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

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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 thermostet composites, including polyamides, polyimides, poly diallyl 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 3. In this formula, Z is a functional group intended to be reactive with the polymer portion of the composite material. X is a hydroxygeal group, typically alkox, which is displaced during the reaction with the substrate portion of the composite.

The strongly electropositive nature of silicon tends to polarize the carbon-silicon bond in positions beta to the silicon Z. This phenomenon occurs particularly if its electron withdrawing contributes to nucleophilic elimination of an ethylenic group. Fluorocarbons have a tendency to decompose at 40°C. In mild basic conditions, although they are more stable than the beta substitution materials, alpha substitution is decomposed by an electrophilic mechanism. Accordingly, most commercially 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 hydrolyzate (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).

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 CH₃ C₆H₄ CH₂ CH₃ 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 styril, and a dimine functional silane. See box, number key 4.

Test results
The thermal stability of the aliphatic-bridged aromatic silanes was evaluated by preparing cured hydrolyrates and observing the 25% weight loss by TGA (nitrogen, 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 mats. Laminates containing 30% resin were prepared under recommended processing 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 styryl silane exceeded that achieved by methacryloxy silane by 16%. The differential increased to 20% after 200°C exposure. Initial strengths of the polyester composite were greater with methacryloxypropyltrimethoxysilane than the styrylylsilane. After 200°C exposure the methacryloxysilane lost over 25% of its strength while the styryl silane lost less than 5%.

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

| 1 | Z CH₂CH₂SiX₃ | (beta substitution) |
| Z CH₂SiX₃ | (alpha substitution) |
| Z CH₂CH₂CH₂SiX₃ | (gamma substitution) |
| Z CH₂(β)SiX₃ | (aromatic substitution) |
| 2 | H₂N CH₂CH₂NHCH₂CH₂CH₂Si(OMe)₃ | 390°C. |
| CICH₂CH₂CH₂Si(OMe)₃ | 360°C. |
| H₂C = C (CH₃) CO₂CH₂CH₂CH₂Si(OMe)₃ | 395°C. |
| 3 | H₂N(β)Si(OME)₃ | 485°C. |
| Me-β-Si(OMe)₃ | 530°C. |
| HOOC-β-Si(OMe)₃ | 510°C. |
| 4 | CICCH₂(β)CH₂CH₂Si(OMe)₃ | C-T2902 |
| H₂C = CH(β)CH₂CH₂CH₂Si(OMe)₃ | PSX083 |
| H₂NCH₂CH₂NHCH₂(β)-CH₂CH₂Si(OMe)₃ | PSX084 |

1 Numbers are parentheses designate references at end of article.
2 Based on a paper presented at the 35th SPI KPC Institute Conference in New Orleans.

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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 coupling 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