

Commercial Applications of Sol-Gel-Derived Hybrid Materials

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Introduction

Sol-gel processing readily yields both inorganic and hybrid organic-inorganic materials. Commercial applications of sol-gel technology preceded the formal recognition of this technology as an important field of study. Likewise, successful commercial hybrid organic-inorganic polymers have been part of manufacturing technology since the 1950s. As our understanding of polymer chemistry, processing, and structure-property relationships has grown, materials scientists have learned to create hybrid materials that display unique properties. Those materials that demonstrate viability in the marketplace either possess singular properties that enable new end-use applications or are well outside the cost-performance envelope of existing commercial materials. Looking at current hybrid polymers that have won niches in the marketplace suggests directions for future successes. The sol-gel-derived materials discussed here represent only a portion of

successful hybrid materials.¹ An important premise in this article is that a “commercial” product is one that is both offered for sale and *used* in the regular production of a device or item in general commerce. There appear to be many hybrid materials with significant commercial potential that have not yet achieved commercial status.

No generally accepted definition has been determined for the bewildering variety of materials that are described as “hybrid organic-inorganic polymers.” A narrow definition is that (a) they consist of clear regions or morphologies in which organic structures (C, H, N, O) dominate as well as separate regions in which distinct structures imposed by heteroatoms dominate, and (b) they exhibit physical properties which are not a linear or geometric average of these regions. For example, poly(vinyltrimethylsilane) and poly(trimethylsilylpropyne), two polymers of interest in permselective (differential-

permeation) membrane technology, are not considered hybrid polymers because they have no distinct region that is associated with the silicon heteroatom. On the other hand, dimethylsiloxane-bisphenol A carbonate block polymers are considered hybrid polymers, since they display independent glass-transition temperatures associated with the inorganic and organic regions. The minimum dimensions in which clear distinction of physical properties associated with a region or domain appear are in the range of about 1 nm. For example, in block polymers with siloxane linkages, this correlates with 4-6 units. In nanocomposites, this correlates roughly to the dimensions of a silsesquioxane cube. A well-considered discussion of the definition of hybrid organic-inorganic structures in this context has recently been presented.²

The only inorganic polymers that have achieved commercial status, or that have been seriously considered for commercial applications, have been derived from the Group IVA and IVB elements, of which silicon is preeminent. Most commercial hybrid polymers derive from the introduction of organic substituents into an amorphous polyoxymetallate structure that is associated with silicates and siloxanes. A scheme for naming these structures based on the number of oxygens bound to each metal atom has been adopted (see Chart 1). A metal with four oxygen substitutions is termed a “Q” resin (Figure 1a). A metal with three oxygens and one organic substitution is termed a “T” resin (Figure 1b). A metal with two oxygens and

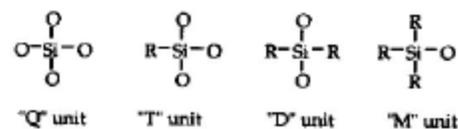


Chart 1.

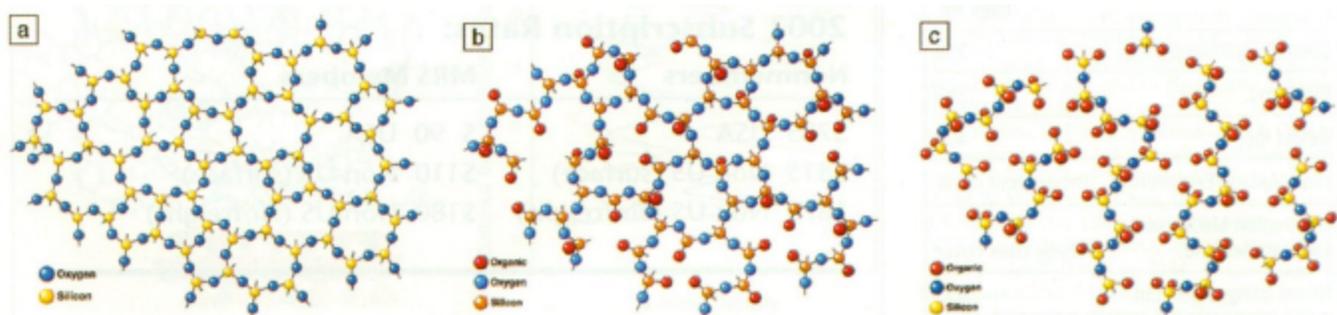


Figure 1. Hybrid organic-inorganic polymers can be visualized as successive organic substitutions of polyoxymetallates. (a) A “Q” structure, where four oxygen atoms are bound to a metal atom (silicon dioxide, or quartz in the example of silicon), gives rise to (b) a less rigid “T” resin when there is one organic substituent on each metal atom, and (c) linear “D” resins when there are two organic substituents on each metal atom (exemplified in the case of silicon by silicone oils).

two organic substitutions is termed a "D" resin. For silicon, a pure Q resin is SiO₂ or quartz, a T resin is a silsesquioxane, and a D resin is a linear siloxane (Figure 1c). Finally, "M" is a terminating siloxy group.

In the context of sol-gel chemistry, a less rigorous definition of hybrid organic-inorganic materials has been accepted in which T resins, and Q resins modified by T and D structures, are allowed. The ceramic community conceptualizes these resins as organic modified silicas and has dubbed them "ormosils."³

Thin-Film and Coating Materials

Zinc-rich inorganic paints are examples of early and still viable commercial applications of sol-gel technology.⁴⁻⁶ Based on Q inorganic silicate structures, these antecedents of modern sol-gel coatings have been in production for over 50 years. They are employed as corrosion-resistant primers and high-temperature coatings for steel. They are formulated from oligomeric condensates of tetraethoxysilane, designated by industry as ethylsilicate 40, and zinc powder. Current manufacturers and trade names include Carboline Carbozinc®, and Devco Catha-Cote®. In principle, two major paths exist for modifying Q structures of this type to create organic hybrids. One path introduces substitutions onto some or all of the silicon atoms, creating a T resin or organo-silsesquioxane structure. The second builds a Q structure core and transitions to an organic-rich T, D, or wholly organic structure.

In the early 1950s, Brady and co-workers at Dow Corning produced a series of low-molecular-weight phenylsilsesquioxane-alkylsilsesquioxane copolymers of low molecular weight and high hydroxyl functionality.⁷ Structure 1 shows a typical structure. The phenylsilsesquioxane copolymers can be converted by reaction into a variety of standard alkyd resin formulations.⁸ The result is a range of high-performance, weather-resistant coatings used, for example, on superstructures for naval aircraft. Similarly, alkoxy functional silsesquioxane resins are incorporated into a variety of polyester formulations used in coil

coating applications.⁹ Compositions that incorporate D units are used directly as release resins for baking pans and utensils.¹⁰ In other variations, ormosils modified by organic resins in a graft inter-penetrating polymer network technology are offered as protective coatings.¹¹ Ameron PSX® coatings are an example.

Modified T resins retain important roles in electrical component coatings such as resistors and molding compounds, as well as spin-on dielectrics in microelectronic interlayer dielectric and planarization applications (Figure 2). They typically have simple methyl or hydride substitutions, but more complex structures than resins used in organic coatings. The materials are prepared by controlled hydrolysis of alkyltri-alkoxysilanes¹² (Reaction 1). An early version, sold under the name Glass-Rock® by Owens-Illinois, was used to seal cathode-ray tubes. Subsequently, the name was changed to Techneglas® by NEC and the product was offered specifically for dielectric applications. Similarly, a range of compositions is offered under the name Accu-Spin® by Honeywell for spin-on glass applications. Pure methylsilsesquioxanes have dielectric constants in the range of 2.9-3.2 at 60 Hz and have become the starting-point compositions for interlayer dielectrics of interest for microelectronic features below 0.18 μm.

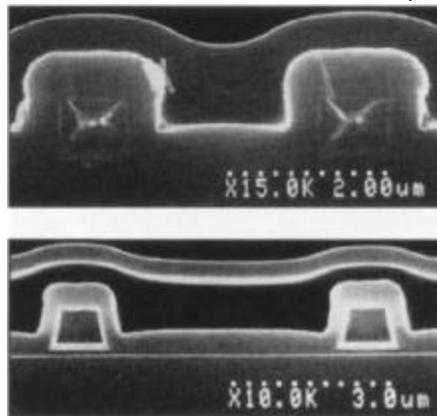
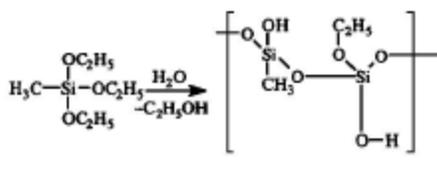
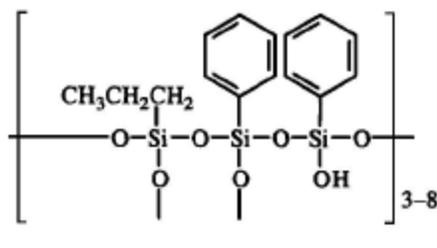


Figure 2. Two examples of spin-on oxides, originally used in planarization, which in hybrid form are used as interlayer dielectrics.



Approaches for reducing the dielectric constant below 2.9 include mesoporous and composite versions.

Structures generated by chemical vapor deposition (CVD) analogous to Q-T resins produced by hydrolysis-condensation are marketed under the trade names Black Diamond® and Coral® by Applied Materials and Novellus, respectively. Typically, trimethylsilane or other methylhydrosilanes are introduced into a deposition chamber containing the substrate in the presence of an oxidizing atmosphere.¹³ At elevated substrate temperatures (>300°C), N₂O and O₂ are used in a plasma-assisted oxidation. The first step in the oxidation of these materials is thought to be the conversion of the hydride substituent to an oxygen substituent, either by direct oxidation of the silyl hydride or through a methyl-substituted silyl radical intermediate. The next stage is the further oxidation of the molecule, resulting in the removal of methyl groups and the formation of films dominated by O-Si-O bonds that maintain some Si-C bonds. The atomic percent of carbon in low-k (where k is the dielectric constant) films (C/(C+Si+O)) is usually in the range of 3-20. Nitrous oxide methods and oxygen methods have been reported.¹⁵ If deposition is to be accomplished at temperatures below 300°C, ozone has been used successfully.¹⁶

Commercial optical hard coats illustrate the broad scope of silsesquioxane or T-resin technology. While simple unmodified methylsilsesquioxane resins of controlled molecular weight and hydroxyl content were the earliest examples of abrasion-resistant coatings, current hard-coat technology rarely uses these materials. For example, cohydrolysis with tetraethoxysilane incorporates Q units into silsesquioxanes. The introduction of an epoxy-substituted monomer (glycidoxypropyl-trimethoxysilane) allows better wet-out and adhesion to polycarbonate lenses and the incorporation of silica sols. A large number of ormosils have been offered as scratch-resistant coatings and antireflective layers for eyewear.¹⁷⁻²⁰ Many of the antireflective coatings substitute metals such as titanium for silicon in the Q portion of the structure. Companies that offer lens coatings include Essilor (Silor®), SDC, American Optical, and Gentec.

While these materials fit the marginal definition of hybrid organic-inorganic polymers, other approaches to optical hard coats match the narrower definition. In the prominent examples, trialkoxysilanes are reacted with a silica sol of low dimensionality and then diluted with alcohol. In the most successful versions, the

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trialkoxysilane is methacrylate-functional, and additional reactive acrylates are added.²¹⁻²³

A new variant on the technology is a thermal- or UV-driven cure system that allows the formation of hybrid systems from modified T resins. The technology exploits the rearrangement reaction of siloxanes substituted at the β position with electron withdrawing groups (Reaction II). The technology disclosed by Arkles and Berry^{24,25} initially described thermally driven chloroethylsilsequioxane rearrangements, but more recent commercial versions are based on acetoxyethylsilsequioxanes. Copolymer versions of the technology lead readily to hybrid structures. Pure or modified silicon dioxide patterns can be written by thermal-cure microcontact printing or UV laser (Figure 3).²⁶ The technology has been introduced to the market under the trade name Ceramic® SI by Gelest. It is finding applications in the formation of dielectric structures in technologies such as flat-panel displays.

Clear Scratch-Resistant Automotive Coatings

A dramatic new high-volume application for hybrid organic-inorganic polymers is in large-volume automotive coatings (Figure 4). In current automotive finish technology, coloration is provided in a pigmented base coat. A clear scratch-resistant overcoat is applied, which must not only satisfy optical and mechanical requirements, but must increasingly provide protection from environmental factors such as UV and chemical attack. In a technology introduced by Dupont as Generation 4®, this is accomplished by utilizing two hybrid polymer systems that cross-link simultaneously during cure to form a polymer network that is partially grafted and partially interpenetrating. Hazan disclosed the enabling technology.²⁷ A high cross-link density acrylate tetrapolymer core, which includes an alkoxyethylsilane group (typically methacryloxypropyltrimethoxysilane) and residual unsaturation, is generated, which provides a high-modulus, scratch-resistant function. The high cross-link density core polymer is dispersed in a second, low cross-link density terpolymer also containing an alkoxyethylsilane, which primarily provides film-

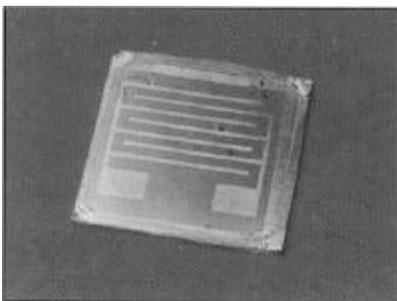


Figure 3. Microcontact-printing-generated silicon dioxide patterns on silicon from β -chloroethylsilsequioxanes give the ability to "build up" rather than "etch back" to create dielectric structures (courtesy R. Composto, Laboratory for Research on the Structure of Matter, University of Pennsylvania).



Figure 4. Automotive finishes such as that on the Honda Civic have depth, luster, and environmental resistance that is the result of a complex mixture of hybrid organic-inorganic materials cured into mixed-graft interpenetrating polymer network systems.

forming properties. Melamine-formaldehyde resins and catalysts are blended into the polymer dispersion, allowing the cure reactions shown in Schemes I and II.

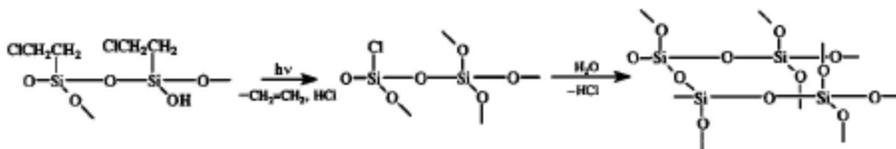
The superior scratch and environmental-etch resistance of these coatings led to their acceptance as topcoats for eight of the ten top-selling automobiles for 1997, including the Ford Taurus, Toyota Camry, and Honda Civic/Del Sol.

Particle, Adhesive, and Composite Technology

The Stöber process²⁸ is a benchmark for the sol-gel preparation of silica particles. A number of extensions of the technology to hybrid systems through the introduction of T and D units have led to particle structures with wide ranges of compressive moduli. Low-modulus particles have been used as components for cosmetic foundations²⁹ under the name Tospearl®. Intermediate-modulus materials are impact modifiers for thermoplastics [e.g., poly(vinyl chloride)] and thermosets (e.g., epoxies).

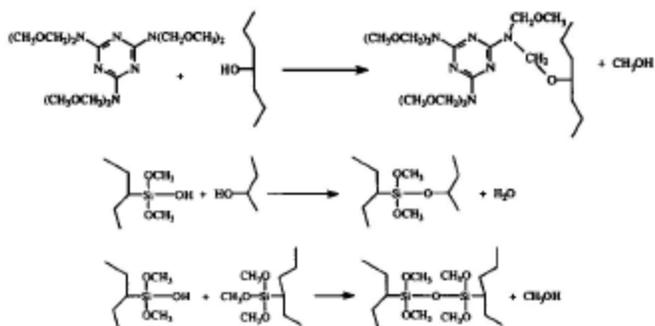
High-modulus mesoporous particles with a Q:T ratio of 2:1 for utilization in reverse-phase high-performance liquid chromatography (HPLC) have been developed by Cheng and Fisk (Figure 5).³⁰ They offer better pH stability than conventional silicas and lower concentrations of surface silanols. In commercial examples, 5- μm particles have an average pore size of 125 Å and a surface area of 180 m²/g, and are typically treated with an octadecyl-functional silane for reverse phase separations. They are marketed under the name Xterra® by Waters. Another application in separation science is SolGel Wax, offered by SGE. A Q-silicate-poly(ethylene oxide) hybrid is bound to glass capillaries for gas chromatography, offering greater thermal stability than conventional poly(ethylene oxide) phases used for the analysis of alcohol, ester, and aldehyde mixtures.

MQ resins are the best examples of commercial hybrid organic-inorganic materials with nanoscale dimensions. These resins are clusters of silicate Q groups terminated with trimethylsilyloxy M groups or hydroxyl groups. Most commercial resins have molecular weights of 2000-10,000 with M: Q ratios varying from 1:1 to 0.6:1 and hydroxyl contents from 0% to 3%. A computer-generated molecular structure of a commercial MQ resin is depicted in Figure 6. In general, there are two methods of preparing these resins, one based on tetraethoxysilane³¹ (Reaction III) and one based on sodium silicate^{32,33} (Reaction IV). The largest application for MQ resins is in pressure-sensitive adhesives (PSAs).^{34,35}

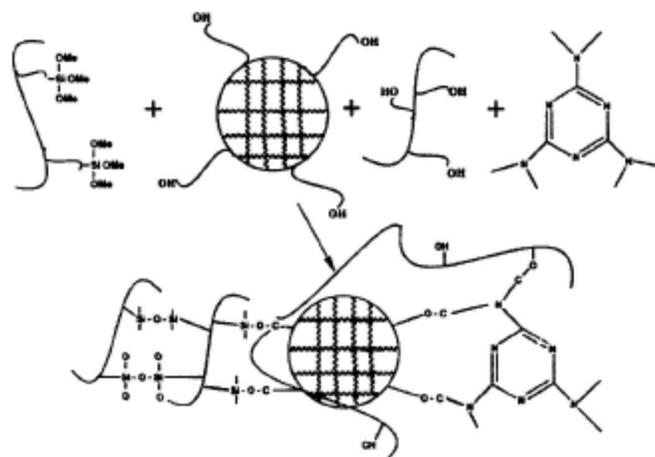


Reaction II.

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Scheme I. Clear, scratch-resistant automotive top-coat chemistry.



Scheme II.



Reaction III.

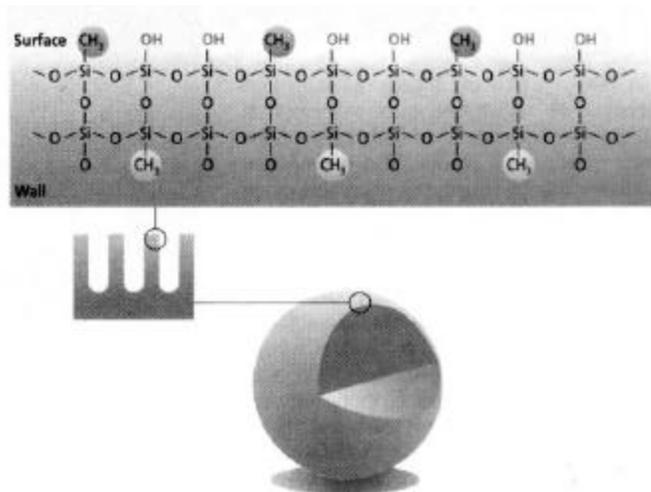


Figure 5. Mesoporous hybrid particles are derivatized for high-pressure liquid chromatography (courtesy T. Walter, Waters Corp.).

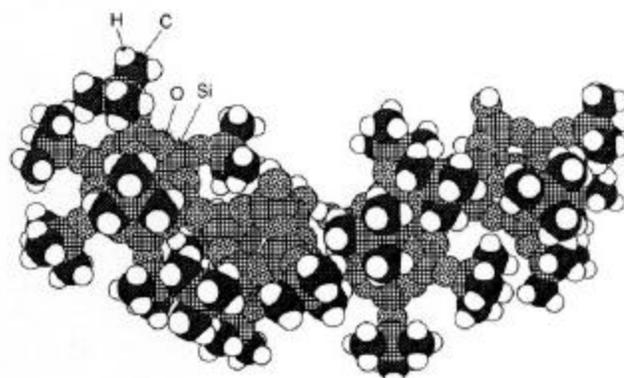


Figure 6. Molecular structure of a typical MQ resin used in pressure-sensitive adhesives [$M_{0.82}Q_{0.17}Q_{0.82}$]₃₂, based on reaction of sodium silicate with trimethylchlorosilane (courtesy J. Wengrovius, General Electric).

Silicone PSAs are visualized as microphase distinct blends or interpenetrating polymer networks of MQ resins with high-molecular-weight linear polydimethylsiloxanes. The MQ resin is the tackifier, and the dimethylsiloxane wets-out substrates before they are cross-linked.

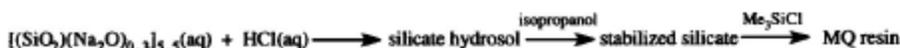
Other applications for MQ resins are in cosmetics, water-repellents, and additives for paper release coatings.³⁶ Hydride- and vinyl-functional MQ resins are used as reinforcing components for clear silicone platinum cure elastomers.^{37,38}

Cross-Linkable Polyethylene (XLPE) through Siloxane Bond Formation

Polyethylene has a desirable balance of electrical, mechanical, and processing properties that has led to its acceptance as a wire and cable insulation material. The continuous operating temperature of polyethylene has been increased from 70°C to more than 90°C by peroxide and radiation cross-linking. These methods, which have shortcomings in production efficiency, product homogeneity, and process safety, have been largely supplanted by methods that incorporate pendant alkoxy-silanes. The

alkoxy-silanes cross-link by a hydrolytic mechanism to form silsesquioxane networks. The technology is widely accepted in wire and cable insulation, including telephone and medium-voltage power cables (Figure 7). It also has applications in heat-shrinkable tubing and compression-resistant foam.

There are two major embodiments of the technology. One is a graft technology in which vinyltrimethoxysilane is peroxide-grafted to a polyethylene backbone prior to or concomitant with cross-head extrusion of the cable. The grafting is done prior to the cross-head extrusion of the cable in the Sioplas® process, which represents a two-step post-polymerization process technology.^{39,40} The grafting is done concomitant with cross-head extrusion of the cable, in the Monosil® process, which represents a one-step post-



Reaction IV.

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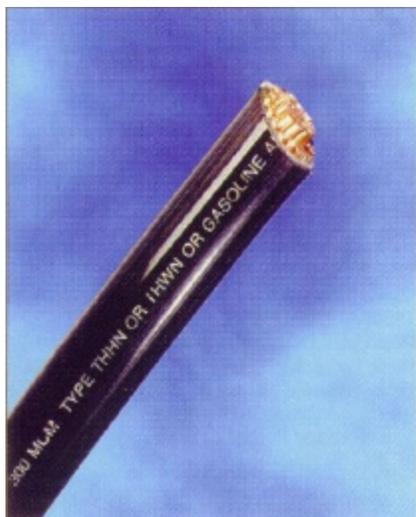
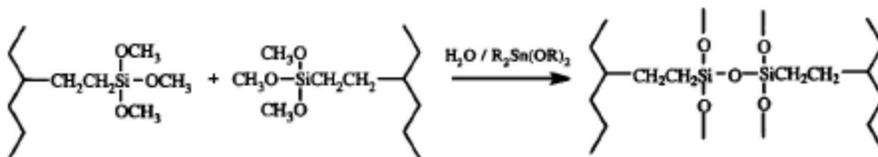


Figure 7. Cross-linked ethylene propylene diene monomer (EPDM) cable insulation is an example of a hybrid technology in which the organic phase dominates.

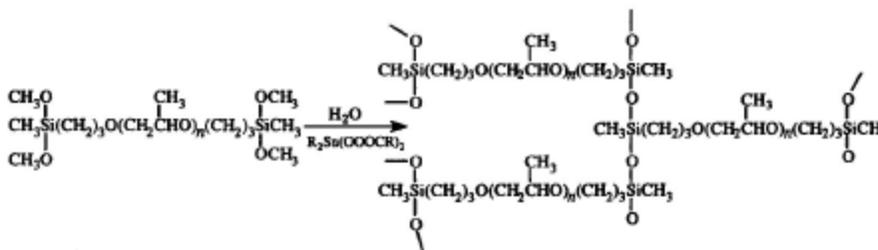
polymerization process technology.⁴¹ Q In both processes, a tin-catalyzed hydrolytic cross-linking after the final extrusion completes the process (Reaction V). Companies that practice the graft technology include Equistar (formerly Quantum Chemicals). Cable processors that practice both graft and cross-link technology include BICC, Alcan, and Okonite.

The success of silane graft technology for cross-linkable high-density polyethylene (HDPE) was based in part upon the ability to fabricate products in conventional thermoplastic-process equipment with relatively little new capital investment. As product benefits became recognized and markets grew, it became possible to consider copolymerization technology, which has a much greater capital barrier for commercialization. The enabling technology was patented by Mitsubishi.⁴³ It is a peroxide-initiated polymerization at 2500 atm of 0.5-3% vinyltrimethoxysilane with ethylene, which generates copolymers with properties similar to graft copolymers. In some cases, high-temperature properties appear to be further enhanced, presumably due to the elimination of reactive tertiary carbon sites.

Companies that have commercialized copolymer technology include Neste (VISICO®), Union Carbide (SI-LINK®), and AT Polymers (Aqua-Link®). A similar technology based on polypropylene has been offered by Mitsubishi (Linklon® PP).⁴⁴



Reaction V.



Reaction VI.

Moisture-Cure Room-Temperature Vulcanizing (RTV) Sealants

A technology that is parallel in concept to cross-linkable HDPE is based on an end-group functionalization of polypropylene oxide.⁴⁵ The result is a liquid polymer that cures in the presence of moisture to form conformable low-cost sealants and caulks (Reaction VI). The technology has been commercialized by Kaneka.

Conclusion

Sol-gel-derived hybrid inorganic-organic polymers are achieving broader commercial status. A review of these materials in a historical context shows that as control of structure and properties has advanced, new applications have followed.

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