

Silylated Polyether: Application In Adhesives And Sealant.

Muhammed Saieed E, Fatehbadur Lodh

Cochin University Of Science And Technology(Cusat)

Abstract

Hybrid polymer is formed by Combining two distinct polymers. The resulting polymer has properties of both components that were not achievable in a polymer alone. By reacting with another substance, one resin can improve certain of its properties without sacrificing the original resin's qualities. For adhesives, sealants, and coatings, silylated polyester and polyether hybrids are essential to the industry. They are low toxic compared to solvent-based goods, silicones, and polyurethanes. The synthesis, characteristics, and uses of these silylated hybrid system are thus covered in a large body of literature. Worldwide, a variety of sealants, adhesives, and coatings are derived from hybrids of silylated polyether polymers. Silane terminated polyether-based sealants combine silicones' resistance to weathering with the strength of polyurethanes. These polymers have gained significant attention not only because of their unique performance and application features but also because they are solvent- and isocyanate-free. This article reviews the various hybrid chemistries, their functions in silyl terminated polyether based adhesives and sealants. It also offers chemistry of silylated polyether polymers and information on various end applications.

Keywords: Silylated, Polyethers, Adhesives, Coatings, Sealants

Date of Submission: 16-04-2024

Date of Acceptance: 26-04-2024

I. Introduction- Different Types Of Hybrids

Hybrid polymers can be developed by combining two different polymers. They frequently include combining a polymer with inorganic substances (such as metal or ceramics) or organic substances. For instance, epoxy-resin-based compounds are durable, quickly cure at room temperature, adhere well to most surfaces, and show chemical resistant to a diluted acids, alkalis, and solvents. The resulting polymer has properties of both components that were not achievable in a polymer alone. It is possible to enhance some properties of an epoxy resin by mixing in a polysulphide component without compromising the epoxy system's current performance capabilities. Reduced viscosity, increased adhesion, flexibility, improved on impact strength, thermal shock resistance, improved water and corrosion resistance, controlled damping properties, and improved chemical resistance are some of the benefits of such modifications. By hybridising these materials, many kinds of polymers, such as polyurethanes, alkyds, acrylics, polyesters, silicones, etc., can perform better or provide desired results. The development of hybrid polymer technology has led to the release of numerous hybrid systems onto the market. Although coatings are the focus of most of the research in this field, other products utilised in the building industry can also benefit from it. Research is being carried out by numerous polymer industries and academic institutes, and new findings are often published. The popularity of hybrid polymers stems from their distinct and often odd features coupled with easy and cheap production methods that lead to significant cost savings over similar silicon-based systems.

Adhesives and coatings commonly use aqueous polyurethane dispersions (PUD). Their films have excellent flexibility, abrasion resistance, and low-temperature impact resistance. Polyurethane (PU) coatings have been available for a while, but the increasing need for low volatile organic content (VOC) materials has driven the development of new environmentally friendly products and procedures. Water-borne PU synthesis is a highly prevalent process in the coatings industry today, albeit the cost of these products is usually higher than that of other products. It is common practice to combine the superior chemical properties of the PU resin with the inexpensive acrylic component in applications where finances are limited number. The most common type of polyol in commercial PUD is aliphatic di-isocyanate. Difunctional materials, like polyester grades, are utilised because they have a range of qualities, including adhesion, solvent resistance, high to low modulus, strong UV resistance, and respectable hydrolysis resistance. New innovations in urethane/acrylic dispersion are primarily focused on improving adhesion to plastic surfaces, resistance to chemicals, solvents and abrasion. Even at low temperatures, the films maintain their exceptional mechanical qualities and the perfect ratio of hardness to flexibility. Additionally, polyurethane coatings withstand scratches well. Nonetheless, these hybrid-based paints offer a higher end gloss than pure PU-based paints. Compared to pure acrylic-based paints, hybrids have better optical qualities after weathering. It was successful in producing nanosized PU/ Poly (butyl methacrylate)

(PBMA) hybrid latex particles (50 nm) with a variety of compositions using a redox-initiated mini-emulsion polymerization process. The use of small-size latex particles will result in films with better mechanical and aesthetic properties. An intraparticle chain extension approach was applied to the urethane prepolymer, which resulted in the polyurethane chains being stretched to increase the molecular weight of the PU and acting as a "crosslinker-like" moiety by binding the pendant urethane chains together. Along with the Fourier-transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance (¹H-NMR), and thermal properties (Differential Scanning Calorimeter (DSC), Thermogravimetric analysis (TGA)) of various PU/acrylic hybrids with varying percentages of acrylic dispersions, the PU prepolymer and the comparable pure acrylic latex were discussed. The outcomes demonstrate the high degree of compatibility between the two components. Because of the hybrid's composition of 30–40 weight percent acrylics, it displays interesting properties like better heat stability and decreased density. A lower T_g acrylic polymer has been used in the development of new PU/acrylic systems, allowing for the preparation of a wide range of compositions for film-forming hybrids and the determination of the maximum amount of acrylic component in a PU matrix without phase segregation [4]. Investigations were conducted into the effects of different initiators, surfactants, PU/AC ratios, Dimethylol propanoic acid (DMPA), and other parameters on the latex qualities. Particle size increased dramatically in latexes made with 0.1% surfactant when compared to surfactant-free polyurethane-acrylic (PU-AC) latexes, regardless of the kind of surfactant used). Nevertheless, by increasing the amount of surfactant in the mixture, latexes with smaller particle sizes and a narrower particle size dispersion developed. Polymers are often reinforced with inorganic fillers for making composite materials. Sol-gel technology has recently opened new avenues for the production of polymer-metal oxide hybrid materials. In this reaction, the metal alkoxides are hydrolyzed, and the hydrolyzed intermediates are then polycondensed. Polymers break down below 500°C, whereas metal oxides have exceptional thermal resilience. Compared to metals and metal oxides, polymeric materials typically have a higher thermal expansion coefficient. Metal oxides are brittle and strong, while polymers are flexible. The process for manufacturing silica-polyimides hybrid materials is explained in this article. It involves hydrolyzing and polycondensing tetramethoxysilane (TEOS) in a polyamic acid solution, then heating it to 270°C. The hybrid films' density, decomposition temperature, and modulus increased together with the concentration of silica; nevertheless, the films' tensile strength decreased in that sequence. The transparent-opaque shifting points shifted to areas with larger silica levels when the matrix polyimide's ethoxy-silyl group concentration increased. Increasing the silica level while lowering the ethoxysilyl content. Aminophenyl trimethoxysilane (APTMS), an organically substituted alkoxysilane that provided the sites for bonding between the resin and the silica phase, was included in the study. The APTMS was selected because of its exceptional thermal stability, ability to hydrolyze tetramethoxysilane, and capacity for polycondensation. In these sol-gel procedures, high temperatures promote the amino groups to react with the carboxylic acid groups of polyamic acid. Additionally, the effects of the size distribution of the silica (SiO₂) particles and coupling agent on the characteristics of the polyimide/silica (PI/SiO₂) hybrids were studied. The coupling agent γ -glycidyloxypropyltrimethoxysilane (GOTMS) significantly enhanced the compatibility between the two phases of PI/SiO₂ hybrids. GOTMS significantly decreased the size of the silica particles in the PI/SiO₂ hybrids. As a result, the PI/SiO₂ hybrids' characteristics were significantly enhanced. Diamine 4,4-diamino-4-hydroxy triphenyl methane (DHTM) was added in a ring-opening polyaddition to dianhydride pyromellitic dianhydride (PMDA) to produce soluble polyimide. This process was then explored for cyclodehydration using xylene-water azeotropic distillation. In less than 10 % SiO₂, the mechanical characteristics of the hybrid films improve, and the creation of physical crosslinking and interfacial contact can be attributed to these improvements. The T_g of the hybrid materials rose by 15-20°C with an increase in inorganic content, according to DMA experiments.

Epoxy resin of bisphenol-A type and silane alkoxide were used for the development of organic/inorganic hybrid composites [15]. A hybrid coating produced by epoxy-silica hybrid materials using a sol-gel/amine curing reaction of GPTMS for steel application. The ratio of amine hydrogen to epoxy groups roughly corresponds to the maximal extent of ring opening. As a result, the development of organic networks increases as diethylenetriamine (DETA) concentration rises. For low DETA formulations, heat curing is therefore necessary to finish the organic network. An extensive and extensively cross-linked organic network that prevents the development of an inorganic network is produced by a high concentration of DETA [16]. The GPTMS-TEOS (tetraethylorthosilicate) hybrid coatings were developed from sol-gel technology. This was done with organic concentrations (20% to 87%) and hydrolysis water contents in order to examine the effects of these parameters on the corrosion protection qualities of ormosil films. The films' resistance to corrosion was tested using salt spray experiments and Potentiodynamic scanning. The outcomes demonstrated that, in comparison to the untreated aluminium alloy substrate, the hybrid coatings offered superior barrier and corrosion protection [17]. High activation energy hybrids provide a high level of thermal stability [18]. A possible method was developed for hybrid system of vinyl-acrylics and alkyds [19-20]. Alkyd resin was mixed into an acrylic solution to form an alkyd-acrylic hybrid with an ultimately solids content of 75–80% [21-22]. The evolution of the crosslinked network and its relationship to the compatibilization of the alkyd and acrylic phases were studied as well by

simulating the large-strain deformation of alkyd-acrylic latex films using a combination of the Upper Convected Maxwell 25 model and the Gent model 26 [23]. Synthesis of hybrid binders by free radical polymerization of acrylic monomers using unsaturated alkyd resin was investigated by emulsion polymerization [24-25]. An acrylic prepolymer containing carboxylic groups and a long-oil alkyd resin underwent a melt co-condensation reaction to successfully synthesise hybrid aqueous alkyd-acrylic dispersions with 40% solid content that absence of surfactant and organic solvent [26]. The melting condensation reactions between medium-oil alkyd resin and acrylic pre-polymers with carboxylic groups produced the VOC-free aqueous hybrid alkyd-acrylic (50/50 wt/wt) dispersion. Following that, an aqueous ammonia solution neutralises the carboxylic groups, initiating the process of self-emulsification [27].

II. Silane Terminate Hybrids

Silane terminated prepolymers perform a major industrial role in adhesives, sealants, and coatings. Their low toxicity in comparison to silicones, polyurethanes, and solvent-based products makes them extremely significant. Silane terminated polyether (MS polymers) and silane terminated polyurethane (SPUR) are the basis for a large number of sealants, adhesives, and varnishes used worldwide. The advantages of silicone-based products and conventional polyurethane are combined in a hybrid system that minimizes the inherent disadvantages of each material by combining an organo-polyurethane content with an inorganic-alkoxysilane content. Most wood flooring adhesives on the market today are consist of SPUR, where the flexibility of the cured substance and adhesion of substrate are becoming more and more important [28]. Silanes are widely used as surface modifiers to promote coating adhesion, and precursors in the chemical industry [29]. Tri-alkoxysilanes, also called silane coupling agents, bond an inorganic substrate (surface) with an unpolymerized resin matrix via two reactive functionalities at the ends of their molecular chain. Before silane may form a bond with the inorganic substrate at room temperature, it must first be activated by an acid to make silanol (SiOH). Alkyl and aryl silanes are the two groups of moieties that are attached to the silicon atom in the structure of an alkoxy silane. The X stands for the alkoxy moieties, which are mainly methoxy or ethoxy. Methanol or ethanol is generated when these moieties react with different hydroxyl groups [30]. Two distinct reactive functional groups found in organofunctional silanes can pair and react with a range of inorganic and organic substances. They so make it easier for different materials to stick together. To form a bond through the hydrogen bond on the surface of the substrate, Silane group must first undergo hydrolysis [30–32]. Figure 1 illustrates the mechanism of hydrolysis.

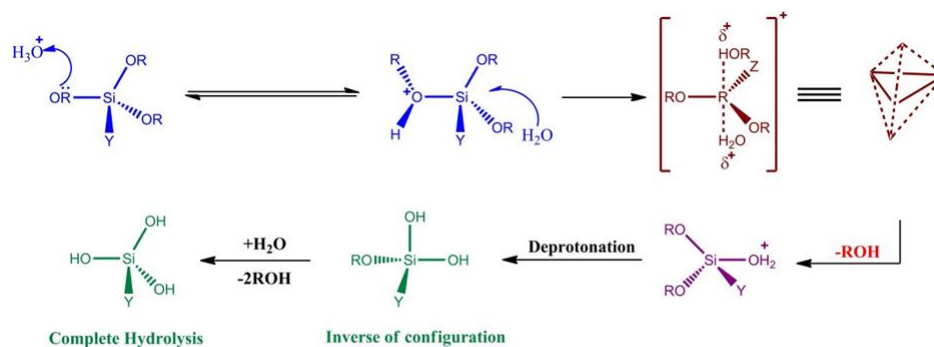


Figure 1: Mechanism of acid hydrolysis of silane: organofunctional group (Y) and alkoxy group (OR).

The humidity, temperature, concentration, pH, solvent system, and molecular structure of silane all affect how quickly it hydrolyses. The rate of hydrolysis may be impacted by the bulkiness of alkoxy groups. Silane coupling agents with large alkoxy groups sterically prevent water from moving towards the silicon atom. In both acidic and alkaline conditions, the rate of silane hydrolysis increases; however, for alkoxy silanes, at a pH of neutral, the rate of hydrolysis approaches a minimum. Attack of nucleophilic hydroxyl or deprotonated silanol group occur on alkoxy silane in alkaline medium and silanol in hydrolysis and condensation reaction. It occurs by SN₂ mechanism. Steric and inductive factor affect the polymerization reaction. Hydrolysis reaction is more sensitive to the steric and inductive effect whereas condensation reaction is more sensitive to the steric effect. The alkoxide and silanol are first protonated in a fast step in acidic medium. After this silicon atom become more electrophilic and are susceptible to backside attack by water or neutral silanol in hydrolysis ad condensation reaction. Here also rate of reaction is affected by steric and inductive effect [29]. The Arrhenius rule states that temperature enhances the pace of the hydrolysis reaction, making temperature an important element. The rate of

hydrolysis is influenced by the kind of co-solvent present in the solvent mixture. The rate of hydrolysis is influenced by the hydrophilicity of the solvent. As methanol, ethanol, and propan-1-ol lose some of their hydrophilicity, the rate of hydrolysis reduces [30–34]. Two distinct reactive functional groups found in organofunctional silanes can couple and react with a range of inorganic and organic substances. Consequently, they promote adherence and strengthen the connection between unsuitable materials. γ -alkoxysilanes undergo a significantly slower process of moisture-induced crosslinking than α -alkoxysilanes, which are highly reactive (figure 2). A siloxane network develops as a result of the interaction with water. The silicon atom (X) possesses a functional organic group in addition to the alkoxy groups. A silane can also attach itself via X to an organic molecule. This is the process of making silane-terminated prepolymers. How long the chain of hydrocarbons is a significant structural characteristic of the reactive organic group of organofunctional alkoxy silanes.

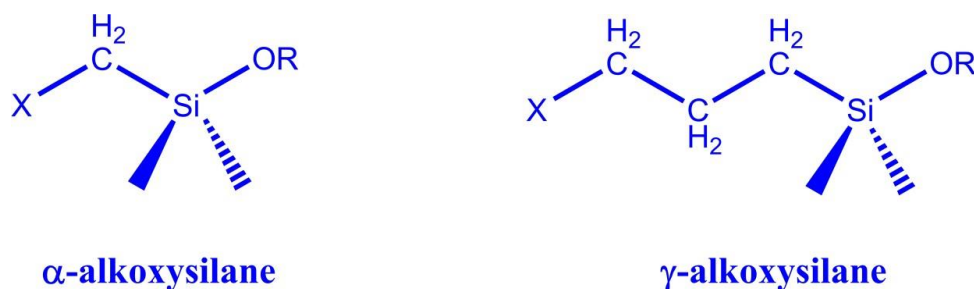


Figure 2: Organofunctional alkoxy silanes: α and γ -alkoxysilanes

When X is positioned in the γ -position about the Si atom, the propylene group in the reactive organic group ($-\text{CH}_2-\text{CH}_2-\text{CH}_2-$) of the γ -silanes. γ -silanes serves as a spacer between organofunctional group and silicon atom. In α -silanes, the methylene group ($-\text{CH}_2-$), which is significantly shorter, is present between the silicon atom and X. Length of the hydrocarbon chain and degree of bonding between the alkoxy group and silicon atom determines the rate of crosslinking in the presence of moisture. The reason for the α -effect in α -alkoxysilanes is the electrical interaction between the donor electron and the silicon atom at the α -position. The electron density is shifted from the donor to the silicon atom by back-bonding, weakening the Si-O bonds. The alkoxy groups separate and hydrolyze more quickly [35].

III. Silane Terminated Polyether Hybrid

A resin consisting of α -silane terminated polyether is used; the fully cured glue possesses both strength and elasticity, which makes it ideal for a variety of uses. The novel resin is extremely reactive due to the α -effect. Polymers ending with α -silane usually undergo rapid crosslinking. In α -silane terminated polyether's, even the dimethoxysilyl and triethoxysilyl end groups exhibit greater reactivity compared to the trimethoxysilyl end groups in γ -silane terminated polyether's. One benefit of difunctional silanes is that during the crosslinking process, they release less methanol. Furthermore, compared to trifunctional silanes, they yield a lower crosslinking density, which promotes the production of a more elastic vulcanizate.

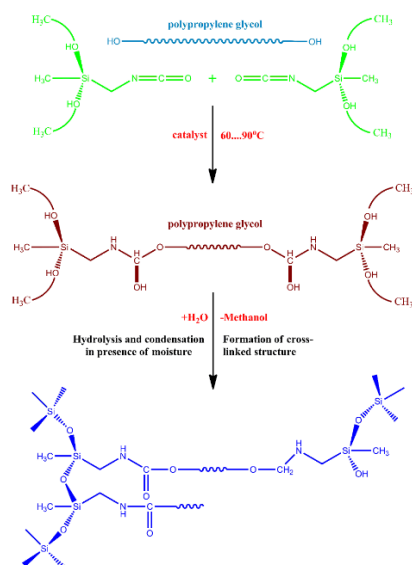


Figure 3: Synthesis Of A Silane Terminated Prepolymers.

As illustrated in figure 3, alkoxy silanes possessing an isocyanate group at the α - terminus have demonstrated exceptional efficacy in interacting with organic polymers. This is due to three factors: 1) It is possible to bond to a variety of organic base polymers due to the isocyanate group; 2) It is simple to control the bonding process; and 3). The final α -silane terminated polymer has no free isocyanate groups since the end silyl groups are permanently bonded to the polymer chain by a strong bond and references on silane terminated polyether synthesis listed in table 1 [36-40] .

With dimethoxy-methyl silyl end groups, the 1st generation of MS Polymer shows exceptional elastic behavior. Later, faster curing systems were created by substituting trimethoxysilyl groups for dimethoxymethyl silyl groups; as a result, elongation decreased. The morphology can be controlled by the polyacrylate-modified second-generation MS Polymer. Rearranging the polymer's structure and backbone can change the suitability of the polymers both before and after curing. This can also affect the polymer's glass transition temperature (T_g). Within a polyether matrix, acrylic domains are created, and these domains greatly increase strength. Additionally, the acrylic domains will give plastic substrates better adhesion and references on modified silane terminated polyether listed in table 1 [41-46].

Table 1: List of references for silane terminated polyether's.

Sr. no	Invention Description	Year	References
1	The invention described about Silyl terminated polyether with epoxy incorporated within its polyether backbone.	2022	47
2	The invention describes the hydroxyl silane and hydroxyl silane terminated polyether polymer and it's method of preparation.	2019	38
3	The article described about Alkoxy silyl group-containing adhesive sealant with improved tear propagation resistance.	2016	54
4	Sealant based on silyl-terminated polyether having very good waterproof performance and adhesion.	2015	56
5	The Invention described adhesive for polyurethane of silyl-terminated polyether modification and preparation method thereof and application.	2012	42
6	The invention relates to adhesive for polyurethane of silyl-terminated polyether modification and preparation method thereof and application.	2012	57
7	The invention described about the silyl-modified polymers and methods of producing same.	2011	37
8	Silicon containing organic polymer with hydroxy or hydrolyzable group bonded to a silicon atom which form a siloxane bond to organic polymer.	2011	59
9	The Invention described silicon polyether copolymers and a Process for their preparation.	2010	55
10	The invention discloses a method for synthesizing silyl-terminated polyether.	2010	43
11	The invention relates to the compound method of polyether's, relate to a kind of method of synthesizing silyl-terminated polyether.	2010	58
12	The invention describes about process for producing polyether's having alkoxy silane-terminated end groups-1991	1991	39

Tatsuro et all invented silyl terminated polyethers incorporated with epoxy co-polymer epoxidized o-, m-, or p-methoxyphenol monomers and its derivative in its backbone. They also described process of its synthesis and its potential application. Incorporation such co-monomer in backbone resulted into increase in the mechanical and physical property of sealant [47].

The silane terminated polyether polymer prepared using primary amino silane as a terminating agent has very poor storage stability and became a yellow with the time. This defect is overcome by He Zhiqiang et all in its invention. They discover a process of the hydroxyl silane terminated polyether polymer and the preparation method of same, wherein the termination process is easy to control and is not easy to yellow [38].

M.Lebet et all describes in their invention about synthesis of silyl terminated polyether and its process of synthesis. They incorporated an alkoxy silyl in the backbone as well as on peripheral segment. Incorporation of alkoxy silyl in central results in improvement in network formation which also demonstrated by improved elasticity and tensile stress [48].

Lin Chunxia and their team provide invention of good silyl-terminated polyether sealant of kind of a cementability which has excellent water resistance and methods of its preparation. The seal gum prepared by this method shows excellent water resistance and water tolerance on most of base materials, particularly on stainless steel substrate. This was a measure shortcoming of existing seal gum [50].

Jiang Hongwei et all invented sealant of blend of silyl terminated polyether and polyurethane and its process of preparation. Resultant sealant shows better low temperature resistant i.e. on similar low temperature it shows better elasticity. Invented sealant does not required any adhesion promoter and reduced plasticizer dosages [51].

Kiyoshi Miyafuji et al developed a sealant with a curable composition with the use of non-organotin condensation catalyst. Developed sealant showed excellent elongation properties and initial tack properties without impairing the rapid curability of the polymer [53].

IV. Applications Of Silane Terminated Polyethers

Given their wide range of applications, adhesives, sealants, and coatings need a variety of characteristics to perform their specific functions. Eco-friendly building methods are widely used in modern construction because of their low environmental toxicity [54-55]. These sealants and adhesives prevent shrinkage after full drying, which typically happens in solvent-based products. In addition, there is less release of volatile chemicals. Because of their superior abrasion resistance, outstanding flexibility, hardness, and excellent adherence to a wide range of materials, polyurethanes have become increasingly popular in the commercial adhesive, sealant, and coating industries. They are beneficial for goods like sealants, adhesives, and coatings because of their qualities. The benefits of silicone sealants and polyurethane are combined in so-called Silyl-Terminated Polyethers Hybrid [56].

In practice, binding the two specimens together additionally allows for the use of a sealant. This is referred to by experts as elastic adhesive or sticky sealant. In addition to having the capacity to transfer forces, an all-rounder of this type should be elastic to allow for component movement. As an example, consider assembly adhesives, which need to be both flexible and strong [52]. Today, the bodywork of a bus, railway car, camper, mobile home or refrigerated truck, for example, could not be assembled without elastic adhesives. Additionally, the use of elastic adhesives in shipbuilding and aviation construction is growing. In order to prevent yellowing in coatings, it is usually advisable to use a tin-free catalyst, which corresponds to the α grade. When it comes to liquid coating materials for waterproofing patios, balconies, and roofs, polyurethane technology also reigns supreme. When the items cure, solid materials that stick well to the substrate and produce a waterproof membrane with no joints or seams develop. Usually, to strengthen the membrane, a nonwoven polyester fabric is added while the liquid waterproofing method is being applied. Transparent coatings are necessary if patios and roofs need to be sealed while maintaining their original appearance. Polyurethanes (PUR) and silane-terminated polymers are the two primary polymer classes from which the binders utilised in elastic adhesives are derived. Isocyanate chemistry is used in polyurethane crosslinking. The alkoxy silane units affixed to the ends of the chains cause silane-terminated prepolymers to crosslink. But they don't have the same elongation at break and adherence to different surfaces as vulcanizates made from adhesives made with silane-terminated polyethers [58-59].

V. Conclusions

Although combining various resins to create finish products can be difficult, the adhesive, sealant, and coatings sectors are paying close attention to this trend due to the possible rewards of success. Since they combine the finest qualities of silicone and polyurethane while mitigating their drawbacks, silylated prepolymers are referred to as "hybrid" polymers. The hybrid polymers crosslink to generate thermosets with remarkable strengths, due to the technology of silylated polyethers. As a result, the new hybrid polymers provide the adhesives industry a desirable substitute for binder that meets strict technical specifications and is both user- and environmentally friendly. These polymers have gained significant attention not only because of their distinct performance and application features but also because they are solvent- and isocyanate-free. In this article, we covered the chemistry, benefits, and drawbacks of silylated polyethers for use in adhesives, sealants, and paints at the same time knowledge on several end uses. The futuristic hybrid technological innovations are more important to meet the demands of the market both now and in the future.

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