

High-heat silane coupling agents are an aid to resin processing

By Barry Arkles* and William Peterson*

Ethylene-bridged aromatic silanes with various organic functionalities have been developed for use as coupling agents at high processing temperatures. The silanes show coupling activity in a variety of thermoplastic and thermoset composites, including polyamides, polyimides, polydiallyl phthalates, and unsaturated polyesters

The general order of increasing thermal stability for organosilane coupling agents is shown in the box on this page under number key 1.

In this formula, Z is a functional group intended to be reactive with the polymer portion of the composite material. X is a hydrolyzable group, typically alkoxy, which is displaced during the reaction with the substrate portion of the composite.

The strongly electropositive nature of silicon tends to polarize the silicon-carbon bond in positions *beta* to the silicon Z. This phenomenon occurs particularly if its electron withdrawing contributes to nucleophilic elimination of an ethylene group. Fluoroethylsilanes have a tendency to decompose at 40°C. in mild basic conditions. Although they are more stable than the *beta* substitution materials, *alpha* substitution decomposes by an electrophilic mechanism. Accordingly, most currently available commercial coupling agents possess functionality at the *gamma* carbon. This class of silane materials has provided sufficient thermal stability for application to most resins. Examples, together with the thermogravimetric analysis temperature (TGA) at which there is a 20% loss of hydrolysate (1)¹, are given in the accompanying box, and are identified under number key 2.

The introduction of resins which process at temperatures in excess of 350°C. or receive continuous exposure to temperatures in excess of 150°C. exceeds the thermal stability of *gamma* substituted silanes.

It has been demonstrated that extremely thermally stable silane coupling agents can be prepared when aromatic groups are bound to the silicon (2,3).

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1: Numbers in parentheses designate references at end of article.

Based on a paper presented at the 35th SPI RP/C Institute Conference in New Orleans.

They are identified under number key 3 in the box.

The principal drawback of aromatic silanes of this type is economics. The chemistry involved is usually multi-step and low-yield, discounting the materials as commercially significant.

We have recently introduced a new series of silanes, with thermal stability intermediate between *gamma* and aromatic materials. They are ethylene-bridged aromatics: Z CH₂ C₆H₄ CH₂ CH₂ SiX₃ (ethylene-bridged aromatic substitution). These materials have significantly greater thermal stability than the *gamma* functional silanes. Stability is marginally lower than the fully aromatic silanes. The ethylene-bridged aromatic silanes have demonstrated utility in resins processing at temperatures up to 400°C. and with continuous exposure to 200°C. They include a chloromethyl, a styryl, and a diamine functional silane. See box, number key 4.

Test results

The thermal stability of the aliphatic-bridged aromatic silanes was evaluated by preparing cured hydrolysates and observing the 25% weight loss by TGA (ni-

trogen, 5°C./min.). The 25% TGA weight loss exceeds 425°C. for all materials tested (Table I). The chloromethyl derivative had the greatest stability (495°C.), while the diamine demonstrated the least stability (435°C.).

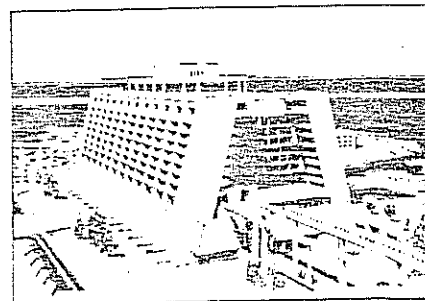
Thermoset composites were prepared from heat-cleaned glass-fiber mat. Laminates containing 30% resin were prepared under recommended process conditions. Flexural strength was measured as molded, after 200°C. exposure for 100 hr. and after a 2-hr. boil (Table II). For DAP compositions initial strengths achieved with the styrylethyl silane exceeded that achieved by methacryloxysilane by 16%. The differential increased to 20% after 200°C. exposure. Initial strengths of the polyester composite were greater with methacryloxypropyltrimethoxysilane than the styrylethylsilane. After 200°C. exposure the methacryloxysilane lost over 25% of its strength while the styrylethylsilane lost less than 5%.

Thermoplastic composites prepared with water-sized chopped glass strand were extrusion compounded prior to injection molding. The flexural strengths and tensile strengths of specimens were

1	Z CH ₂ CH ₂ SiX ₃ Z CH ₂ SiX ₃ Z CH ₂ CH ₂ CH ₂ SiX ₃ Z CH ₂ (\bigcirc)SiX ₃	(<i>beta</i> substitution) (<i>alpha</i> substitution) (<i>gamma</i> substitution) (aromatic substitution)
2	H ₂ N CH ₂ CH ₂ NHCH ₂ CH ₂ CH ₂ Si (OMe) ₃ ClCH ₂ CH ₂ CH ₂ Si (OMe) ₃ H ₂ C = C (CH ₃) CO ₂ CH ₂ CH ₂ CH ₂ Si (OMe) ₃	390°C. 360°C. 395°C.
3	H ₂ N(\bigcirc)Si (OEt) ₃ Me(\bigcirc)Si (OMe) ₃ HOOC(\bigcirc)Si (OMe) ₃	485°C. 530°C. 510°C.
4	ClCH ₂ (\bigcirc)CH ₂ CH ₂ Si (OMe) ₃ H ₂ C = CH(\bigcirc)CH ₂ CH ₂ CH ₂ Si (OMe) ₃ H ₂ NCH ₂ CH ₂ NHCH ₂ (\bigcirc)CH ₂ CH ₂ Si (OMe) ₃	C-T2902 PSX083 PSX084

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Designation	Functionality	TGA ^a	Boiling point, °C.
C-T2902	Chloromethyl	495°C.	165°/1.5 mm.
PSX083	Vinyl (styryl)	460°C.	185°/3 mm.
PSX084	Diamine	435°C.	

a: Temperature of 25% weight loss of hydrolysate in thermogravimetric analysis (5° C./min. in nitrogen).

Silane	Flexural strength, p.s.i.		
	Molded	200°C.	Wet
Diallyl phthalate resin			
C-M8550 ^b	58,200	62,100	58,400
PSX083	67,400	74,800	68,100
Unsaturated polyester			
C-M8550	93,800	69,200	91,000
PSX083	82,600	79,800	76,200

a: Specimen treatment before test: molded = as-molded condition; 200°C. = after exposure for 100 hr.; wet = after 2 hr. in boiling water.
b: C-M8550 is methacryloxypropyltrimethoxysilane.

Silane	Polysulfone		Polyamide-imide		Nylon 6/6	
	T.S., p.s.i.	F.S., p.s.i.	T.S., p.s.i.	F.S., p.s.i.	T.S., p.s.i.	F.S., p.s.i.
C-A0700 ^a	18,600	25,250	27,400	31,000	27,200	39,500
C-T2902	14,400	19,600	28,200	37,700	23,500	33,600
PSX084	19,400	25,700	29,700	38,600	27,900	39,800

a: C-A0700 is aminoethylaminopropyltrimethoxysilane.

determined by ASTM D790 and D638 (Table III). The amine-functional high temperature silane (PSX084) produced the best results across the board, with values higher than those previously reported (4,5). The differential versus the nonaromatic amine control (C-A0700) increased with increasing process temperature of the resins, i.e., polyamide-imide > polysulfone > nylon-6/6. The chloromethyl aromatic group has lower reactivity than the amine groups in the polyamide-imide resin tested; yet in C-T2902 it gave superior results when compared to the nonaromatic amine. This indicates that the thermal stability of the nonaromatic amine silane is inadequate for resins processing at temperatures in excess of 350°C.

Conclusions

This new series of ethylene-bridged aromatic silanes has improved thermal stability compared with currently available commercial materials. Vinyl functional materials of this class demonstrate cou-

pling-agent activity in DAP and polyester resins; maintenance of composite strength has been found to be superior to that of materials which are based on nonaromatic silanes.

In our evaluations, diamine silane produced greater composite strength than the nonaromatic amine. Chloromethyl silane gave greater coupling in polyamide-imide than nonaromatic amine, indicating the latter's inadequate thermal stability for high-temperature resin compounding.

References

- 1) E.P. Plueddemann, MODERN PLASTICS, 43 131 (Aug. 1966).
- 2) E.P. Plueddemann, Air Force report AFML-TR-65-316 (1965).
- 3) E.P. Plueddemann, SPI RP/C Proceedings, 22, Paper 9A (1967).
- 4) B. Arkles and J. Theberge, SPI RP/C Proceedings, 30, Paper 17E (1975).
- 5) B. Arkles, ChemTech 7, 766 (1977). ■

Official rules

1. Fill out the official entry blank or a 3" x 5" card handprinted with your name and completed address. Be sure to include with your entry only the weight of the actual part made only from Nylon 66 or reinforced Nylon 66. YOUR ENTRY MUST BE AN INJECTION MOLDED PART PRODUCED FOR COMMERCIAL USE WITHIN THE LAST FIVE YEARS. HOWEVER, IT DOES NOT HAVE TO BE A PART MADE FROM MONSANTO'S VYDYNE NYLON MATERIAL.

2. Mail your entry to: Vydyne[®] Makes All Sizes Contest, P.O. Box 115, New York, NY 10046. Enter as often as you like but each entry must be mailed separately. All entries must be received no later than April 30, 1981 in order to be eligible to win.

3. Winners will be selected in three ways: (1) The largest part by weight, (2) The smallest part by weight and (3) A sweepstakes drawing from all entries received. All parts must be made from Nylon 66 or reinforced Nylon 66. Winners will be selected by Marden-Kane, Inc., an independent judging organization whose decisions are final. In the event there is more than one entry received in a category with the identical weight, then the winners will be selected in a random drawing. Winners will be required to submit their winning part to Monsanto for verification and sign an affidavit of eligibility and release. Winners will be notified by mail. Only one prize will be awarded to an individual for all three categories. All taxes are the sole responsibility of the prize winners.

4. Prize Structure: A trip to Walt Disney World for four people for 3 nights and 4 days. Trip includes round trip air transportation (coach) from airport nearest winner's home, accommodations at the Monsanto Suite at The Contemporary Hotel, admission to Walt Disney World for 3 days plus \$200.00 spending money. Total approximate retail value: \$2,000.00. No prize substitution permitted and winners must take their trips by December 31, 1981.

5. Contest open to all persons 18 years or older of the Continental USA who are employed by a company that uses or molds parts made of nylon material, except employees and their immediate families of Monsanto Company, its subsidiaries, its advertising agency and Marden-Kane, Inc. Void where prohibited by law. All federal, state and local regulations apply.

6. For a list of winners send a stamped self-addressed envelope to Vydyne Winners List, P.O. Box 386, New York, NY 10046.