

Designing Soft Reactive Adhesives by Controlling Polymer Chemistry

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Abstract

Soft reactive adhesives (SRAs) are polymer-based materials (e.g., polyurethanes, polysiloxanes, polydienes) designed to be further vulcanized or slightly cross-linked through external activation (heat, moisture, oxygen, UV-visible irradiation, etc.), either at the time of their application or within a subsequent predefined period. They are used mainly as mastics, or sealing compounds, in a wide range of industrial and commercial fields such as construction, footwear, and the automotive industry. Generally deposited as thick films, SRAs behave as structural adhesives; their low elastic moduli accommodate large strains between the bonded parts without incurring permanent damage. Other outstanding attributes of SRAs are their resistance to solvents, their ability to withstand aggressive environments, and their ease of use. This article discusses examples of SRAs and, more specifically, shows how the cross-linking chemistry, mainly through step-growth polymerization, provides their primary advantages.

Keywords: chain polymerization, polyurethanes (PURs), silicones, soft reactive adhesives (SRAs), step-growth polymerization.

Introduction

Chemists working in the field of reactive adhesives, that is, adhesives that require a chemical reaction to cure, must provide technological solutions that fulfill two main conditions:

- The viscosity of the adhesive must be low enough to allow easy wetting of the adhesive on the substrates to be bonded and fast interfacial interactions; and
- The transformation of the uncured liquid adhesive into a solid bonded joint must be fast (by means of chain or step polymerization, initiated or activated under mild conditions).

These principles are the key to finding the best compromise between the characteristics of a formulated polymer-based adhesive and the behavior of bonded joints. Reduced viscosity for better wetting may lead to a weaker bond, so a compromise between properties is often needed. Using the example of soft reactive adhesives (SRAs), we will show how polymer chemistry is able to provide adhesive manufac-

turers with some innovative solutions. SRAs can be considered as structural adhesives; their low elastic moduli and high adhesion properties accommodate the relative motion of the substrates without damage. This behavior is useful in a wide range of applications for adhesives, mastics, and sealants in many industrial fields, for example, in the automotive, construction, and electronics industries.

Background

Various reactive adhesive systems can be designed through good control of polymer chemistry. Two main polymerization mechanisms can be used: chain polymerization, based on the reactivity of monomers such as acrylates and cyanoacrylates; and step-growth polymerization, characterized by addition or condensation reactions, which are involved in the synthesis of polyurethanes or polyepoxides.

In the case of chain polymerization processes, highly reactive adhesives can

be obtained by using cyanoacrylate monomers. The corresponding bonded joints are formed by anionic polymerization initiated by the moisture located at the surface of the substrates.¹ Anaerobic adhesives are more complex systems in which the initiation step is induced by the absence of oxygen; then, the *in situ* formation of charge-transfer complexes leads to a free-radical polymerization process.² Unsaturated polyester adhesives, which are widely used in composites, are another example; these thermosetting joints are obtained by opening a double bond located in the polyester backbone followed by the chain copolymerization of a mix of vinyl monomers, both initiated by free radicals.³ The advantages of these systems include the rate of the polymerization process (a high initiation rate, combined with the high reactivity of the vinyl or acrylic monomers) and the low viscosity of such monomers, which allows easy and complete spreading of the adhesive on the bonding surfaces without the use of any additional volatile solvent. Unfortunately, one significant disadvantage is the potential presence of toxic residual monomers if conversion is incomplete.

Step-growth polymerization leads, for example, to the formation of polyurethane or polyepoxide joints, based on the formation of covalent bonds between mutually reactive functional groups. In the case of polyurethanes, groups such as alcohol and isocyanate are used; for polyepoxide compounds, amine and glycidyl groups are effective. The polymerization proceeds by an addition mechanism that is generally activated by temperature or moisture, and the resulting polymer does not contain any volatile compounds. The thermomechanical properties of these thermoset joints can be controlled by the nature of the polymer backbone chosen and, obviously, by the average molar mass between cross-links. The final properties of the cured adhesive must be suitable for the required applications (e.g., the joint must be able to sustain large levels of strain mismatches and moderate shear stresses and only fail with a considerable amount of viscoelastic dissipation).

The monomers are packaged as one- or two-component systems. One-component systems contain all reactive compounds in one mixture; two-component systems separate the adhesive compound from the catalyst until they are ready to be used. For classical two-component systems, polymerization starts after mixing the curing agent with the prepolymer (a functional oligomer). In this case, the mixing stage is of primary importance: in order to achieve good mixing before coating—and as much

as possible, to avoid the presence of residual functional groups—sophisticated automatic mixing equipment is sometimes required, such as inline mixing tubes. One-component systems are based on functional prepolymers that become reactive through external activation (temperature increase, reaction with moisture, UV-visible irradiation, etc.). The applications of such adhesives range from structural joints to sealants. One of their advantages is that a high level of adherence and stress resistance can be attained even before conversion is fully completed.

To guide the choice of such systems for a specific application, users generally establish precise specifications in terms of

- The viscosity of the adhesive formulation (monomers are liquid, oligomers are more viscous), to ensure good bond formation and hence the development of interfacial interactions;
- The setting time for the transformation of the adhesive into the bonded joint (efficiency of the chain extension and optimization of conditions to enhance conversion yields and complete the reaction of functional groups); and
- The required thermomechanical properties of the final joint.

This article focuses on the chemistry required to build soft thermosetting joints used as mastics or sealants, especially in the case of one-component systems. But we also decided to present two examples of two-component adhesive systems in order to convince the interested reader of the versatility of polymer chemistry.

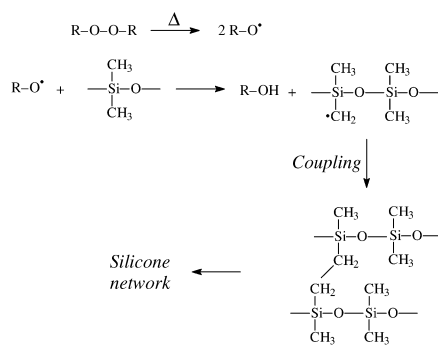
Chemistry of Polysiloxanes

Silicones⁴ are highly deformable, due to the flexibility of the $-\text{Si}-\text{O}-$ backbone. These polymers are useful at both high and low temperatures and are available as one- or two-component systems. Silicones are often chosen for their excellent resistance to weathering and their ability to accommodate relative displacements of the substrates without damage. This is why silicones are mainly used as mastics or sealants.

Two examples of one-component adhesive systems will be described next to illustrate the mechanisms involved in the construction of silicone-like bonded joints, which are highly deformable under mechanical stress.

High-Temperature One-Component Silicones

To obtain a reactive adhesive, poly(dimethylsiloxane) (PDMS) oligomers (Reaction 1) are mixed with peroxide.⁵ The mixture is stable at room temperature and can be manipulated under a variety of



Reaction 1. Typical free-radical high-temperature curing of silicones.

conditions. An increase in temperature induces the thermolysis of the peroxide. Afterwards, the reactive free radicals abstract one hydrogen from the methyl groups. The high reactivity of the alkyl radicals induces coupling reactions, resulting in a large number of interchain junctions and even cross-linked PDMS.

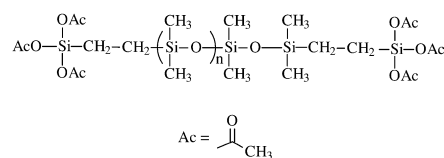
Manufacturers have also developed various functional PDMS precursors such as α,ω -divinyl-PDMS, which have significant functional groups on the first (α) and last (ω) monomers. Such compounds are mainly used as a two-component adhesive precursor, for which the cross-linking reactions involve telechelic vinyl end groups. In this case, the cross-link density, resulting from the reaction at room temperature of Si-H groups with the vinyl functional polymer, is better controlled than in the case of a statistical abstraction of methine protons.

Setting time and ease of implementation guide the choice between the two systems described here. In both cases, the conversion rate and the final cross-link density will control the thermomechanical properties of the adhesive joint.

Moisture-Curing One-Component Silicones

These adhesives are designed to react at low temperature. The transformation from adhesive to bonded joint is initiated by a reaction with water when the adhesive is coated on the substrate.⁶ The compound α,ω -di(triacetoxy)-PDMS (Structure 1) is the primary one-component silicone precursor proposed by silicone manufacturers that works at low temperature (a process called RTV, room-temperature vulcanizing) (Reaction 2).

The triacetoxysilane functions are highly reactive with water. The hydrolysis of such functions forms trihydroxysilane intermediates (the remaining acetic acid gives such sealants their characteristic



Structure 1. Chemical structure of α,ω -di(triacetoxy)-poly(dimethylsiloxane).

vinegar smell). Because of the high reactivity of silanols, the final step is the condensation of two silanols to form silicone bridges (Reaction 2).

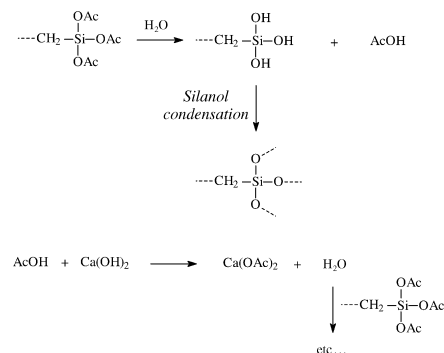
Reactive fillers such as calcium hydroxide may be introduced in such adhesive formulations. They can react with the remaining acetic acid and regenerate water (Reaction 2). Then, new triacetoxysilane functions can again be hydrolyzed.

The mechanical properties of silicone-bonded joints are similar to those of elastomeric joints, which exhibit low moduli and high deformability. One major drawback of these systems is that fillers or additives used in such adhesive formulations must have a very low moisture content in order to prevent any cross-linking during storage or before coating.

The application of these silicones as mastics or sealants requires good weathering properties. The very low surface free energy of PDMS provides, at the interface with the substrate, good resistance to degradation by moisture. Additionally, the long setting time—a couple of days—for these systems is not really a handicap in the construction industry, which is their main domain of application.

Chemistry of Polyurethanes

We focus here on the preparation of thermoset-like polyurethanes⁷ (PURs). Their main use in adhesives is for thermoplastic applications requiring hot-melt



Reaction 2. Moisture-curing one-component silicone.

properties (e.g., in the manufacturing of footwear).⁸ The chemistry of polyurethanes is based on addition reactions between alcohols and isocyanates. The nature and the functionality of the monomers control their reactivity and cross-link density.

In the case of PUR adhesives, two-component formulations have distinct disadvantages: the uncured adhesive is difficult to handle because of the high reactivity of isocyanates with water, and low-molecular-weight diisocyanate precursors are toxic. Various one-component strategies have been developed to circumvent these difficulties.

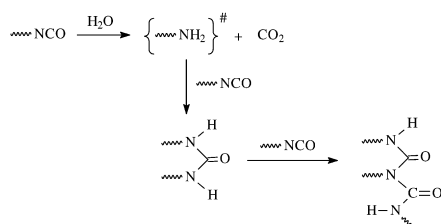
Moisture-Curing One-Component Polyurethanes

By varying the molar ratios of the monomers, it is straightforward to prepare α,ω -diisocyanate-PUR. In this case, the free isocyanate chain ends react with water to produce amine functions and CO_2 . Such amine functional groups are nucleophilic and able to further react with free isocyanates, leading to urea functional groups (Reaction 3).⁹

The PUR network is built by these successive reactions. The thermomechanical properties of the joints are not only governed by the average molar mass between cross-links, but also by the number of hydrogen bonds between urea bridges, resulting in strong mechanical resistance and good adherence properties in the bonded joints. One major disadvantage is the formation of CO_2 , which can interfere with adhesive properties.

These adhesives are mainly used in the automotive industry as joints and sealants to bond large modules like windshields, roofs, or wheel wells.

It is important to note that the amine intermediate, formed *in situ* during the hydrolysis process, can also be used to react with epoxides; in this case, hybrid polyurethane–polyepoxide materials can be obtained. The resulting properties are a combination of the properties of each polymer backbone.



Reaction 3. Reactivity of isocyanates with water.

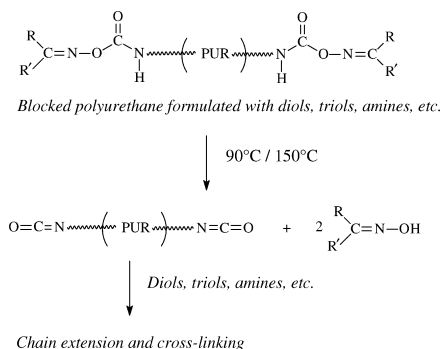
Blocked Polyurethanes

A large number of polymer structures can be designed with the chemistry of α,ω -diisocyanate-PUR. Because of the high reactivity of isocyanates, it is easy to convert them into specific organic functionalities and then design new adhesive architectures. For example, isocyanates react with oximes to give new α,ω -difunctional-PUR,¹⁰ as shown in Reaction 4.

The major advantage is that oxime functions will prevent the isocyanate from reacting with active hydrogen species such as alcohol and amine at low temperatures and will also promote a reaction at high temperature in the presence of active hydrogen species (Reaction 4). The deblocking step is induced by the mutual influences of temperature and the presence of active hydrogen species in the formulation. The major drawback of such formulations is the releasing of moieties in the joint before cross-linking, which can interfere with the adhesive and thermomechanical properties. These adhesives are designed for niche applications.

Other Reactive Polyurethanes

Water-Dispersed Polyurethanes. In the effort to comply with recent environmental legislation, at least in Europe, water-dispersed polyurethanes¹¹ are considered good candidates for replacing solvent-based polyurethanes. In this case, the main challenge for a chemist is to propose solutions that will prevent the reaction of water with free isocyanates. To that effect, α,ω -diisocyanate-PUR, bearing sulfonate side groups as stabilizers, can be easily dispersed in water, since the free isocyanates are efficiently protected in the micelles and are not hydrolyzed during their storage. The curing agent, a water-soluble amine present in the water, may then react with the isocyanate moiety by a



Reaction 4. Chain extension and cross-linking in blocked polyurethanes (PURs).

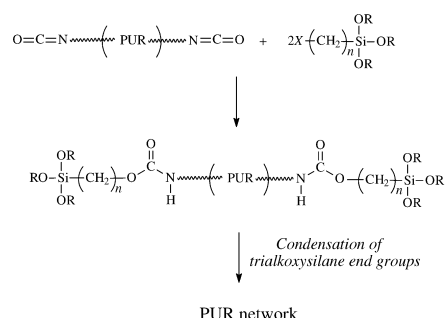
condensation reaction during the film forming process. These adhesives are commonly used to bond porous substrates in the paper and textile industries.

Hybrid Polyurethanes. Hybrid systems can be designed to produce adhesives tailored for specific applications. The principle is based on the covalent association of two or more polymer backbones, each of which brings its own properties. For example, blocked polyurethanes can easily react with amines to form amino-terminated PURs that are able to further react with epoxy groups. It is possible to convert isocyanate chain ends into acrylic functional groups. In this case, the free-radical polymerization of acrylic-terminated PURs leads to new adhesive materials. Another idea that has been developed is to transform the isocyanate chain ends into trialkoxysilane functions (Reaction 5).¹²

The condensation of trialkoxysilane chain ends results in siloxane bridges and produces new properties that are intermediate between those of silicones and conventional PURs. Furthermore, the disappearance of free isocyanate groups removes the toxicity problem, and some of the residual trialkoxysilane functions can also react with the surface and act as an adherence promoter, leading to high adherence to stainless steel and glass (e.g., for bonding windshields). A last example concerns reactive PUR-based hot melts; a small quantity of free isocyanate carried by the polymer backbone may react with moisture and create covalent cross-links. In this case, a hot-melt thermoplastic prepolymer cures slowly and naturally after coating and becomes a thermoset joint.

Chemistry of Polydienes

Polydienes, and particularly polychloroprene, are well known for their excellent adhesive properties on various substrates. Generally packaged as organic



Reaction 5. Chain extension in hybrid α,ω -trialkoxysilane polyurethane (PUR).

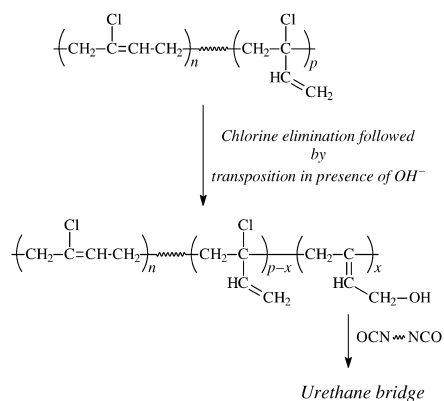
solutions, polydienes develop strong adhesion during solvent evaporation. The mechanisms involved are based on inter-diffusion theories. To enhance these properties, chemists have proposed creating chemical cross-links using classical organic modification of the polychloroprene backbone.

Polychloroprenes are synthesized by classical emulsion polymerization. Few transfer reactions of chlorine to water (which is the dispersing phase) occur during the propagation step, leading to the formation of only a few side-chain alcohol functions (Reaction 6).

These polychloroprenes react with polyisocyanate moieties to create urethane bridges between polydiene backbones.¹³ The resulting thermomechanical properties of such joints are identical to those of classical polydienes, but the urethane bridges and the large density of entanglements significantly improve the level of adherence and shear resistance, respectively. These two-component formulations are particularly well suited for joining or repairing raw polymeric materials, such as neoprene and poly(vinyl chloride) used in inflatable rubber boats, for which high adhesion properties and low-modulus polymers are required.

Chemistry of Polysulfides

Polysulfides are raw adhesive materials¹⁴ commonly used as mastics. The sulfide repeat unit in the polymer backbone



Reaction 6. Extent of cross-linking in two-component polychloroprene adhesives.

brings its own chemical resistance for applications in aggressive media such as acidic or basic solutions and organic solvents, which tend to degrade polymers.

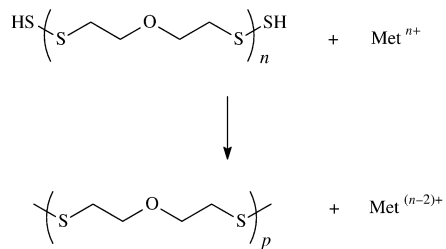
The synthesis of polysulfides is a well-known process, leading to high-molar-mass polymers. To obtain low-molar-mass adhesive precursors, polysulfides are reduced by sodium sulfite, which forms mercaptan-terminated polymers. These are liquidlike polymers, easily coated on various substrates and transformed to rubbery solids in the presence of an oxidizing agent (i.e., lead dioxide, calcium peroxide, etc.) (Reaction 7).

The curing process, that is, the chain extension, involves the oxidation of terminal $-SH$ groups to form disulfides.

This last example shows another way to control the chain extension process, based in this case on oxidation by metals. These adhesives are commonly used in the automotive industry, especially to seal fuel tanks.

Concluding Remarks and Future Trends

Based on the ideas described in this article, there is no doubt that polymer chemistry provides the tools required for the design of well-defined adhesive architectures to respond to the increasingly precise needs of industry. New architectures are built, on the one hand, by the association of various polymerization processes and control of the reactivity of functional side-chain or end-chain groups, and on the other hand, by the degree of chain extension or cross-linking. The chemistry suited for soft reactive adhesive applications must typically involve mild reaction conditions and complete chain extension



Reaction 7. Chain extension in polysulfide prepolymers. Met^{n+} and $Met^{(n-2)+}$ represent various oxidation states of a metal.

with a minimum of residual extractable compounds.

It seems that the challenge for the materials science of adhesives is to go beyond chemistry and propose hybrid or nano-structured systems that could provide an answer to specific applications. These complex materials would be composed of distinct phases with an internal organization that can be adapted to the specific substrate. One can imagine a hydrophilic/hydrophobic system where one or the other of the phases can segregate to the interface, depending on the nature of the substrate, effectively creating an adaptive adhesive. Along the same lines, some additional areas of development can be imagined, for example, the preparation of new adhesive systems using innovative polymer architectures such as stars, dendrimers, and hyperbranched polymers, leading to nano-to-mesoscale supramolecular organizations.

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