Development of Nanosilica-Thermoset Matrix Resins for Prepreg Composites

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ABSTRACT

A review of the prepreg thermoset matrix resin development activities at 3M and commercial status of these systems will be provided.

Keywords: fiber-reinforced composites, nanosilica, thermosets, sporting goods, prepreg, tooling, epoxy, bismaleimide.

1.0 INTRODUCTION

The matrix material properties of continuous fiber reinforced composites have a primary effect on both composite compression strength and intra- and interlaminar cracking resistance. Matrix stiffness is a primary variable affecting composite compression strength because fiber microbuckling, a major compression failure mechanism, depends on the amount of support provided by the matrix to the fibers. This has been studied extensively both experimentally and theoretically [1-7]. Fiber waviness, matrix stress-strain curve nonlinearity, and the fiber/matrix interface strength have been identified as important factors [6, 7], but virtually all work on compression mechanisms includes the role of the matrix constitutive behavior. The matrix fracture resistance, along with adequate fiber/matrix interface strength, is important in resisting both interlaminar and intralaminar cracking. The requirements of high matrix stiffness for adequate composite compression strength and high matrix fracture resistance for adequate composite cracking resistance can force compromises since some strategies for increasing fracture resistance of resins reduce modulus [8, 9].

Incorporation of hard particles into polymers increases modulus, and can increase fracture resistance [9]. Micron-scale inorganic fillers have been used to modify cured resin properties, but when processed into fiber-reinforced composite structures, these large particles are filtered out by the reinforcing fibers, as illustrated in Figure 1. Another undesirable effect of conventional fillers is increased resin viscosity during cure, which can compromise composite processing.

2.0 TECHNOLOGY OVERVIEW

In recent years research has focused on the development of novel thermoset prepreg matrix resins

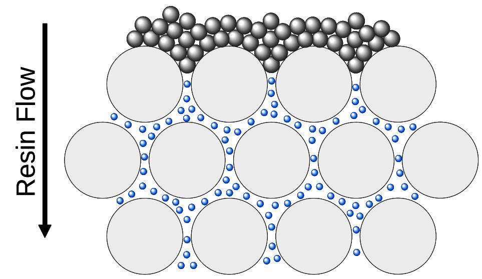

Figure 1. Illustration of filtering of larger particles by fiber array and infiltration of smaller particles between fibers.

based on silica nanoparticle technology [10-16]. The use of surface-functionalized inorganic particles much smaller than conventional micron-scale particle technology circumvents particle filtration. Emphasis is on very high loading of particles, up to 50% by weight which is possible due to the the highly compatible nature of the functionalized particles. The nanosilica particles form non-aggregated dispersions at all loading levels.

The non-agglomerated compatibilized nanosilica can be evenly dispersed throughout a fiber composite structure without filtration by the fiber array, as displayed in Figure 2. Shown is a representative composite laminate made with resin having 36 wt% nanosilica of nominally 154 nm diameter. The particles have penetrated between 7μm diameter carbon fibers.

An additional differentiating feature of these materials relevant to fiber composites is the simultaneous increase in both modulus and fracture resistance, as well as improvement of other resin properties [10-19].

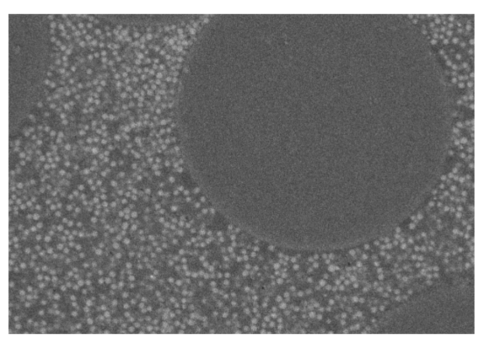

Figure 2. SEM image of a polished 7 micron diameter carbon fiber composite cross-section showing distribution of 154 nm diameter silica particles

3.0 TECHNICAL REVIEW

This review summarizes work towards the development of nanosilica-filled matrix resin technologies for prepreg manufacturing processes. Specifically, this paper describes:

i) The unique properties of epoxy nanocomposite resins with high weight fractions of nanosilica, emphasizing the effect of silica concentration on 121 °C (250 °F) and 177 °C (350 °F) cure temperature resin systems and composite properties and commercial embodiments;

ii) The development of low temperature-curable 3M^{TM} Fortified Tooling Prepreg 140F Resin, an out-of-autoclave epoxy prepreg for composite tooling applications; and

iii) Extensions of the nanosilica resin technology in bismaleimide (BMI) chemstries and development of 3M^{TM} Fortified Tooling Prepreg BMI Resin for composite tooling applications.

3.1 Effect of Nanosilica Concentration on Neat Resin and Composite Properties.

Initial work examined the effect of nanosilica on: a) the processability of a model 121 °C-cured epoxy novalac system for prepreg, b) the quality of nanoparticle dispersion, c) neat resin physical and mechanical properties, and d) carbon fiber laminate mechanical property enhancements [11-12]. This work represented the first evaluation of the effects of nanosilica inclusion at high silica loading levels (ca. 45 wt%). Representative data for this study is shown in Table 1.

Table 1. Cured Resin Property Data [11-14]

Property	Novolac 121 °C System		TGDDM/4,4 ’-DDS 180 °C System	
Silica (wt%)	0	45	0	45
Tensile Modulus (GPa)	3.5	7.2	3.8	7.8
Fracture Toughness (MPa-m$^{1/2}$)	0.61	0.93	0.57	0.76
CTE (µm/m/°C)	48.0	31.7	40	25
Cure Exotherm (J/g)	471	258	665	220
Cure Shrinkage (%)	0.62	0.33	0.76	0.42
Barcol Hardness (H_B)	42	73	57	79
Density (g/cc)	1.25	1.54	1.27	1.53

Nanocomposite resins with high weight fractions of nanosilica offer dramatic enhancements in both resin modulus and fracture toughness. The tensile modulus was more than doubled. Figure 3 illustrates results of the dynamic mechanical analysis of cured samples with varying silica content displaying the storage modulus, E’, vs. temperature plotted on a linear scale. As anticipated, the modulus increased monotonically with increasing silica content throughout the range explored in this study.

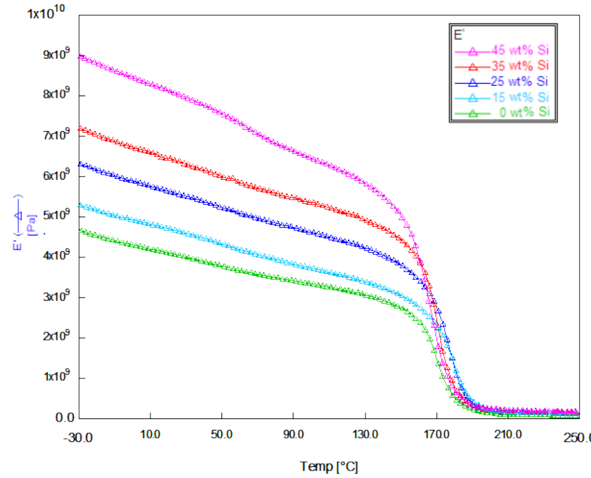

Figure 3. Dynamic mechanical spectra of cured resins

Results of resin fracture testing are given in Table 1. The critical plane-strain stress intensity factor, K_{IC}, increased monotonically with increasing nanosilica content. The incorporation of 45 wt% silica increased K_{IC} by about 50%. Figure 4 shows the fracture surfaces near the precrack for the unfilled control resin and the 45 wt% silica material at low and high magnifications.

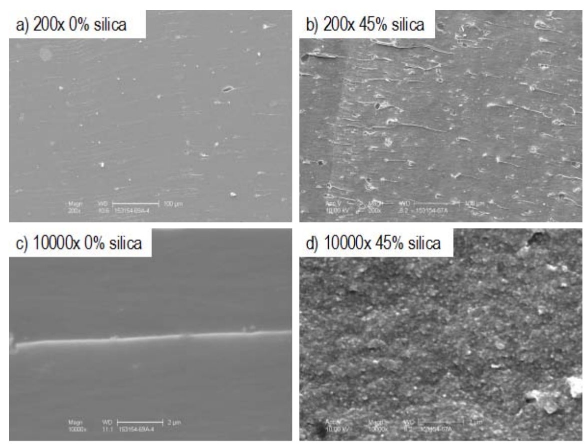

Figure 4 Fracture surfaces of unfilled control and resin with 45 wt% nanosilica. Crack propagation was from left to right [11-12].

The unfilled control has a very smooth surface as examined at both low and high magnifications, with fine ridges typical of unmodified epoxy. The low magnification image of the fracture surface of the 45 wt% silica resin (Figure 4b) shows whitening at the edge of the precrack due to a change in texture. Significantly coarser ridges emanate from the precrack, and “tails” are seen at the undissolved curative particles. The high magnification Figure 4c shows the nearly featureless surface of the unfilled control, apart from a fine tear ridge. In contrast, the filled material shown in Figure 4d reveals a surface that is rough on the submicron scale.

Additionally, other resin properties desirable for fiber-reinforced composites were improved including monotonically increased hardness, reduced coefficient of thermal expansion (CTE), water uptake, cure exotherm and resin shrinkage (Table 1). These enhancements were accompanied by a controllable increase in resin viscosity, and without influence on the resin's glass transition temperature.

A drawback to nanosilica modification of epoxy resins is the increased density of the resultant system because the density of silica is higher than that of the base resin. But because fibers are typically about 60% of the volume of a composite, the fiber composite density is increased 5-7% even at high particle loadings. 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 strategies can result in an overall reduction in part weight for equal strength or stiffness.

The incorporation of nanosilica loading levels up to 45 wt% produced prepreg resins with suitable characteristics for the prepreg manufacturing process. Carbon fiber prepreg composites incorporating these matrix materials display monotonically increasing shear stiffness, compression strength, and flexural strength with increasing nanosilica concentration. Representative composite data is found in Table 2.

Table 2. Carbon Fiber Laminate Property Data.

Property	**Novolac 121 °C System**			**TGDDM /4,4'-DDS System**
Silica (wt%)	0	36	45	38
In-plane Shear Modulus (GPa)	4.74	6.52	6.63	7.21
Compression Strength (GPa)	1.78	1.92	1.98	2.0
Short Beam Shear Strength (MPa)	93.1	113.8	119.1	120.0
0° Flexure Modulus (GPa)	126.9	143.9	124.7	155.1
0° Flexure Strength (GPa)	1.53	1.68	1.93	1.54

In 2009, 3M introduced 3M™ Matrix Resin 3831, a 36 wt% silica content nanocomposite epoxy resin system designed for use in composite prepreg manufacturing processes [20]. This introduction was followed by the development and launch of a similar, yet lower-tack nanocomposite epoxy resin, 3M™ Matrix Resin 3832. Additionally, 3M™ Prepreg based on these resins was recently commercialized. These commercial systems display the performance characteristics elucidated in the previously mentioned 121 °C epoxy concentration study [11-12].

Initial implementation of this epoxy nanocomposite resin in the sporting goods market has made producing stronger, lighter-weight carbon fiber composites structures such as fishing rods and marine spars possible. Real world application-based testing of carbon fiber reinforced composite designs containing 3M™ Matrix Resin 3831 have shown dramatic increases in strength such as a 30-50% strength increase in marine spars and a 60-90% strength increase in fishing rods where compression-dominated bending failures occur. This increase in composite compressive properties offers composite engineers greater design flexibility in optimizing the strength, weight, and performance of carbon fiber prepreg structures

In an effort to further understand the applicability of this technology, the first evaluation of the effects of nanosilica on a 180 °C (ca. 350 °F) cure prepreg resin system was also examined [13,14]. Specifically, this work outlines the effect of nanosilica inclusion on the neat resin and prepreg properties of tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) cured with 4,4'-diaminodiphenylsulfone (4,4'-DDS). In addition, carbon fiber laminates made with unidirectional prepregs of this resin at 38 wt% silica were used to establish the viability and characteristics of DDS-cured elevated temperature composites with high nanoparticle loadings. A summary of the resin data from this study is found in Table 1. These enhancements are compared with results from previous work on a nanosilica-filled dicy-cured composite, showing that the desirable properties obtained for modest temperatures by that system can be extended into higher-glass transition temperature systems (Table 2).

3.2 Extension of the Nanosilica Resin Technology

3.2.1 3M™ Fortified Tooling Prepreg 140F Resin

Recently development efforts have concentrated on the application area of composite tooling, with particular emphasis on the development of a low temperature, out-of-autoclave (OOA) cure epoxy prepreg systems designed for 180 °C cure applications, referred to as the 3M™ Fortified Tooling Prepreg 140F Resin (FTP 140F) [15]. Consistent with previous prepreg resin studies, nanosilica modification produced unique cured resin and composite property improvements as shown in Tables 3 and 4 respectively.

Properties of carbon fiber laminates made with fabric prepregs at silica loading levels of 43 wt% revealed significant improvements in compression strength, in-plane shear modulus, and 0° flexure modulus. Additionally, composite properties of particular importance to the area of composite tooling, such as coefficient of thermal expansion, hardness, shrinkage, and exotherm control have been greatly improved through silica incorporation. These properties are necessary for producing thick, durable tools that have enhanced fidelity to the tool master along with dimensional stablity and reduced residual stresses. For example, the difference in in-plane and through-thickness CTE causes angular distortion of unconstrained curved laminates, such as L-stiffeners. If such parts are constrained, interlaminar tensile stresses are produced. The effect of reduced coefficient of thermal expansion as shown in Table 4 on thermal distortion of curved parts (“spring-in”) was demonstrated [15].

Table 3. Effect of Nanosilica Concentration on Composite Tooling Resin Properties.

Property	Epoxy		BMI	
	Control	**FTP 140F**	**Control**	**FTP BMI**
Silica (wt%)	0	43	0	40
Tensile Modulus (GPa)	3.1	6.3	4.0	8.3
Tensile Strength (MPa)	56.8	67.2	70.6	89.7
Tensile Strain (%)	2.6	1.0	1.7	0.9
Fracture Toughness (MPa-m$^{1/2}$)	0.51	0.72	0.44	0.96
CTE (μm/m/°C)	46	36	40	24
Cure Exotherm (J/g)	594	231	233	139
Cure Shrinkage (%)	0.75	0.5	0.66	0.33
Barcol Hardness (H_B)	36	73	55	81

Table 4. FTP 140F Carbon Fiber Laminate Properties

Property	Control	FTP 140F
Silica (wt%)	0	43
In-plane Shear Modulus (GPa)	3.7	5.1
Compression Strength (GPa)	0.70	1.01
Short Beam Shear Strength (MPa)	53.7	61.6
0° Flexure Modulus (GPa)	57.5	62.3
Nanoindentation Modulus: Resin Region (GPa)	3.9	7.7
Nanoindentation Hardness: Resin Region (GPa)	0.2	0.4
Vickers Hardness: Resin Region (HV)	29	58
CTE (μm/m/°C)	72	40

3.2.2 3M™ Fortified Tooling Prepreg Bismaleimide (FTP BMI) resin system.

BMI matrix systems represent the other major class of resins used in high temperature composite tooling applications. BMI resins are commonly used in high production rate composite tooling campaigns due to their high glass transition temperatures and their robustness when subjected to thermal cycling.

As part of effort to develop a portfolio of composite tooling resins to meet the varied needs of this application space, the viability of nanosilica-modification of bismaleimide resins was examined. Specifically, the effect of nanosilica inclusion on the neat resin and prepreg composite properties of a model diallyl bisphenol A /diphenylmethane bismaleimide system was examined [16]. Consistent with previous work, bismaleimide nanocomposite resins with high weight fractions of nanosilica offer significant enhancements in both resin modulus and fracture toughness. Carbon fiber prepreg composite laminates incorporating 40 wt% nanosilica in the FTP BMI resin displayed improvements in composite properties such as compression strength and in-plane shear over an unfilled control. The presence of nanosilica enhanced other important composite tooling properties such as hardness and reduced the coefficient of thermal expansion. Representative cured neat resin and carbon fiber laminate property data are shown in Tables 3 and 5 respectively.

Table 5. FTP BMI Carbon Fiber Laminate Properties

Property	Control	FTP BMI
Silica (wt%)	0	40
In-plane Shear Modulus (GPa)	4.5	5.8
Compression Strength (GPa)	0.7	0.9
Modulus Nanoindentation: Resin/Fiber Region (GPa)	4.8/14.7	15.3/16.8
Hardness Nanoindentation: Resin Region (GPa)	0.3	0.8
Vickers Hardness: Resin Region (HV)	41	56
z-azis CTE μm/m/°C	33	28

4.0 SUMMARY

Nanosilica modification of thermoset matrix resin at high silcia concentrations offer dramatic and simultaneous enhancements in both resin modulus and fracture toughness. Carbon fiber prepreg composites incorporating these matrix materials display increasing shear stiffness, compression strength, and flexural strength. These improvements in composite properties offer designers opportunities to produce stronger, lighter composite structures. Additionally, improvements in resin properties made through nanosilica inclusion, such as hardness, cure exotherm, cure shrinkage, and coefficient of thermal expansion produce composite tooling structures with enhanced durability. 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.

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