Susan H Tilford, *Barry Arkles* and *Jonathan Goff*, Gelest, discuss the company's first offering in its new production line of Sivate enhanced silanes

Sivate enhanced amino functional silane

One of the most widely used silane coupling agents is 3-Aminopropyltriethoxysilane (1). It is used in industrial applications, for example coatings and composites, to treat siliceous and other inorganic oxide (aluminium, titanium, etc) surfaces and microparticles for improving the adhesion and mechanical strength of phenolic, epoxy, urethane, polyamide, urea-formaldehyde and polycarbonate formulations. In advanced technology applications, particularly diagnostics, it is employed to immobilise antibodies, enzymes and DNA. Aminopropyltriethoxysilane is often referred to by the abbreviations APTES, AMEO, A-1100 or GAPS. The well-recognised commercial success of this technology has stimulated interest in further extending the property enhancement, particularly life-time, for more demanding applications.

Gelest recently introduced Sivate E610, which combines the versatile functionality of APTES with the adhesion and durability boosting properties of dipodal silanes. Sivate E610 is a proprietary blend of APTES (1), a bridged hydrophobic dipodal silane (2), and an aminoalkyl functional dipodal silane (3) **(Figure 1)**. Together the dipodal silanes improve substrate bonding by limiting adsorption of water at the interface, while maintaining reactivity consistent with APTES resin interaction. This enhanced silane formulation provides improved hydrolytic stability and superior mechanical properties compared to using APTES alone.

Silane surface modification occurs by the hydrolytic deposition process depicted in **Figure 2**[1]. A conventional silane coupling agent, such as APTES has three hydrolysable groups (R' = Et) and an organofunctional group (R = aminopropyl). Exposure to moisture results in hydrolysis of the alkoxy groups to generate a silanol compound and liberate alcohol. The silanol species condense into oligomers and hydrogen bond with the hydroxyl groups on the substrate. There is a degree of reversibility to this reaction, and the covalent Si–O bonds that form on the substrate are susceptible to hydrolysis.

Dipodal silanes, such as compounds 2 and 3, have two sites for attachment to the substrate, which leads to an increase in the cross-linked density of the surface coating[2]. Each dipodal silane has the ability to form six oxane bonds to the substrate. The additional bonding sites in combination with the increased coating density, which reduces the ingress of water, results in a dramatic improvement in hydrolytic stability[2,3]. The intrinsic hydrolytic stability of dipodal silanes is calculated to be ~10,0000 times greater than conventional silanes. Additional benefits of the densely bonded siloxane layer include: increased adhesive strength, improved film-forming properties, enhanced durability, improved chemical resistance and better mechanical properties in composite applications.

For coating applications, dipodal silanes are known for providing corrosion protection for metal substrates. It is well-understood that dipodal silanes are self-priming and they can be used to replace phosphate and chromate conversion coatings[4,5]. The dense, hydrophobic barrier that is formed on the metal surface improves corrosion resistance.

To demonstrate the improvement in barrier properties using Sivate E610 compared to APTES, coatings were

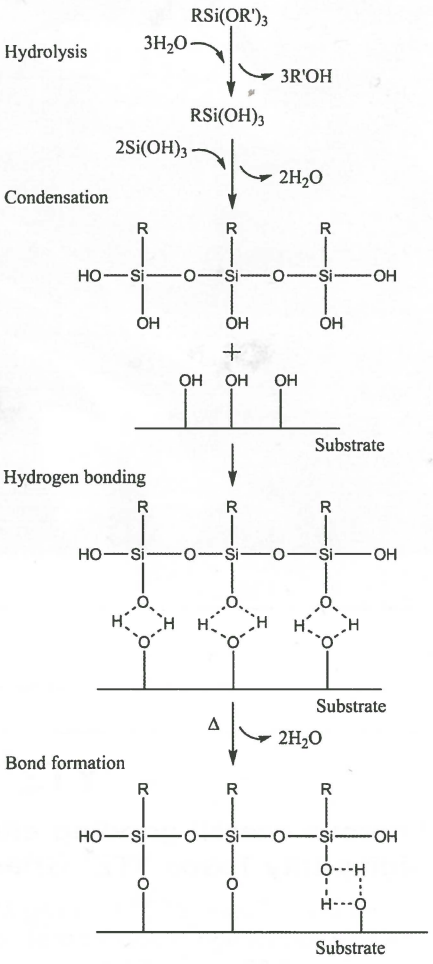
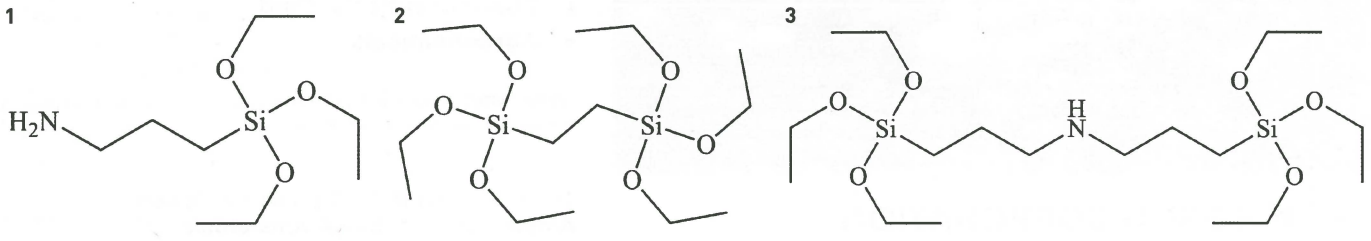


Figure 2. Surface modification using conventional silane coupling agents

applied on cold-rolled steel by depositing 4-6wt% aqueous silane solutions and curing for four hours at 150°C to generate 80-120nm thick coatings. The microporosity of the coating was

Figure 1. Sivate™ E610, a proprietary blend of silanes 1, 2 and 3



Silane	Rp (ohm-cm^2)
None	<1
APTES	2
SIVATE™ E610	20

Table 1. Electrochemical Impedance Spectroscopy (EIS) of silane coatings on cold-rolled steel

Silane	0hr	5hr	24hr	100hr
None	100%	45%	40%	40%
APTES	100%	88%	80%	77%
SIVATE™ E610	100%	96%	92%	90%

Table 2. Relative Flexural Strength of epoxy resin with silane treated fused silica filler (85°C/85% RH)

examined by Electrochemical Impedance Spectroscopy (EIS) and is reported in **Table 1**. APTES was similar to the control, which was bare cold-rolled steel, while the Sivate E610 coated steel showed a reduction in electrolyte transport through the coating pores.

In a different experiment, filled epoxy composites were prepared with 70wt% fused silica, which was treated with either APTES or Sivate E610. The control was untreated silica filler. The Flexural Strength of the moulded composites was measured after ageing at 85°C and 85% Relative Humidity (RH). The relative Flexural Strengths are shown in **Table 2**. The initial measurements for the control and the samples containing silane are similar but the control sample loses more than half its strength after a few hours of exposure. The silane samples are still displaying significant retention of properties even after 100hr, especially the Sivate E610 sample.

Sivate E610 is ready-to-use and is intended to be a 1-to-1 replacement for APTES. The silane blend can be applied as 100% actives or diluted in solvents, such as ethanol, isopropanol, heptane, or toluene. Sivate E610 can be used as a primer or as a coupling agent for thermoset and thermoplastic composites and it can be applied to metallic, as well as siliceous substrates and particles.

Coatings and composites with Sivate E610 will have enhanced durability when exposed to a wide range of harsh conditions and, particularly, in aqueous environments.

Sivate E610 is the first offering in Gelest's new product line of Sivate Enhanced Silanes. It has the potential to improve properties, performance, and durability in a wide variety of applications that currently use conventional amino functional silanes.

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Authors: Susan H Tilford, Barry Arkles, Jonathan Goff
Gelest, Inc., 11 Steel Road E, Morrisville, PA 19067, USA
Website: www.gelest.com

Recycle-friendly PETG shrink sleeves

Sun Chemical has launched its SunLam™ De-seaming Adhesive for shrink-labelled containers. This new de-seamable adhesive helps recyclers improve recycled polyethylene terephthalate (rPET) yield without process changes.

Developed in partnership, Sun Chemical and Eastman extensively tested SunLam on labels made with Eastman Embrace™ LV copolyester. It has received a 'Responsible Innovation Acknowledgment' by the Association of Plastic Recyclers (APR) after passing stringent testing outlined by the APR.

By changing from a traditional solvent to SunLam De-seaming Adhesive, shrink labels deseam and release during the whole bottle wash step of the wet recycling process, without sacrifice of label performance. The label removal occurs prior to colour, infrared and manual sorting, thus preventing shrink-labelled PET bottles being removed from the rPET stream due to misidentification.

The efficacy of SunLam De-seaming Adhesive was tested on bottles with shrink sleeves made from Eastman Embrace LV copolyester. The tests utilised whole bottle wash equipment at commercial recycling facilities and yielded results of greater than 95% label removal, with results typically exceeding 99%.

"When the challenge of removing shrink labels during PET recycling was brought to the industry's attention by the APR and the National Association for PET Container Resources in 2012, Eastman stepped up to the challenge and organised a consortium to collaborate on ways to solve this issue," said Ronnie Little, Market Development Manager, Eastman. "PET bottle bales typically contain five percent shrink-labelled PET bottles. Many of those labels do not come off in the PET recycling process, reducing rPET yield. We're pleased to have partnered with Sun Chemical in this process to develop a technology that satisfies the consumers' desire to recycle, a brand's goal to be both responsible and recognisable and the APR's mission to eliminate barriers to successful commercial recycling."

"Consumers and brand owners alike expect PET bottles to be recycled but unfortunately, far too many end up in landfills because the label wouldn't come off," said Russell Schwartz, Chief Technology Officer, Sun Chemical. "At Sun Chemical, we consider it our responsibility to address issues in the industries in which we participate and to provide leadership in resolving problems our partners and customers face. On learning of these concerns, we initiated a major project to solve this industry-wide challenge. We are pleased to introduce the environmentally friendly SunLam De-seaming Adhesive as part of our contribution to the circular economy."

By using SunLam De-seaming Adhesive, brand owners can continue to benefit from the superior performance of Eastman Embrace LV copolyester. They need not sacrifice full body shrink sleeve label coverage, shrinkage or quality. Brand owners can continue to use full-body shrink labels on their containers. An additional 20% of label surface area is regained with full-body shrink labels, compared to the portion of the bottle that must be left uncovered to avoid near-infrared or colour missorting, as bottles with full wrap shrink sleeves could get rejected by the NIR or colour automated sorting equipment. **PPCJ**