NANOSILICA-MODIFIED EPOXY MATRIX RESIN FOR PREPREG COMPOSITE TOOLING APPLICATIONS

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ABSTRACT

Modification of composite matrix resins with spherical nanoscale silica has been shown to produce desirable changes in matrix coefficient of thermal expansion, cure shrinkage, cure exotherm, and hardness, as well as resin mechanical properties including modulus and fracture toughness. This study examines the effect of incorporating 43 wt% nanosilica into a tooling-specific prepreg resin on both resin and carbon fabric composite properties. Surface hardness is quantified by both macroscale and nanoscale testing. The effect on thermal distortion of curved composite laminates is illustrated.

1. INTRODUCTION

Fiber-reinforced polymer matrix composite materials are attractive materials for tools used for the manufacture of composite parts. Low coefficients of thermal expansion similar to composite parts and high stiffness ensure dimensional fidelity. High specific strength and stiffness as well as design flexibility allow composite tools to be significantly lighter than metal tools, with easier handling in manufacturing settings and reduced thermal mass. Tool faces for curved surfaces can be formed by laying up a tooling composite laminate on a model made from an easily-machined material such as high density foam, partially curing the tool face at a temperature appropriate to the model material, and then completing the tool face cure with a high temperature free-standing post-cure. The tool face can then be integrated into an overall support structure. Together the material properties, design flexibility, and manufacturing options enable cost-effective, high-performance tools.

Composite tooling also places special demands on material properties that are uniquely important for this application. Dimensional accuracy and stability affect the difficulty of part design and manufacturing concerns such as demolding, multi-part fit-up, and accuracy of secondary part manufacturing operations. The durability of the tool can determine the tool lifetime as well as the necessity of maintenance and repair—factors profoundly affecting the overall cost of manufacturing composite parts. Durability is a multifaceted concern. Resistance of the tool surface to damage affects the part surface finish. Progressive matrix damage due to thermal cycling can lead to mechanical and dimensional compromise of a tool. Maintaining vacuum integrity is a prime concern. The overall ruggedness of a tool can be a concern during handling in a manufacturing environment. In addition, tooling prepregs are often reinforced with high fiber areal weight carbon fabric, sometimes with high resin content. Often the thickness of laminates

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used for tooling composites is significantly greater than usual for composite parts. Cure exotherm for thick-section constructions can be a consideration.

Many of the advantages and special requirements for composite tooling materials depend on the matrix resin properties and performance. Unfortunately, most of the properties of conventional epoxy and bismaleimide resins can be varied only in a narrow range. In bulk applications of polymers, inorganic fillers are often used to increase stiffness and hardness, decrease cure shrinkage and the coefficient of thermal expansion (CTE), and modify other properties relevant to tooling. However, conventional inorganic filler technology is not appropriate for fiber composite matrix resins because the particles are filtered out of the resin during fiber impregnation. In addition, the increase in resin viscosity from high levels of conventional fillers is too great for composite processing.

However, the improvements from inorganic particle incorporation can be realized in fiber-reinforced composites by using nanoscale inorganic particle technology. Appropriately surface-functionalized spherical nanoscale particles enable production of non-aggregated dispersions in epoxy resins with levels over 50 wt%. Unlike larger inorganic particles, these can be evenly dispersed throughout a fiber composite structure without filtration by the fiber array. Past work by the present authors and others has shown that the incorporation of spherical nanoscale amorphous silica can improve matrix resin properties that translate into improvements in fiber reinforced composite processing and properties [1-8]. Composite matrix resin mechanical properties including modulus and fracture toughness showed significant, monotonically increasing improvement with increasing nanosilica concentration. Desirable changes in coefficient of thermal expansion, cure exotherm, and hardness were also measured. Silica concentration levels did not adversely affect the cured glass transition temperature or prepreg processability. Properties of carbon fiber laminates made with unidirectional prepregs of varying silica loading levels revealed significant improvements in compression strength, in-plane shear modulus, and 0° flexure strength. In general, the benefit of matrix modification with nanosilica is increased with increased loading levels.

Previous work by the present investigators has demonstrated the benefits of incorporating a high loading (up to 45 wt%) of nanoscale silica into epoxy matrix materials for unidirectional carbon fiber prepregs for both 121 °C (250 °F) and 180 °C (350 °F) curing [1-4]. The properties reported for the prepregs suggests the advantages of nanosilica modification for tooling.

This study focuses on implementation of nanosilica matrix technology in a tooling-specific fabric-reinforced prepreg. As noted previously, the specific curing characteristics required for tool manufacturing are varied, requiring a portfolio of prepreg systems designed for use in composite tooling applications. The intent here is to establish the viability and characteristics of elevated temperature composites with high nanoparticle loadings, cured by low temperature initial cure cycles suitable for autoclave and out-of-autoclave (OOA) processing. The present work uses a developmental nanosilica-filled (43 wt%) epoxy resin designed for initial low temperature (63 °C, 140 °F) cure, high temperature post-cure (200 °C), and suitable for out of autoclave processing, referred to as Fortified Tooling Prepreg 140F epoxy (FTP 140F). This study examines the
processibility of the resin for prepreg, the quality of nanoparticle dispersion, and neat resin physical and mechanical properties, and tooling-relevant properties of carbon fiber fabric laminates made with this resin as well as an unmodified control resin. Emphasis was placed on composite properties of particular importance to composite tooling, including surface hardness and dimensional stability.

2. EXPERIMENTAL

2.1 Materials and Resin Sample Preparation

Resin samples were generated by use of FTP 140F containing 43 wt% silica of nominal particle size 86 nm and cured with an imidazole curative. A control sample containing no silica was also made. Resin/curative mixtures were blended into the pre-warmed (60 °C), nanosilica-filled epoxies with a DAC 600 SpeedMixer (Flacktek, Landrum, SC) at 2350 rpm for 45 seconds to produce well-dispersed blends. These blends were degassed under vacuum for 3-5 minutes prior to being poured into appropriate molds for neat resin testing. The samples were cured in a forced air oven for 14 hours at 63 °C and then for an additional 2 hours at 200 °C.

2.2 Uncured Resin Test Methods

Rheological analyses of these nanosilica-epoxy resin/curative systems were conducted on an ARES rheometer (TA Instruments, New Castle, DE) in parallel plate dynamic mode. Samples 50 mm in diameter (50 mm diameter top and bottom plate) and 1 mm thick were heated from 50 °C to 180 °C at 2 °C/min, at a frequency of 1 Hz and a nominal strain of 2%.

The cure exotherm was obtained using a modification of ASTM D3418-08, conducted on a TA Q2000 differential scanning calorimeter (DSC, TA Instruments). Uncured resin samples were heated from -30 °C to 330 °C at 10 °C/min.

Linear shrinkage of the resins during cure was measured using ASTM D2566-86. All interior surfaces of a semi-cylindrical steel trough mold of dimensions 2.54 cm diameter by 25.4 cm length were coated with mold release.

2.3 Cured Resin Test Methods

Resin silica content was determined using a 5 to 10 mg cured sample placed in a TA Instruments Q500 thermogravimetric analyzer (TGA) (TA Instruments). Samples were heated in air from 30 °C to 850 °C at 20 °C/min. The noncombustible residue was taken to be the resin’s original nanosilica content.

The glass transition temperature, T_g, of cured resins were obtained by Dynamic Mechanical Analysis (DMA) using an RSA2 Solids Analyzer (Rheometrics Scientific, Inc, Piscataway, NJ) in the dual cantilever beam mode. Experiments were performed using a temperature ramp of -30 °C to 350 °C at 5 °C/min, a frequency of 1 Hz, and a strain of 0.03 to 0.10%. The peak temperature of the tan delta curve was reported as the T_g.
Density of cured resin specimens was measured by ASTM D792-86, Test Method B where n-heptane (d = 0.684 g/cc) was used as the immersion liquid. For each material, four specimens were measured and the average density was reported in g/cc.

Barcol hardness ($H_B$) was measured according to ASTM D2583-95 (Reapproved 2001). A Barcol Impressor (Model GYZJ-934-1, available from Barber-Colman Company, Leesburg, VA) was used to make measurements. For each specimen, between 5 and 10 measurements were made and the average value was reported.

Coefficient of thermal expansion (CTE) measurements were performed using a TMA Q400 (TA Instruments) with a macroexpansion probe. A force of 1.0 N was applied and the specimen lengths were measured at room temperature. The specimens were cycled from 0 °C, to 180 °C five times. The CTE was taken to be a curve fit from 0 °C to 170 °C on the fifth heat for composite laminate samples. For neat resin specimens CTE was taken to be a curve fit from 0 °C to 50 °C on the second heat.

Fracture toughness was measured according to ASTM D5045-99 using a compact tension geometry, wherein the specimens had nominal dimensions of 3.18 cm by 3.05 cm by 0.64 cm with $W = 2.54$ cm, $a = 1.27$ cm, and $B = 0.64$ cm. A modified loading rate of 1.3 mm/min (0.050 in/min) was used.

The tensile strengths, failure strains, and moduli of the resins at room temperature were measured according to ASTM D638 using a “Type I” specimen. The loading rate was 1.3 mm/min (0.05 in/min). Five specimens were tested for each sample.

A Hitachi H-9000 transmission electron microscope (TEM) was used to examine prepared samples. Cured samples for TEM observation were microtomed at the thickness of 87 nm at room temperature.

Samples for nanoindentation analysis were cut from the larger neat resin plaques and affixed to metal pucks with a stiff double-sided adhesive tape. The sample surfaces were polished with a lapping pad by hand and a cross sectional polisher to smooth the surfaces.

Nanoindentation studies were performed using an MTS Nanoindenter XP with a DCM module using Continuous Stiffness Measurement (CSM). Load and displacement of a Berkovich diamond probe into the surface were used to calculate the sample modulus and hardness over hundreds of depths for a single indentation. Each sample was loaded to a maximum force of approximately 17 mN. Data was averaged over indentation depths from 500-1000 nm. Nanoscratching was performed by applying a normal load to the sample while simultaneously monitoring the lateral force required to move the probe forward and the depth of the probe relative to the surface. A cube-corner diamond probe was used for scratch testing experiments using an edge of the cube-corner as the leading edge. Three passes over the same area for each scratch were employed. The probe first maps the topography of the surface by tracing the length of the region to be scratched with a minimal force of 10 µN. Then the probe returns to the origin to perform the nanoscratch with an initial force of 10µN, then ramping linearly to 100 mN over the next 500 nm. Finally, the probe unloads the force to 10 µN to profile a further 100 nm of
The probe returns again to the origin to profile the indentation post-scratch to determine the depth of the scratch under a loading force of 10 μN.

2.4 Carbon Fiber Composite Sample Preparation

Fabric prepreg for the FTP 140F system resin system was produced using T300-3k and T700-12k 2x2 twill carbon fabric. The 127 cm wide fabric prepregs had nominal fiber areal weights of 200 g/m² and 670 g/m² for the T300 and T700 fabrics, respectively.

For comparison, commercially available control prepregs made with conventional epoxy matrix resin and T300-3k and T700-12k 2x2 twill carbon fabrics were obtained. The fiber areal weights were the same as for the FTP 140F prepregs.

Composite laminates for mechanical testing were prepared using typical autoclave and vacuum bag techniques to achieve porosity-free samples. Laminates were heated from room temperature to 63 °C at 5 °C/min using 0.6 MPa of pressure. The laminates were cured at 63 °C for 10 hours, then were allowed to slowly cool to below 37 °C before removal. The resulting laminates underwent a free-standing post-cure at 200 °C for 4 hours and then were allowed to slowly cool to below 37 °C before removal.

Four types of laminates were made from the control and FTP 140F prepregs. Laminates a-c were made using the T300 prepreg: a) [0]₈ for compression, b) [0]₁₄ for 0° flexure, c) [-45/+45]₃ₛ for in-plane shear and d) a 1:n:1 tool-face laminate (where n = 6 or 8) fabricated with T300 on the outer plies and T700 on the inner plies. Nominal cured ply thickness for laminates a-c) was 0.129 mm. A wet diamond-blade saw was used to cut specimens.

2.5 Carbon Fiber Composite Test Methods

Images of polished cross-sections were taken using a Hitachi S-4700 Field Emission Scanning Electron Microscope (FESEM) in compositional imaging mode. Compositional imaging uses backscattered electrons to highlight elemental composition with areas of higher average atomic number appearing brighter in images. This mode is helpful to distinguish the nanoscale silica from the surrounding organic material.

Compression strength of the composite laminates was measured according to the Suppliers of Advanced Composite Materials Association recommended method SRM 1R-94 “Recommended Test Method for Compressive Properties of Oriented Fiber-Resin Composites.” Tabs were cut from twelve-ply laminates of a common commercial carbon fiber prepreg tape made using a [0, 90]₃ₛ, lay-up. The tabs were bonded using a scrimmed epoxy film adhesive AF163-2 (3M, Saint Paul, MN) so that a consistent gage section of 4.75 mm was obtained. A “Modified ASTM D695” test fixture (Wyoming Test Fixtures, Inc., Salt Lake City, UT) was used with bolt torques of 113 N-cm. A spherically-seated lower platen and a fixed upper platen were used to compress the specimens at a rate of 1.27 mm/min. Nine specimens of each laminate were tested.

In-plane shear modulus was determined by the procedure of ASTM D 3518. Eight specimens were tested from each panel. A biaxial extensometer was employed.
Following the standard, the shear modulus was taken to be the chord modulus between 2,000 and 6,000 micro-shear-strain.

Flexure testing was conducted following ASTM D790 using a nominal strain rate of (0.10 mm/mm/min). Five specimens measuring 127.0 x 12.7 x 3.2 mm were cut in the 0° direction from the laminate. A span:depth ratio of 32:1 was used.

Hardness was measured by the nanoindentation method described above as well as by using a Vickers Hardness tester, sampling areas of the laminate surface both where the fabric yarns neared the surface and in local resin-rich areas. The Vickers method was used rather than the Barcol hardness test in order to allow distinguishing the type of area that was being sampled, yet make a “macroscale” hardness measurement.

3. RESULTS AND DISCUSSION

3.1 Neat Resin Properties

The TEM micrograph in Figure 1 demonstrates that a non-agglomerated, non-aggregated dispersion was obtained in the FTP 140F system having a nanosilica loading of 43 wt%.

![Figure 1. TEM Micrograph of nanosilica dispersion at 43 wt % nanosilica (at 10,000x instrument magnification)](image)

To illustrate the neat resin property enhancements produced through the inclusion of this high level of well-dispersed nanosilica, the FTP 140F resin system was compared to the unfilled control of otherwise identical epoxy composition. Table 1 summarizes the neat resin data for the FTP 140F resin system and the control system.

Density of the cured resin samples are shown in Table 1. Typical carbon fiber prepregs have fiber volume fractions of about 60%, so the increase in density of prepreg-based composites with nanosilica modification is a few percent [1-4]. As will be seen, the accompanying gain in composite properties offer composite designers latitude in eliminating carbon fiber and other weight- and cost-saving strategies. These can result in an overall reduction in part weight for equal strength or stiffness.
Table 1. Matrix Resin Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Control</th>
<th>FTP 140F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica (wt%)</td>
<td>0</td>
<td>43</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>1.23</td>
<td>1.51</td>
</tr>
<tr>
<td>Complex Viscosity @ 63 °C (Pa-s)</td>
<td>6.5</td>
<td>26.3</td>
</tr>
<tr>
<td>Minimum Complex Viscosity (Pa-s)</td>
<td>0.3</td>
<td>1.5</td>
</tr>
<tr>
<td>Cure Exotherm (J/g)</td>
<td>594</td>
<td>231</td>
</tr>
<tr>
<td>$T_g$ (°C)</td>
<td>232</td>
<td>232</td>
</tr>
<tr>
<td>Linear Cure Shrinkage (%)</td>
<td>0.75</td>
<td>0.50</td>
</tr>
<tr>
<td>CTE (μm/m/°C)</td>
<td>46</td>
<td>36</td>
</tr>
<tr>
<td>Tensile Modulus (GPa)</td>
<td>3.1</td>
<td>6.3</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>56.8</td>
<td>67.2</td>
</tr>
<tr>
<td>Tensile Strain (%)</td>
<td>2.6</td>
<td>1.0</td>
</tr>
<tr>
<td>Fracture Toughness (MPa-m$^{1/2}$)</td>
<td>0.51</td>
<td>0.72</td>
</tr>
<tr>
<td>Barcol Hardness ($H_B$)</td>
<td>37</td>
<td>76</td>
</tr>
<tr>
<td>Nanoindentation Modulus (GPa)</td>
<td>4.9</td>
<td>7.3</td>
</tr>
<tr>
<td>Nanoindentation Hardness (GPa)</td>
<td>0.36</td>
<td>0.45</td>
</tr>
</tbody>
</table>

Resin viscosity at processing and curing temperatures is an important criterion for prepreg resin systems. A significant feature of the nanosilica used in the present study is the ability to use high volume fraction loadings without excessive increases in resin viscosity. The prepreg manufacturing process requires a resin system with viscosity-temperature profile enabling both film formation and sufficient flow to produce low-porosity cured composite laminates. Table 1 shows the viscosity of each of the resins at the film-forming and cure temperature of 63 °C. The viscosity ranged from 6.5 Pa-s for the control to 26.3 Pa-s for the 43 wt% silica sample. The increase in viscosity for the 43 wt% sample was sufficiently low to enable excellent low-void composite laminates to be made from the filled formulation. Also listed for reference is the minimum viscosities reached during the temperature sweep used in the rheological test as described in the section on test methods.

A 61 % reduction of cure exotherm was measured for the addition of 43 wt% nanosilica. In a previous study of dicy-cured or aromatic amine-cured resins, the cure exotherm per mass was found to be reduced proportionally to the organic weight fraction. Introduction of inorganic particles lowered the extent of exotherm during cure by reducing the fraction of curable resin [1-2]. This “inert filler” effect accounts for some of the reduction in total exotherm for the FTP 140F resin system, but additional reduction was measured. Further work is needed to understand the cause of the additional reduction. The observed reduction in cure exotherm may be important for the fabrication of thick parts where heat management during cure is crucial.

The glass transition temperatures measured by DMA tan delta peak were identical (232 °C) for the control and 43 wt% nanosilica resins.
As shown in Table 1, both cure shrinkage and the coefficient of thermal expansion are reduced with silica modification. Reduced coefficient of thermal expansion is desirable for composite matrix materials in order to reduce thermal stresses and part distortion, as will be illustrated. Incorporation of 43 wt% silica lowered the matrix resin CTE by 22%.

Additionally, silica incorporation led to an increase in hardness as seen in both macro-scale and nano-scale measurements. Barcol hardness, which uses an arbitrary scale to quantify the force needed to produce a fixed total (elastic and plastic) surface deformation by a stylus, increased twofold (Table 1). Hardness as quantified by nanoindentation further confirmed the much higher hardness of the FTP 140 resin system as shown in Table 1. The increase in nanoindentation hardness suggests that unlike larger filler particles, the nanoscale silica effectively increases hardness on a very small scale; the material is essentially homogeneous on the scale of the indenter. High hardness is believed to enhance tool surface durability and part surface quality.

Nanoindentation techniques were also employed to quantitatively examine the nominal scratch resistance of the resins, a property associated with hardness. Nanoscratch experiments revealed that the control resin is more susceptible to damage. Figure 2 displays images of scratches produced as described earlier. Figure 2 also shows the depth of the probe during the scratch test as well as the depth of the scratch that was produced. The depth of the probe during motion of the probe under force is the result of both plastic and elastic deformation of the sample. The high modulus of the nanosilica-modified resin reduces the elastic component of deformations. After the load is removed, the sample recovers and the remaining scratch is the result of the plastic deformation of the sample. The FTP 140F resin displays higher scratch resistance as shown by the smaller residual scratch depth and width, reflecting the higher nanoindentation hardness measured.

![Figure 2](image-url)

**Figure 2.** Images of nanoindenter scratches in (a) control and (b) nanosilica-modified resins. On left are traces of indenter depth during scratch testing under increasing load and residual scratch depth.
Table 1 lists the tensile modulus as well as the average stress and strain at failure. The tensile modulus is more than doubled relative to the control resin. The failure stress and strain are believed to be lower bounds on the properties since they are significantly affected by defects in the resin castings. Consistent with previous studies [1-4], nanosilica modification produced similar or higher strength levels with reduced failure strain.

Results of resin fracture testing are given in Table 1. The critical plane-strain stress intensity factor, $K_{IC}$, increased by about 48% with incorporation of 43 wt% silica. The increase in $K_{IC}$ shows that the resin is not embrittled even with a dramatic increase in modulus.

3.2 Composite Mechanical Properties

Figure 3 shows a field-emission SEM micrograph of the polished cross-section of a representative T300/FTP 140F composite laminate from this study having 43 wt% nanosilica of nominally 86 nm diameter. The particles have penetrated between 7 μm diameter carbon fibers and fill the interstitial areas between the fibers. This produces a homogeneous mechanical environment for the fibers.

Figure 3. Field Emission SEM image of a polished carbon fiber composite cross-section showing distribution of 86 nm diameter nanosilica in the FTP 140F epoxy resin.

Composite laminate data for the FTP 140F system and the conventional commercial control material are compiled in Tables 2 and 3.
Table 2. Carbon-fiber Composite Properties (T300 fabric)

<table>
<thead>
<tr>
<th>Property</th>
<th>Control</th>
<th>FV</th>
<th>FTP 140F</th>
<th>FV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica (wt%)</td>
<td>0</td>
<td>-</td>
<td>43</td>
<td>-</td>
</tr>
<tr>
<td>In-plane Shear Modulus (GPa)</td>
<td>3.7</td>
<td>60</td>
<td>5.1</td>
<td>51</td>
</tr>
<tr>
<td>Short Beam Shear Strength (MPa)</td>
<td>53.7</td>
<td>56</td>
<td>61.6</td>
<td>56</td>
</tr>
<tr>
<td>Compression Strength (GPa)</td>
<td>0.70</td>
<td>52</td>
<td>1.01</td>
<td>52</td>
</tr>
<tr>
<td>0° Flexure Modulus (GPa)</td>
<td>57.5</td>
<td>56</td>
<td>62.3</td>
<td>52</td>
</tr>
<tr>
<td>0° Flexure Strength (GPa)</td>
<td>0.94</td>
<td>56</td>
<td>0.77</td>
<td>52</td>
</tr>
<tr>
<td>0° Flexure Strain (%)</td>
<td>1.7</td>
<td>56</td>
<td>1.2</td>
<td>52</td>
</tr>
<tr>
<td>Nanoindentation Modulus: Resin Region (GPa)</td>
<td>3.9</td>
<td>53</td>
<td>7.7</td>
<td>53</td>
</tr>
<tr>
<td>Nanoindentation Modulus: Fiber Region (GPa)</td>
<td>7.6</td>
<td>53</td>
<td>16.3</td>
<td>53</td>
</tr>
<tr>
<td>Nanoindentation Hardness: Resin Region (GPa)</td>
<td>0.2</td>
<td>53</td>
<td>0.4</td>
<td>53</td>
</tr>
<tr>
<td>Nanoindentation Hardness: Fiber Region (GPa)</td>
<td>0.5</td>
<td>53</td>
<td>1.4</td>
<td>53</td>
</tr>
<tr>
<td>Vickers Hardness: Resin Region (HV)</td>
<td>28.6</td>
<td>53</td>
<td>57.6</td>
<td>53</td>
</tr>
<tr>
<td>Vickers Hardness: Fiber Region (HV)</td>
<td>68.3</td>
<td>53</td>
<td>108.5</td>
<td>53</td>
</tr>
</tbody>
</table>

As shown in Table 2, in-plane shear modulus increased 39% over the unfilled control. This property is matrix-dominated, and the increase reflects the value of matrix tensile modulus (Table 1) that is outside the range attainable with unoriented polymers. (Note that the fiber volume fraction of these laminates was not well-matched, yet the in-plane shear modulus was still dramatically increased.)

Short beam shear strength increased approximately 15%. This property was also increased for unidirectional prepreg tapes, e.g. [1].

Compression strength as measured by SACMA SRM-1R is listed in Table 2. The average strength increased with increasing nanosilica content. The apparent strength changed by 44% at 43 wt% silica loading. This is a greater increase than was seen at high silica contents for unidirectional prepreg laminates [1-2]. In contrast to those previous studies, the flex strength did not increase, but was reduced. It is surprising that the flex strength, which is usually governed by compression failure mid-span, did not show an increase. It is possible that the very high hardness and modulus of the nanosilica-filled matrix resin lead to an increased stress concentration under the central loading roller, triggering early failure through a combination of in-plane compression and contact stresses. The increased flex modulus may be caused by the increased elastic support given to the fabric which consists of wavy fiber tows. This local stiffness is seen in the nanoindentation modulus. The nanoindentation modulus of the laminate surfaces depends on the proximity of the indentation location to fiber tows near the surface, as seen in Table 2. Because of the well-distributed stiff particles as seen in Figure 3, the nanoindentation modulus is much higher relative to any corresponding area in the unfilled control laminate surface.

As previously mentioned in the resin data section, silica incorporation leads to an increase in surface Barcol hardness (Table 1). To examine the translation of enhanced
neat resin hardness to improved composite laminate hardness, nanoindentation and Vickers hardness were measured. Both nanoindentation hardness and Vickers hardness depend on the indentation location relative to fiber tows near the surface. Resin rich and fiber-dominated areas of the laminate were examined and results are summarized in Table 2. Vickers hardness for the resin-rich regions of the nanosilica-containing laminate displayed a 100% increase in hardness in comparison to the control. Additionally, the FTP 140F laminates displayed a 59% hardness increase in the fiber-rich regions. Similar determinations of nanohardness via nanoindentation revealed hardness improvements for the FTP 140F laminate of 100% and 280% in the resin- and fiber-rich regions respectively. The high hardness is desirable to enhance tool durability and part surface quality.

The enhanced flexural modulus creates opportunities for light-weighting composite tooling structures. For example, Table 3 displays flexural modulus data for a control 10 ply 1:8:1 tool-face laminate in comparison to an 8 ply 1:6:1 FTP 140F system laminate illustrating essentially equivalent values. This approach offers composite tool designers reduced build times, labor and material costs in addition to lighter-weight tools.

Table 3. Lightweight Flexural Strength Comparison

<table>
<thead>
<tr>
<th>Si (wt%)</th>
<th>Fabric</th>
<th>0° Flexure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FV</td>
<td>Lay-up</td>
</tr>
<tr>
<td>0</td>
<td>T300/T700</td>
<td>62.2</td>
</tr>
<tr>
<td>43</td>
<td>T300/T700</td>
<td>63.0</td>
</tr>
</tbody>
</table>

3.3 Composite Dimensional Stability

Manufacturing distortion of laminated composites can be attributed to several factors, including reversible thermo-elastic deformation and irreversible matrix cure shrinkage [9]. The differences between the in-plane and through-thickness properties drives angle changes in curved parts such as angle brackets and stiffeners. An equation capturing the effect of anisotropic material properties is [9]

\[
\frac{\Delta \theta}{\theta} = \left[ \frac{(\alpha_{I} - \alpha_{T})}{(1 - \alpha_{T} \Delta T)} \right] + \left[ \frac{(\phi_{I} - \phi_{T})}{(1 + \phi_{T})} \right]
\]

[1]

where

\[
\theta = \text{included angle}
\]

\[
\Delta \theta = \text{change in included angle}
\]

\[
\alpha_{I} = \text{in-plane coefficient of thermal expansion}
\]
\[ \alpha_T = \text{through-thickness coefficient of thermal expansion} \]

\[ \Delta T = \text{change in temperature} \]

\[ \phi_I = \text{in-plane, isothermal fabrication shrinkage} \]

\[ \phi_T = \text{through-thickness, isothermal fabrication shrinkage} \]

The laminate in-plane CTE and cure shrinkage are dominated by the stiff, low CTE carbon fibers; the through-thickness CTE and cure shrinkage are more sensitive to changes in the matrix CTE and cure shrinkage. The data in Table 1 shows that the high loading of nanosilica significantly reduces both of these neat resin properties.

Measurements of curved part distortion were made to illustrate the effect of the changes. In addition to the flat laminates used for mechanical property measurements, curved specimens were made to investigate out-of-plane thermal deformations. A thick-walled aluminum pipe (length = 203.2 mm, diameter = 76.2 mm) was cut in half along its axis to make two half-cylinder molds. Rectangular pieces of 2x2 twill prepreg (15.24 cm x 20.32 cm) were laid over one mold positioned on a flat plate with a stacking sequence of [(T300)/(T700)$_6$/(T300)]. The parts were vacuum bagged and cured out-of-autoclave at 63 °C for 9 hours resulting in semi-cylindrical parts with a nominal 6.3 mm thickness. Strips approximately 25 mm wide were cut normal to the part cylindrical axis to produce specimens with an arc slightly less than 180 degrees. These were post-cured free-standing for 2 hours at 200 °C. Specimens for measurement of through-thickness CTE were cut from flat areas trimmed from the parts to form semi-cylindrical specimens. The laminate through-thickness CTE values were determined by best linear fit of the TMA expansion data between 25 and 140 °C.

Two-dimensional Digital Image Correlation (DIC) was used to measure the change in shape of the specimens in response to changes in temperature. This is an optical technique that tracks the displacements of randomly-distributed speckles applied to an object in a series of digital images [10]. The curved edge of each strip was first painted white, and then decorated with speckles of black spray paint. Figure 4 shows a specimen after preparation.

The displacement measurements were made using a commercial DIC system made by Correlated Solutions, Inc. (Columbia, SC). Specimens made using the control and nanosilica-modified prepregs were imaged at room temperature. Each specimen was then equilibrated at 200 °C in an oven, then removed from the oven and allowed to cool as the surface temperature was monitored by a thermocouple attached to the outer surface of the strip. An image was captured when the surface reached 140 °C, an arbitrary but convenient elevated temperature. Ideally the high-temperature image would be captured when the specimen is known to be at a single temperature, with no thermal gradients. Because imaging while in an oven was not easily done, the assumption was made that specimens would cool at similar rates, and for a given surface temperature the distribution of temperature would be similar enough to allow comparison. In this way, changes in angle due to thermal expansion can be illustrated in a relative sense.
Figure 4. Image of a curved composite cross-section showing speckle pattern applied for digital image correlation

Table 4 lists the through-thickness coefficients of thermal expansion determined by fitting TMA data between 25 and 140 °C and the change in included angles calculated from the DIC displacement data. The change is calculated using the post-cured specimen at room temperature as a reference. Many literature studies of curved laminate distortion consider the distortion of 90° angle brackets (e.g.,[9]). For comparison, the change in angle per 90° is tabulated as the equivalent spring-in for a 90° angle.

<table>
<thead>
<tr>
<th>Property</th>
<th>Control</th>
<th>FTP 140F</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTE (μm/m/°C)</td>
<td>72</td>
<td>40</td>
</tr>
<tr>
<td>(\frac{\Delta \theta}{\theta})</td>
<td>0.00769</td>
<td>0.00407</td>
</tr>
<tr>
<td>Equivalent spring-in for 90° angle (°)</td>
<td>0.692</td>
<td>0.367</td>
</tr>
</tbody>
</table>

The level of thermal deformation is relatively lower for the nanosilica-containing specimen, illustrating the effect of lowering the through-thickness CTE. The consequence of this change depends on the situation. If a part is constrained during a thermal change, interlaminar and in-plane stresses will result. For an unconstrained curved part, the displacements caused by angular changes will depend on the part size and geometry.

4. SUMMARY

The properties of a low-temperature curable resin and corresponding tooling prepreg designed for high temperature use (180 °C, ca. 350 °F) and containing 43 wt% nanosilica
was studied and compared to an otherwise identical unfilled resin and an unfilled control prepreg system. Neat resin property improvements relevant to composite tooling applications were observed, including lower CTE, cure shrinkage, and cure exotherm, higher modulus and fracture toughness, and higher hardness. Composites made using the highly filled resin exhibited several improved mechanical properties, including hardness. The reduction in through-thickness CTE was shown to result in reduced thermal distortion of a curved part.

5. FUTURE WORK

The effect of nanosilica incorporation on the characteristics of composite tooling prepreg will require further study. The nanocomposite matrix technology described here is being extended into additional resin systems for prepreg that take advantage of the unique attributes of highly-filled matrix materials, with particular emphasis on composite tooling applications [11]. The translation of matrix properties to composite properties will likely depend on the base resin characteristics as well as the particular fabric reinforcement being used. Part distortion is likely to depend on the cure schedule as it affects the degree of cure occurring at given temperatures. The role of isothermal cure shrinkage is another topic for study. Understanding the surprising decrease in cure exotherm that was observed is a particular need arising from this study. Quantification of the resistance to microcracking during thermal cycling of nanosilica-modified tooling laminates is one of the most important areas of future work.

6. ACKNOWLEDGEMENTS

We would like to thank Mary Buckett and Mary Swierczek of 3M’s Corporate Research Analytical Laboratory for their assistance with the SEM/TEM images, Rachel Wilkerson for neat resin testing and Daniel Quinn for neat resin sample preparation.

7. REFERENCES


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