White Paper

Conductive Anodic Filaments:
The Role of Epoxy-Glass Adhesion

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All glass fibers used in glass ply production have a form of sizing applied before the weaving process to ensure sufficient lubrication and prevent fracture. In conventional glass production, fibers are drawn from molten glass and a starch-oil sizing is applied. This sizing provides mechanical integrity and lubrication for subsequent processing. Warp yarns, corresponding to the grain direction in the laminate, are then coated with a second sizing for additional protection. The sizing applied to the glass fibers is subsequently removed by a thermal decomposition process and the fabric is coated with a silane finish to provide a chemical coupling between the glass surface and the resin matrix.

Bonding between the glass fiber and the epoxy resin is ensured through the application of a silane finish. Depending on the laminate manufacturer, the silane finish may be applied by the glass fabric supplier or in-house. The silane finish is often applied before the impregnation of the epoxy resin. There are several factors that drive the effectiveness of silane in retarding or preventing CAF events. These include degree of coverage, density of coverage, and ratio of bound to unbound siloxanes .

Bonding Process

The precise nature of the mechanism in which silane increases adhesion is not entirely understood. Silane coupling agents modify the interface between organic resin surfaces and non-resins to improve adhesion. It is thought that the silane coupling agents form bonds with the glass surfaces and resin matrix through the silane functional group. Hydrolyzed silanes condense to oligomeric siloxanols and eventually form rigid cross-linked structures. The bonding to a polymer matrix may take various different forms. Bonding may be covalent where the siloxanol is compatible with the liquid matrix resin. The solutions might also form an interpenetrating polymer network as the siloxanols and the resins separately cure with only limited copolymerization.

The interfacial region between the glass fiber and epoxy resin varies from tightly bound siloxanes at the fiber wall to unbound siloxanes blending into the epoxy matrix. Unbound siloxanes permit penetration of the epoxy resin into the interface region and strengthens the epoxy-glass bond, while tightly bound siloxanes restrict moisture absorption. The proper ratio of bound to unbound siloxanes results in the optimum interface.

A further optimization process involves balancing the degree of residual stress present at the interface. As an example, a method of increasing adhesion is to improve the reactivity of surface treating agents with the epoxy resin by varying the number and kinds of the organic functional groups on the silane coupling agents . However, the improved reactivity with resins can result in a rigid and thin layer on the interfaces that can induce residual stress at the interface. The use of surface treating agents together with long chain polysiloxanes will reduce the residual stress, but will tend to decrease intrinsic interfacial adhesion because

- The reactivity of surface treating agents with long chain polysiloxanes is poor under usual treating conditions
- Long chain polysiloxanes have no alkoxyl groups reactive to base materials
- The hydrophobic groups, such as methyl groups, on long chain polysiloxanes disturb the impregnation of base materials with the long chain polysiloxanes.

Silane Chemistry

The choice of silane chemistry and other finish additives is often driven by compatibility with the epoxy resin formulation and is considered highly proprietary by most laminate manufacturers. These coupling agents will influence fiber-resin interaction through changes in surface properties such as surface energy and bonding site availability. The coverage of the silane will be driven by the weave, surface preparation of the glass, and the application process. The amount and composition of silane also depends on process factors, such as pH and cure conditions. Combined, material selection and manufacturing parameters will drive the final quality of the interfacial bond.

There are numerous types of silanes available for laminate production. Some older examples are shown in Table 1. More recent formulations include epoxysilane coupling agents, such as γ-glycidoxypropyltrimethoxysilane, aminosilane coupling agents, such as

N-β-(N-vinylbenzylaminoethyl)-γ-aminopropyltrimethoxysilane, hydrochloride, cationic silane coupling agents, vinylsilane coupling agents, acrylsilane coupling agents, and mercaptosilane coupling agents. These may be used individually or in a combination of two or more in desired ratios. Hexcel- Schwebel and Dow Corning currently have a significant share of the silane marketplace for glass ply production, with Dow Corning's Z-6032, vinylbenzylaminoethylaminopropyltrimethoxysilane [C6H4-CH2-NHC2H4NHC3H6-Si(OCH3)3)] especially popular due to its high water resistance and status as a universal coupling agent (successful with various epoxies).

However, changes in silane selection are ongoing as epoxy chemistry is constantly modified, fillers are added to FR-4 formulations, and cost is the dominant driver in material selection within the electronics supply chain. As an example, Z-6032 tends to have a higher price due to some rare raw materials and product instability that requires cooling during transportation and storage.

Table 1: Examples of some common silane coupling agents used in FR-4 epoxy laminates

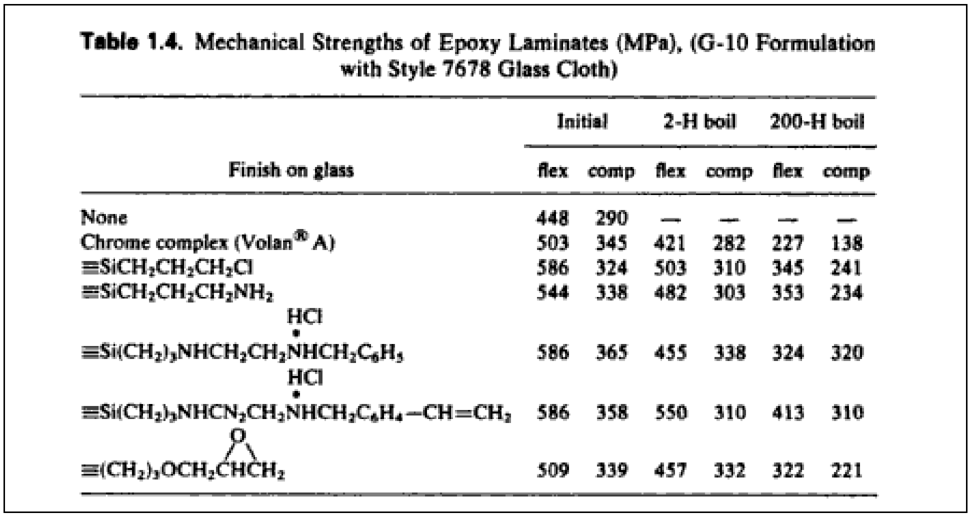

Table 1.4. Mechanical Strengths of Epoxy Laminates (MPa), (G-10 Formulation with Style 7678 Glass Cloth)

	Initial		2-H boil		200-H boil	
Finish on glass	flex	comp	flex	comp	flex	comp
None	448	290	—	—	—	—
Chrome complex (Volan® A)	503	345	421	282	227	138
$\equiv SiCH_2CH_2CH_2Cl$	586	324	503	310	345	241
$\equiv SiCH_2CH_2CH_2NH_2$	544	338	482	303	353	234
$\equiv Si(CH_2)_3NHCH_2CH_2\overset{HCl \cdot}{N}HCH_2C_6H_5$	586	365	455	338	324	320
$\equiv Si(CH_2)_3NHCN_2CH_2\overset{HCl \cdot}{N}HCH_2C_6H_4-CH=CH_2$	586	358	550	310	413	310
$\equiv (CH_2)_3OCH_2\overbrace{CHCH_2}^{O}$	509	339	457	332	322	221

Glass/Epoxy Interfacial Characterization and Control

After the impregnation of the glass fabric with the epoxy resin, direct characterization of the interfacial chemistry is difficult and often not performed. As such, reverse engineering of interfacial chemistry is not a practical enterprise. However, laminate manufacturer should have processes and procedures in place to characterize the silane finish and its compatibility with the epoxy resin blends.

If silane finishes are applied by a supplier, the laminate manufacturer should have controls in place to confirm the silane finish. If multiple finishes are used, there should be a process in place to identify each finish. Resin can also be crucial and evidence of systems to ensure adequate control is also necessary. These include resin lot conformance checks for content, molecular weight, and impurities.

Qualification Requirements

The primary process for ensuring good bonding at the glass/epoxy interface, outside of CAF testing, is the use of the test method IPC TM-650 2.6.16 Pressure Vessel Method for Glass Epoxy Laminate. This test method requires exposing laminate coupons to pressure cooker conditions (121C, 100%RH, 15 psi) for 30 minutes and then immersing the coupons in a solder pot heated to either 260C or 288C.

The Pressure Vessel test method is called out in IPC-4101B Specifications for Base Materials for Rigid and Multilayer Printed Boards as an optional test as agreed upon between user and supplier. If the test is incorporated, IPC-4101B recommends that it be used for both conformance and qualification testing, with testing performed on every lot. The test method provides a grading system of 1 to 5, with laminates graded 4 to 5 often rejected by the PCB supply chain.

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