Novel Toughening Agents for Thermosetting Systems for PWB Base Materials

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Abstract:
The proposed revision of IPC 4101 - Specification for Base Materials for Rigid and Multilayer Printed Boards contains new slash sheets describing FR-4 base materials compatible with lead-free assembly. These specification sheets also outline requirements not found currently for FR-4 including Td, T260 and T288. In order to achieve minimum performance criteria, toughening agents have been incorporated into the FR-4 resin systems both for 135 and 170°C materials. Current modifiers for toughening thermosetting systems exhibit significant drawbacks including depression of the glass transition temperature, instability of the formulation and difficulty of use. Core Shell Rubber (CSR) particles have been used successfully for more than 40 years in thermoplastic applications but have had limited success in thermosetting systems due to difficulty in dispersing the solid powder into the resin system.

We have developed a proprietary process for dispersing CSR domains into various thermosetting resins. The CSR particles are perfectly dispersed and remain so during storage under a variety of conditions and after the formulating process is complete. The resulting FR-4 composite exhibits improved inter-laminar adhesion, fracture toughness and lap shear strength without depressing the glass transition temperature or other thermal properties related to the cross link density. The CSR particles are supplied as a 25% concentrate in an epoxy resin chosen by the formulator such as a liquid Bis-A or multifunctional brominated epoxy thus minimizing initial development work.

This paper will discuss the merits and use of these novel toughening agents for thermosetting systems for lead-free compatible base materials.

Introduction:
Core Shell Rubber (CSR) particles have been used to toughen various polymeric systems since the early 1960s. A simplified depiction of a typical CSR particle can be found in **Figure 1**. As the name CSR implies, a spherical core of one composition is covered with a shell of another. The core of the CSR particle is synthesized by an emulsion polymerization process and the chemistry of the core provides the impact modification performance and toughening desired. A shell of a second chemistry is then grafted onto the core with the dual purpose of both protecting the core and generating compatibility with the polymer being modified. The core is typically a butadiene / styrene copolymer similar to rubber and the shell is of an acrylate character. Historically over the last 40 years, literally hundreds of CSR products have been synthesized by various manufacturers differentiated by core composition, shell chemistry, size and geometry. The product is generally furnished as a solid powder comprised of agglomerated CSR particles that have been dried. Powder CSR particles have been successfully used in thermoplastic systems such as PVC and PET. **Figure 2** shows the typical applications of the over 1 million metric tons of CSR used globally each year.

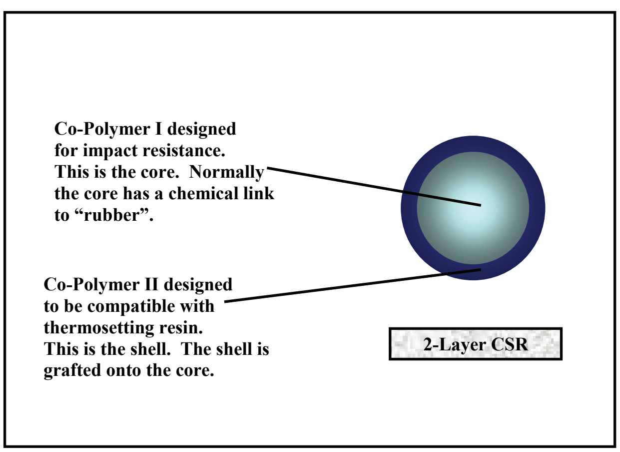

Figure 1 - Design of Core Shell Rubber (CSR) Particle.

	Resin	Application	Volume (mt/yr.)
MBS	PVC PC PBT	packaging (bottle, film) auto (bumper, panel) auto (airbag cover)	250,000
ABS	SAN	auto, appliance	500,000
Acrylic	PVC	window, siding, fence	350,000
Acrylic	PMMA	auto, lighting, signage	10,000

Figure 2 - Applications for CSR as Toughening Agent.

CSR Toughening Properties:
CSR particles toughen a polymeric matrix in several different ways. The first theory is that the core itself acts to dissipate the energy of an impact. The cavitation theory of impact modification is that the core deforms effectively

mitigating the force of the impact itself. This theory is supported by the change of refractive index in the cores of the CSR near the impact area itself. The composition of the core as well as the overall size of the CSR can change the toughening performance of the CSR. The CSR itself can be optimized for the particular application. The second theory of toughening by CSR is that the particles themselves act as crack terminators. Cracks or fissures that start by whatever mechanism are stopped when they meet a CSR particle. Therefore having small and evenly dispersed CSR in the polymeric matrix increases the probability of the crack meeting a CSR particle. The importance of an even dispersion of CSR or any toughening agent is to maximum the number of effective sites for cavitation and crack termination. In addition, a small, homogenously dispersed CSR provides a reproducible result in terms of fracture toughness and adhesion characteristics lot-to-lot or batch-to-batch.

Cohesive type failures in copper clad laminates due to the brittle nature of the resin affect the interlaminar bond (T-260, T-288) and the peel strength of the copper foil to the butter coat of the resin matrix. These performance properties are improved using toughening agents such as CSR. The mechanism of improvement has been attributed to slowing rate of crack propagation within the FR-4 resin itself.

Development of Kane Ace® MX:

Attempts to mix CSR powder with epoxy and other thermosetting resins have resulted in very poor dispersions characterized by rapid settling and inherently non-homogeneous levels of toughness. A lot of effort has been expended trying to mill, grind or shear the solid CSR particles into epoxy resin. Once the particles are agglomerated however, it is impossible to break the solid particle up into the individual CSR domains first synthesized. Kaneka Texas Corporation has developed a process that delivers the CSR particles in various epoxy resins where the individual particles are not agglomerated but are evenly dispersed throughout the liquid resin. **Figure 3** shows a beaker containing a 10% dispersion of solid CSR on the left versus the beaker on the right containing Kane Ace® MX 120 product comprised of a 25% dispersion in Bis A epoxy resin. In this product, the 100 nm CSR particles are evenly dispersed and stable without settling or agglomeration for at least 1 year. Therefore the toughening agent is easily mixed into existing systems and no further agitation is required to keep the CSR in even suspension as a raw material or in the formulated system.

Figure 4 shows a cured composite that has been cross-sectioned and stained to highlight the CSR particles within the matrix. The 100 nanometer particles (0.1 micron) are evenly dispersed providing numerous sites for cavitation and/or crack termination.

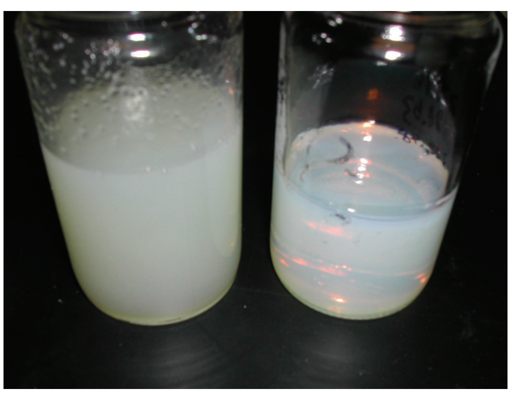

Figure 3 - Dispersion characteristics of 10% solid CSR on left versus 25% CSR MX 120, both in liquid Bis-A epoxy resin.

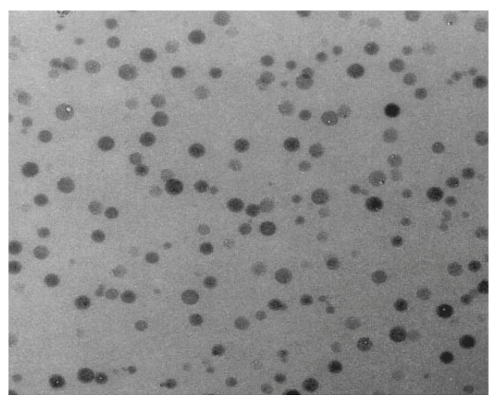

Figure 4 - Cross section showing 100 nm MX 120 CSR in composite polymer matrix.

Performance Testing:

Figure 5 shows the T-Peel Strength test results for the product introduced into a composite formulation. The data shows that that the T-Peel Strength is improved by 3X from 5 lbs. per linear inch width to 15 lbs. per linear inch width by incorporating 5% CSR into the matrix. Increasing the loading to 10% generates a 5 fold increase in T-peel strength with a result over 25 lbs. per linear inch width. **Figure 6** shows the Lap Shear Strength test results for the product introduced into an adhesive formulation. The data shows that that the Lap Shear Strength is improved by 40% from 2800 psi to 4000 psi by incorporating 5% CSR into the matrix. Increasing the loading to 10% generates an 80% increase in Lap Shear Strength with a result over 5000 psi.

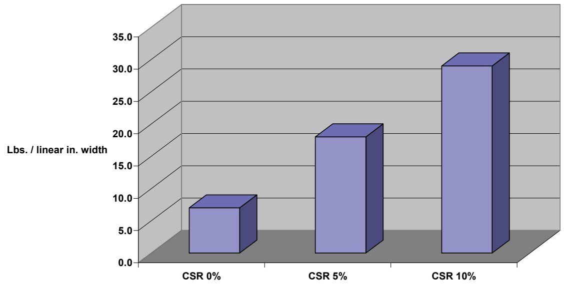

Figure 5 - T-Peel Strength of Bis-A Epoxy Matrix.

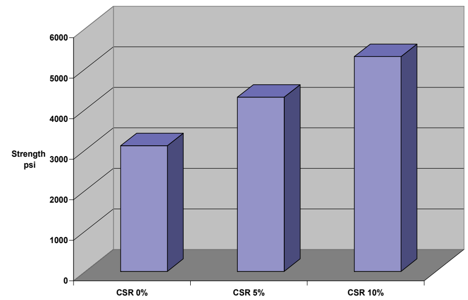

Figure 6 - Lap Shear Strength Bis-A Epoxy Matrix.

Figure 7 shows the Fracture Toughness test fixture as described in ASTM 5095. The test specimen is supported in two places and then the specimen is notched midway between the supports. The test measures both the force and the energy required to propagate this initial crack. This test measures directly the crack termination performance of the toughening agent. Our material was introduced into a composite formulation in the form of a neat casting with diaminodiphenyl sulfone (DDS) or piperidine as the curing agent. The data can be found in **Figure 8** and **Figure 9** for the G1c and K1c

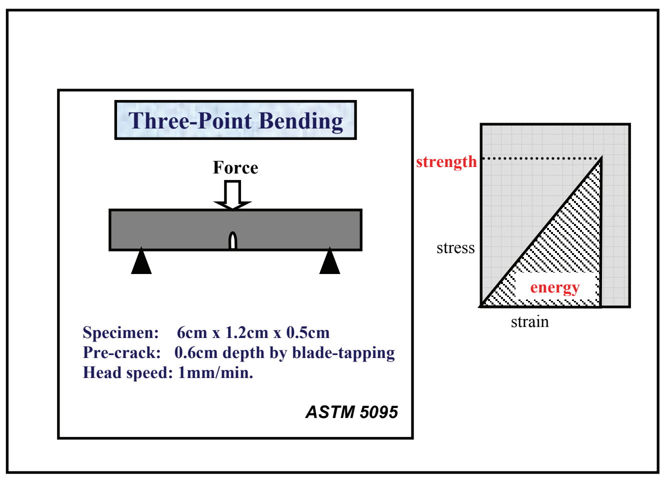

Figure 7 - ASTM 5096 Fracture Toughness Test.

respectively for a 10% loading of CSR particles. The data shows that for the G1c results, piperidine shows a more significant result with a 10X improvement while the DDS cured composite was is still improved by a factor of 2. For K1c results, the force required to propagate the crack was found to be twice the control for the DDS cured sample and a 4X improvement was exhibited for the piperidine specimen

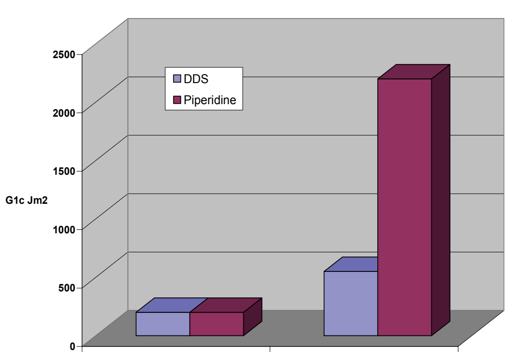

Figure 8 - Fracture Toughness G1c Results.

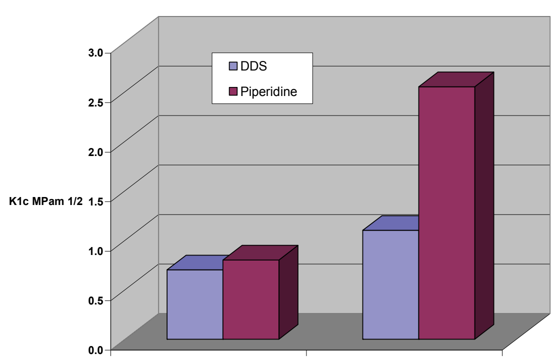

Figure 9 - Fracture Toughness K1c Results.

Epoxy Resins Available:

Figure 10 shows the types of carrier resins that can be used for the production of copper-clad laminates and prepregs for circuit boards. The most common for the domestics market is a brominated, multifunctional epoxy resin which when cured with dicy provides an FR-4 laminate with a glass transition temperature of approximately 170°C. In order to provide base materials compatible with lead-free assembly, phenolic and novolak curing agents have been substituted for dicy. Although these systems provide improved thermal stability for the higher eutectic temperatures of the lead-free solder, the polymeric matrix is generally more brittle resulting in lower T-260 and copper peel strength results. CSR incorporated into the resin system effectively restores the toughness of the overall system to that of the dicy cured products.

Base Resin	CSR Content
Low Viscosity Liquid Bis-A Epoxy Resin	25%
Brominated Multifunctional Epoxy	25%
Standard Liquid Bis F Epoxy Resin	25%
Epoxidized Phenol Novolak Resin	25%
Epoxidized Cresol Novolak Resin	25%
Multifunctional Epoxy TGMDA	25%
Multifunctional Epoxy TGPAP	25%
Cyclo-aliphatic Epoxy	15%
Polypropylene Glycol	25%
Bis-F Epoxy Resin	25%

Figure 10 - Base resins for use with CSR products

Summary:

CSR particles when incorporated into various adhesive and composites systems have demonstrated improved toughness and impact resistance. Performance tests including lap shear, T-peel and fracture toughness have demonstrated that CSR improves the base line characteristics of these polymeric matrixes. The glass transition temperature is not affected by the incorporation of the CSR modifier even at high particle loadings. Performance properties related to the cohesive nature of the polymeric matrix are improved with the use of CSR toughening agents.

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