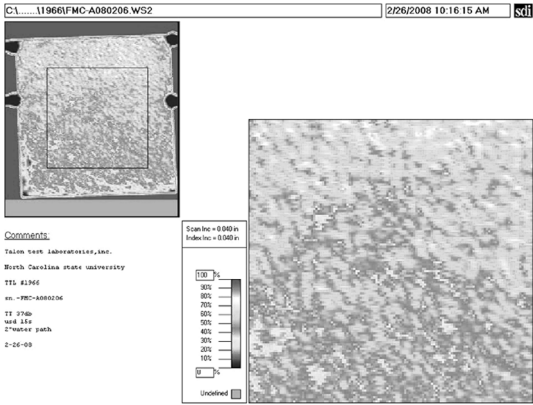
Physical Characterization

C-scan images for representative panels are shown in Figure 3. Panels A-080206 and H-080117 represent uniform parts with some slightly increased porosity, lack of bonding, or other restriction to sound at the panel edges. H-080122 shows dramatic loss in quality (dramatic loss of sound) along the top edge and one lower corner, and significant surface porosity was observed on the panel.

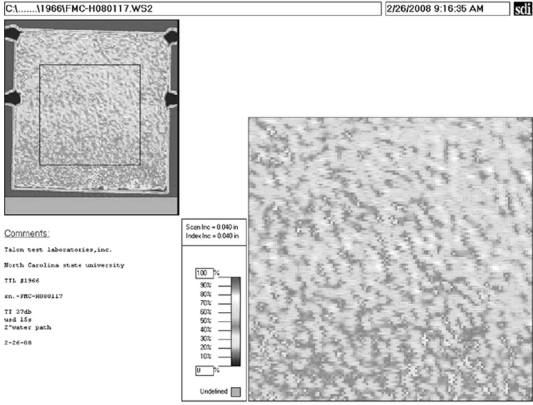
Acid digestion results (Table II) revealed findings similar to the C-scan observations, with panel A-080826 demonstrating low void content (1%) and panel H-080122 displaying a 6% porosity value. Panel AC revealed extremely high porosity (14%), but all other panels were deemed suitable for testing. Note that some intrinsic error exists in the calculation of void content as the density of the resin in the composite is assumed (here, 1.4 g/cm³).

Thermal Characterization

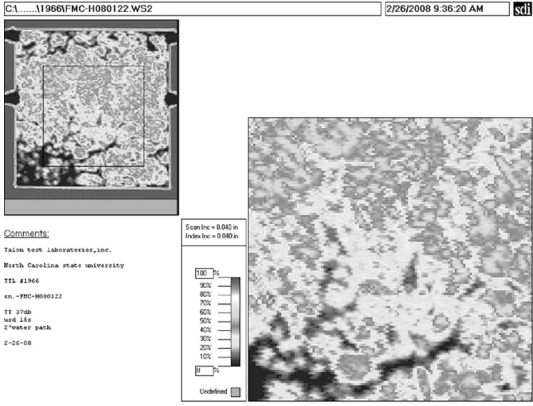
Since the materials are of proprietary but similar chemistry, the mass loss in air (Figures 4 and 5) revealed similar characteristics with



(a)



(b)



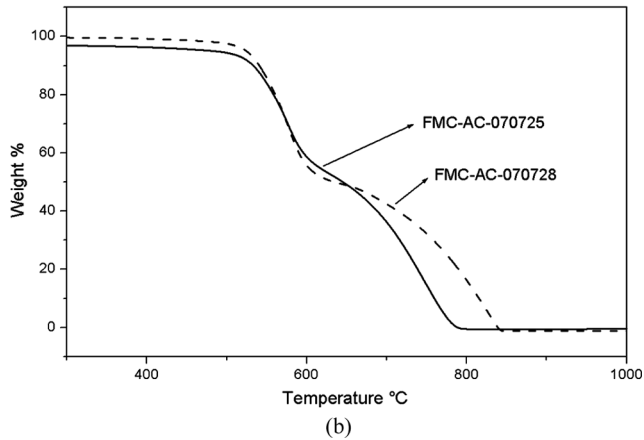
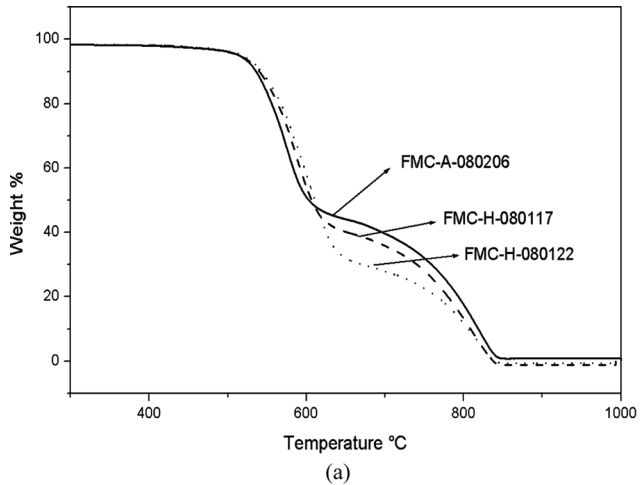
(c)

Figure 3. C-scan images for molding compound (a) A-080206, (b) H-080117, and (c) H-080122.

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Table II. Panel physical properties determined from ASTM D3171

| Panel code | Mass density (g/cm ³) | Fiber volume fraction (%) | Void volume (%) |
|------------|--------------------------------------|------------------------------|--------------------|
| AC-070725 | 1.324 | 32 | 14 |
| AC-070728 | 1.471 | 35 | 5 |
| A-080826 | 1.549 | 41 | 1 |
| H-080122 | 1.430 | 29 | 6 |
| H-080117 | 1.463 | 30 | 4 |

**Figure 4.** (a) and (b) TGA scan of various molding compound panels in air.

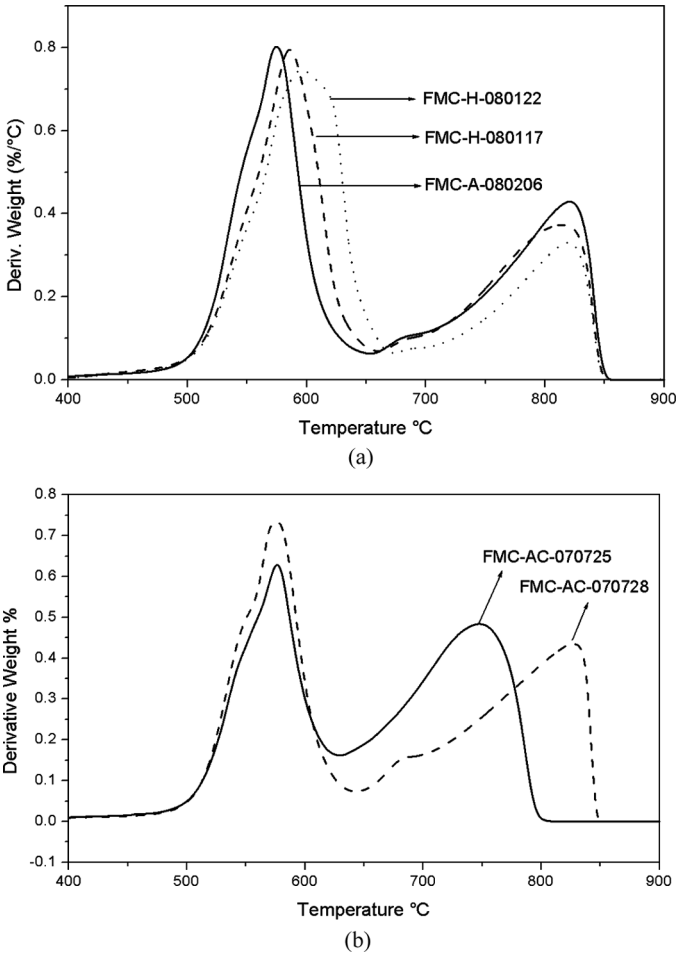


Figure 5. (a) and (b) TGA scan of various molding compound panels in air displaying derivative.

decomposition of the matrix occurring at a significant rate above 550°C and oxidation of the carbon fibers occurring rapidly above 800°C. Differences shown in the maximum oxidation rate above 700°C in Figure 5(b) are likely an artifact of exposed carbon fiber surface area in the specimen in the TGA experiment, not related to the chemical makeup of the material.

Typical DMA spectra for all composite panels are shown in Figure 6, and the quantitative glass transition temperature measurements are summarized in Table III. Material H was found to exhibit

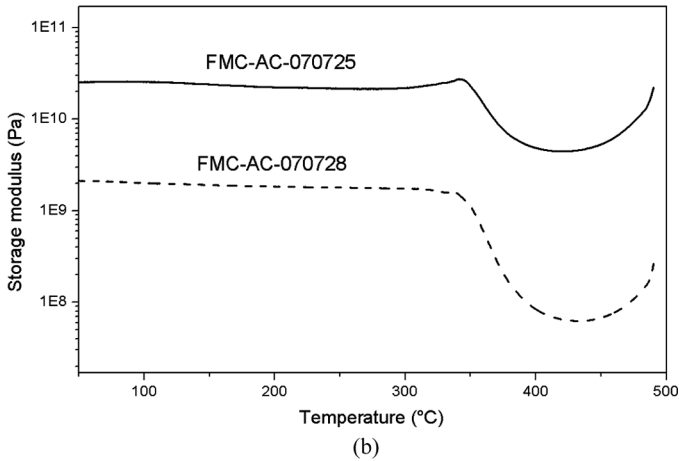
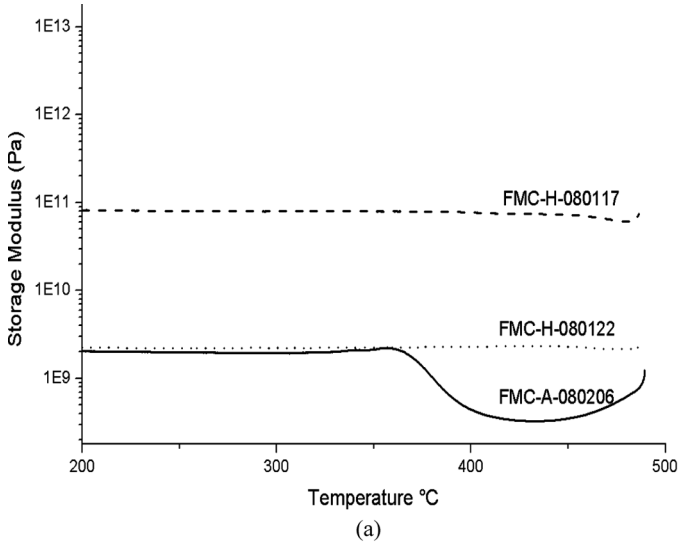


Figure 6. (a) and (b) Dynamic mechanical spectra of composite panels. Storage modulus values are only apparent values.

the highest glass transition temperature of 456°C with less than 1°C variation between the two panels for material H. Material AC exhibited the lowest average glass transition temperature of 344°C, and material A exhibited a glass transition temperature of 362°C. Material chemistries varied primarily in the distance between cross-links, with material H formulated with the highest cross-link density.

Table III. Panel thermal properties

| Panel code | Glass transition temperature (°C) |
|------------|-----------------------------------|
| AC-070725 | 345 |
| AC-070728 | 343 |
| A-080826 | 362 |
| H-080122 | 455 |
| H-080117 | 456 |

Mechanical Characterization

Table IV summarizes the flexural properties of the various materials characterized in this work. As expected from C-scan and acid digestion results, panel AC-070725 exhibited low mechanical strength and stiffness compared to the lower porosity panel AC-070728. These differences were not as apparent when evaluating compression properties (Table V). Compression strength is not as affected by porosity as shear, flexural, or tensile deformation.

Comparing the various materials of nearly equivalent low porosity, the order of flexural strength followed the trend AC ≫ A > H. Flexural

Table IV. Panel flexural properties

| Panel code | Flexural strength (MPa) | Flexural modulus (GPa) |
|------------|-------------------------|------------------------|
| AC-070725 | 240 ± 56 | 19 ± 3 |
| AC-070728 | 376 ± 90 | 28 ± 7 |
| A-080826 | 272 ± 41 | 32 ± 5 |
| H-080122 | 245 ± 36 | 25 ± 4 |
| H-080117 | 137 ± 32 | 20 ± 2 |

Table V. Panel compression properties

| Panel code | Compression strength (MPa) | Compression modulus (GPa) |
|------------|----------------------------|---------------------------|
| AC-070725 | 129 ± 41 | 22 ± 5 |
| AC-070728 | 222 ± 29 | 30 ± 5 |
| A-080826 | 236 ± 21 | 24 ± 6 |
| H-080122 | 191 ± 18 | 17 ± 5 |
| H-080117 | 208 ± 35 | 14 ± 2 |

Table VI. Panel short beam shear properties

| Panel code | Short beam shear strength (MPa) |
|------------|---------------------------------|
| AC-070725 | Not measured |
| AC-070728 | Not measured |
| A-080826 | 49 ± 16 |
| H-080122 | 49 ± 8 |
| H-080117 | 41 ± 8 |

modulus yielded similar values for AC and A within the standard deviation, with the average value $\sim 50\%$ higher than that of material H. Compression strength of all materials was within the standard deviation (with the exception of the high-porosity AC-070725 laminate), averaging 214 MPa. Compression modulus values were similar for materials A and AC, which were approximately 75% higher than that of material H. Short beam shear strength of materials H and A were equivalent within the standard deviation (Table VI).

As noted from cumulative analysis of the results, porosity and matrix properties play critical roles in the performance of these high-temperature molding compounds. Although material H exhibited the highest glass transition temperature of the materials characterized, it also exhibited, in general, the lowest mechanical strength and stiffness, likely owing to its reduced toughness resulting from low molecular weight between cross-links. Panel porosity, resulting from non-optimized processing conditions, reduced the flexural and shear properties of the panels, regardless of matrix chemistry. Overall, the structural performance of the materials in compression, shear, and flexural deformation is excellent when the laminate porosity is low.

CONCLUSION

A series of high-temperature molding compounds based on fourth-generation high-temperature materials were characterized for physical, thermal, and mechanical properties. Fiber molding compounds provided rapid and facile fabrication of composite plates. All materials were found to exhibit excellent thermal properties with high oxidative decomposition temperatures and high glass transition temperatures (343° – 456° C). Flexural, shear, and compressive mechanical properties were good when the void content of the composite panels was less than 5%. Matrix cross-link density was found to influence glass transition temperature

and mechanical performance: lower cross-link density resulted in lower glass transition temperature but higher mechanical performance.

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