

# HIGH PERFORMANCES OF CORE-SHELL (DENDRIMER) NANOPARTICLES IN CARBON FIBER/EPOXY COMPOSITES

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## 1. Introduction

It has been shown that the overall damage resistance and tolerance of a fiber reinforced polymer (FRP) composite part do not simply depend on the properties of individual material components but on the integration of these components in the composite. In other words, toughening the polymer is necessary, but a fracture toughness enhancement achieved in the polymer is not necessarily translated to an increased fracture resistance and tolerance of the composite. The construction or design of the composite material to where the toughening material is located spatially in the cured structure, leading to its interactions with the fibers and the resin matrix, is essentially the key.

Two approaches have been identified to enhance the fracture resistance of FRP composites in response to different types of load. *Interlayer toughening* using thermoplastic micron-sized particles were pioneered by Toray Industries, Inc. The particles embedded in a resin are concentrated outside the reinforcing fiber bed upon curing of the composite. This leads to significant enhancements in compression after impact (CAI) and Mode II interlaminar fracture toughness ( $G_{IIC}$ ) of the FRP composite. The former is a measure of the damage tolerance. The latter is a measure of how well the composite part resists impact loads. In this case, cracks generated due to quasi-static bending of the part experience an interlaminar shear load, which tends to slide one crack face with respect to the other.

The other toughening approach called *intralayer toughening* refers to the technique of populating a tough nano-sized additive throughout the composite material, i.e., in the interlayer area between the fiber beds and inside the fiber bed. This additive retains

its spatial distribution upon curing. This technique has been shown to enhance Mode I interlaminar fracture toughness of the FRP composite ( $G_{IC}$ ), which is a measure of how well the material resists crack opening.  $G_{IC}$  has been shown to be a critical design parameter for composite parts to avoid ply delamination.

Many attempts have been made to improve  $G_{IC}$  by enhancing toughness of a thermosetting resin system such as an epoxy resin. This can be done by embedding the resin with a toughening agent. Current effective toughening approaches rely on using polymeric toughening agents such as block copolymer and preformed core-shell rubber (CSR) particles. Block copolymers such as Nanostrength® by Arkema are typically synthesized from unsaturated carbon-carbon monomers such as methyl methacrylate, butadiene, styrene, propylene, ethylene oxide. Their morphologies in a cured epoxy highly depend on the block copolymer's composition and a cure cycle. Possible structure might be linear (i.e., worm-like), branched, or spherical by the assembly of individual copolymer molecules or group of self-assembled molecules. CSR particles, on the other hand, is an embodiment of self-assembled block copolymer in a solvent, typically having a soft rubbery polymer such as polybutadiene (PB) as core, and a proprietary harder polymer such as polymethylmethacrylate (PMMA), polyglycidyl methacrylate (PGMA) or similar, as shell. For both cases, the toughening effects rely on the rubbery component to induce matrix deformations, such as shear band formation and cavitation, through which crack energy, i.e., stored strain energy ahead a crack tip, is dissipated. For all of these cases, since a very soft material was incorporated in the resin in a large amount either by

weight or volume, the modulus was substantially reduced. This, in turn, leads to a substantial reduction in the compressive properties of the FRP composite [1, 2].

Hard particles from inorganic materials such as glass nanoparticles from Nanopox<sup>®</sup> F400 by Hanse Chemie can be used to avoid such modulus penalty. However, the toughness enhancement is arguably marginal with such hard particles. Combination of polymeric and inorganic tougheners, on the other hand, are expected to improve fracture toughness while retain the modulus. Nonetheless, this strategy often faces difficulties in processing resin and material consistency as two types of tougheners are incorporated into the epoxy [3,4].

Recently, Nguyen et al. [1-2, 5] has shown that when using an amino dendrimer, viz., polyethyleneimine (PEi), to initiate a polymerization reaction of styrene monomers, the resulting copolymer was shown to self-assemble into a spherical core-shell structure, viz., core-shell (dendrimer) particle or CSD particle, having a hard core (polystyrene or PS) and a soft shell (PEi). These particles were found to increase fracture toughness of a low modulus simple epoxy resin system substantially without decreasing the modulus, as seen in the conventional polymeric materials. In fact, the modulus was significantly enhanced. It was rationalized that PEi behaved as a soft reactive shell that provided fracture toughness enhancement, while PS formed a hard core that retained the resin's modulus, which would possibly have been marginally reduced if PEi was used alone. New mechanisms were discovered including dramatic interphase stretching followed by core stretching and breaking.

The present paper discusses a recent development of high performance carbon fiber composite at Toray Composites (America), Inc., (TCA) located in Washington State, USA, by utilizing novel CSD particles. To demonstrate the concept, these particles are incorporated into a model intermediate modulus aerospace grade resin which is then used to make an unidirectional (UD) prepreg. Both the resin's, and the composite's properties at room temperature dry (RTD) and hot wet (HW) are evaluated to show particle's performances.

## 2. Materials and Methods

**2.1. Materials.** Tetra glycidyl diamino diphenyl methane (ELM434), made by Sumitomo Chemical Co., Ltd.), diglycidyl ether of bisphenol A (Epon<sup>™</sup> 825) made by Hexion Specialty Chemicals, Inc. and diglycidyl ether of bisphenol F (Epiclon 830) made by Dainippon Ink and Chemicals, Inc. are epoxy components. Polyethersulfone (Sumikaexcel PES 5003P) made by Sumitomo Chemical Co., Ltd. is used as a viscosity controlling agent for prepregging. 4,4'-diaminodiphenyl sulfone (ARADUR 9664-1) made by Huntsman Advanced Materials is the curing agent. Core-shell rubber (CSR) particles (Kane Ace MX416) made by Kaneka Texas Corporation is used as a comparative toughener. Torayca T800S-24K-10E produced by Toray Industries, Inc. is the carbon fiber.

## 2.2. Methods

**2.2.1. Particle synthesis.** The CSD particles were synthesized in isopropyl alcohol (IPA) according to the procedure outlined by Nguyen et al. [1-2, 5].

**2.2.2. Particle purification and characterization.** The particle dispersion in IPA was centrifuged at 10,000 rpm in a refrigerated centrifuge (Beckman Coulter J2-HS equipped with JA-10 rotor 6x500mL) for 60min. Temperature was kept at 10°C for the whole processing duration. After centrifuged, the solid was collected and re-dispersed in fresh IPA by a mean of mechanical stirring until all the solid was suspended. The centrifuge procedure was repeated to obtain second re-dispersion with final purified particles.

Combustion analysis (Perkin-Elmer 2400 Series II CHNS/O Analyzer) was used to determine the particle composition.

A transmission electron microscope (Tecnai G2 F20) was used to determine particle core/shell structure, while a field emission scanning electron microscope (JEOL JSM-7500) was utilized to observe particle size, particle's surface structure and particle dispersion and micro-failure modes of particle in the cured epoxy and composite. In addition, to determine particle size distribution a light scattering technique (Brookhaven Instruments Corp. ZetaPALS) was used.

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### 2.2.3. Resin preparation.

40g of PES was mixed with 500g of an epoxy blend and allowed to melt at 160°C for 1hr. The mixture was transferred to a jacketed vessel equipped with a vacuum port and an overhead stirrer. Appropriate volume of purified CSD particle dispersion in IPA was slowly added to the epoxy mixture under vacuum at 100°C to achieve the specified particle loading of 10parts per 100parts of epoxy (10phr). IPA vapor was condensed and collected in a flask cooled by liquid nitrogen. The mixture was kept under vacuum for an additional 2hr after no bubbles were observed and no more IPA was collected. After vacuum was removed, appropriate amount of the curing agent was added to the vessel and mixed for 30 min at 60°C. The mixture was discharged to a container.

An amount of the hot mixture was degassed in a planetary mixer (Thinky ARV-310) rotating at 1500rpm for a total of 10min, and poured into a metal mold with 0.25in thick Teflon insert. The resin matrix was heated to 180°C with the ramp rate of 1.7°C/min, allowed to dwell for 2hr to complete curing, and finally cooled down to room temperature. Resin plates were prepared for testing according to ASTM D-790 for flexural test, and ASTM D-5045 for fracture toughness test.

Resin's viscosity was evaluated in a rheometer equipped with a pair of parallel plates (Rheometric Scientific ARES).

### 2.2.4. Composite panel fabrication and testing

To make a prepreg, the resin was first casted into a thin film using a knife coater onto a release paper. The film was consolidated onto a bed of fibers on both sides by heat and compaction pressure. A UD prepreg having carbon fiber area weight of 190g/m<sup>2</sup> and resin content of 35wt% was obtained. The prepregs were cut and hand laid up with the sequence listed in Table 1 for each type of mechanical test, followed an ASTM procedure. Panels were cured in an autoclave at 180°C for 2 hr with a ramp rate of 1.7°C/min and a pressure of 0.59 MPa.

Resin and CFRP samples containing 10phr CSD and CSR particles, herein, are designated CSD and CSR, respectively.

## 3. Results and Discussion

### 3.1. Particle composition and structure.

Presumably purification by a centrifuge has removed unreacted PEi, styrene monomers as well as small particles including PS homogeneous particles. These impurities were expected to make the resin preparation difficult if not removed. The purified particle's composition was determined by combustion analysis with a ratio of N to C of 1.5%, which is approximately translated to 4.1 wt% of the PEi material. That of the unpurified was 2.9% or 8.2 wt% PEi. Particle size was determined to be 50-650nm before they were purified by both electron microscopy and dynamic light scattering techniques. After gone through the centrifugation process, particles were found to be 150-350nm.

Fig. 1 shows the TEM images of PS particle and CSD particle. The particles were immersed in a dilute solution of phosphotungstic acid for 15min before transferred to a TEM grid. A thin shell was evidenced for CSD particle, compared to no shell for PS particle. Nano-sized feature of a CSD particle's surface was observed in a high resolution field emission SEM at 1,000,000x magnification, 300V and a working distance of 1.5mm. Ridges were found on the surface indicating some evidence that the PS-PEi copolymer had folded in the solvent to form a particle.

### 3.2. Resin processing

Nguyen et al. [1-2,5] discussed a common technique to prepare master blend of CSD particle in a model low viscosity epoxy. For the particle synthesis IPA was chosen since it has a high boiling point to drive the polymerization reaction to achieve a high particle yield. In addition, in IPA the particle dispersion was self-stabilized by PEi shells through an electrosteric effect without the need of an additional stabilizer. More importantly, IPA could be removed easily from an epoxy when the particle dispersion was introduced to make a master blend.

In the present study, IPA was also used to disperse purified particle. A stable dispersion with more than 20wt% solid was achieved. Note that other lower boiling point alcohols could be used to disperse the purified particles to reduce processing time,

especially in high viscosity epoxy blends. However, the data was not presented here.

Fig. 2 shows the viscosity profiles of the control, and particle-modified resins. Note that PEi could react with epoxy as temperature increases, which penalizes the viscosity. Yet, the present CSD particle composition and purification method allowed a little increase in the resin's viscosity, similar to that from CSR particles.

A good particle dispersion in a resin is very important to maximize the performances of the particles in both the resin and subsequent composites. Typically, a good and stable dispersion in the resin is necessary to have a good dispersion in the composites. Our present study shows a good dispersion of individual particles was achieved in the resin (Fig. 3). However, some big clumps were also found on the surface of the fracture specimen. It was assumed that they could be aggregated PES domains. However, more work is needed to confirm this.

### 3.3. Particle's performances in the resin and composite.

Table 1 showed a significant increase in  $K_{IC}$  by CSD particles, comparable to that by CSR particles. Yet, as expected, no modulus penalty was observed in the CSD resin for both RT and HW. SEM images in Fig. 3 show that all failure modes responsible for the high performances of the particle as seen in a low modulus simple epoxy system previously [1-2, 5] were retained in this intermediate modulus aerospace resin system. As shown there were interfacial stretching, particle expansion and particle breaking. Potentially, higher particle's performances in the resin can be achieved if an optimized particle composition is obtained, taking into account an ease of resin processing, and a better particle dispersion.

CSD particles show a significant increase in  $G_{IC}$ , however, it is not as high as that by CSR particles though resin's fracture toughness  $K_{IC}$  was similar for both cases. The particle size after fracture as seen in Fig. 3 was found to be about a couple of microns, which makes the migration of these articles into the fiber beds possibly not as efficient as the 80nm unexpandable CSR particles. Potentially since the

PS-PEi copolymer folded to form the particle, this resulting particle might not pack itself tightly enough such that a core might be formed by a loosely packed volume rich in PS, surrounded by PEi as a shell. This would result in a potential swelling or expanding of CSD particles during curing with the epoxy resin, i.e., smaller epoxy molecules could penetrate the loosely packed PS-PEi copolymer and crosslink with PEi in both the shell and core. Consequently, as a load is applied, it pulls the crosslinks out of the particles until the particle debonded. This would also explain the interfacial stretching as evidenced by the teeth-like marks around the particle. However, it was not clear to what extent these particles expanded when the load was applied until fracture. Higher crosslinked particles would lead to a stable particle size and subsequently, can further enhance CSD particles' performance in the composite's fracture toughness, comparable to that of CSR particles. This would also improve the CSD resin's modulus and subsequently allows even a higher increase in OHC (open-hole compression) at RTD and HW than the current level.

Note that a higher amount of PEi in the CSD particle could further increase the particle's performances; however, at the expense of viscosity. Therefore, optimization of particle composition and resin preparation process including a better particle dispersion is also important to maximize particle's performances in carbon fiber/epoxy composites.

### 4. Conclusion

Core-shell (dendrimer) nanoparticles have been shown to provide an ultimate solution for fracture toughness needs in carbon fiber reinforced epoxy composites without penalizing other properties. Such performances would never been achieved with conventional tougheners. Further development for practical particles, i.e., high performance, low cost particles made in an environmentally friendly process, and prepregs are ongoing at Toray Composites (America), Inc., WA, USA.

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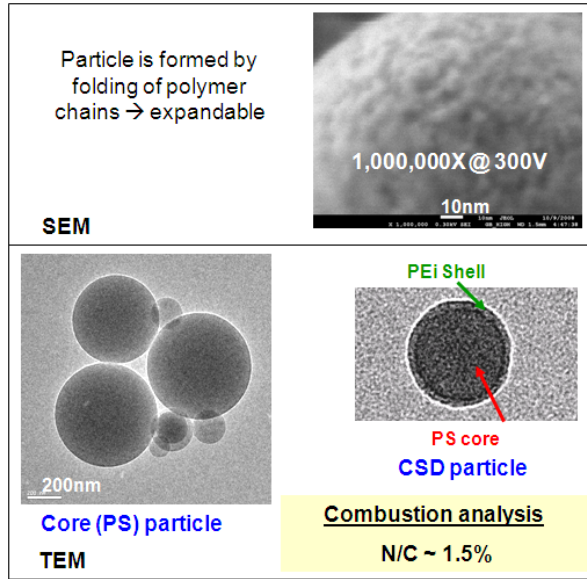


Fig. 1. CSD particle structured characterized by SEM and TEM. Particle surface by SEM appears with ridges indicating that the particle was formed by the folding of the copolymer PS-PEI, while a thin shell of the particle is clearly shown by TEM.

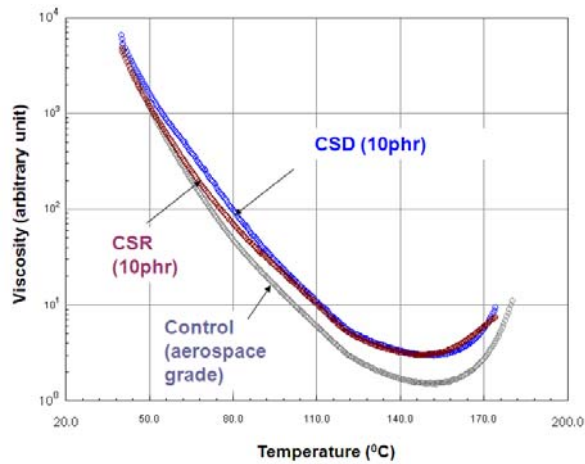


Fig. 2. Viscosity profiles of the control and particle-modified resins. CSD particle modified resin has a similar viscosity penalty as CSR particle modified resin.

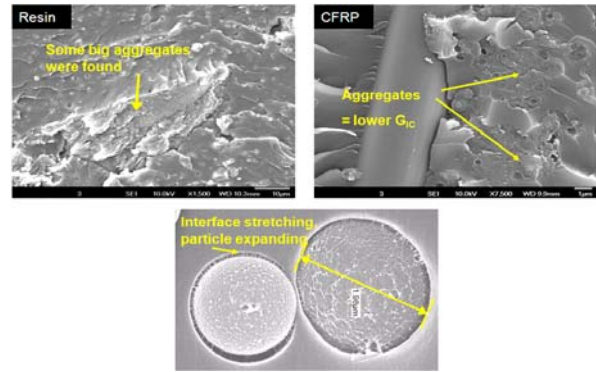


Fig. 3. SEM images of fracture surfaces of resin and composite. Good dispersion with individual particles with some clumps of aggregated PES domains was in the resin while a poorer dispersion was in the composite. Interfacial stretching and particle expansion and breaking were found responsible for the high performances.

Table 1 – Ply configuration and composite testing method used in the present study.

Test	ASTM Test method	Lay up	Test Condition
Tensile	D 3039	(0) <sub>6</sub>	RT
OHC/ RT	D 6484	(45/0/-45/90) <sub>2S</sub>	RT
OHC/ HW	D 6484	(45/0/-45/90) <sub>2S</sub>	Hot

Table 2. Properties of particle toughened aerospace resins and CFRPs

Properties		Control	CSR	CSD
Resin	Fracture toughness ( $K_{IC}$ ), $Mpa.m^{0.5}$	0.61 (0.03)	1.02 (0.06)	1.02 (0.05)
	Flexural modulus RTD, GPa	3.23 (0.05)	2.78 (0.02)	3.22 (0.02)
	Flexural modulus HW, GPa	2.97 (0.07)	2.56 (0.04)	3.05 (0.01)
CFRP	$G_{IC}$ , lb.in/in <sup>2</sup>	2.13 (0.14)	5.7 (0.63)	3.47 (0.2)
	OHC/RTD, ksi	41.3 (0.8)	36.4 (0.6)	40.6 (1.0)
	OHC/HW, ksi	34.4 (0.7)	28.4 (0.8)	33.0 (1.9)

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