TECHNICAL ARTICLE

Maximizing sustainability in SMP sealants with new rheology modifiers

By Edward M. Petrie

For many sealant formulators, **sustainability has become an essential part of their marketing strategy**. Sustainable certifications allow formulators to differentiate themselves by proving that their products meet key environmental standards. Contractors will often select a sealant based on the extent that a product meets these standards.

The prime sealants focus in recent years has been on **reducing the volatile organic compounds (VOCs)** in the formulation, but there are many other pathways to sustainability as listed below.

- Reduce the content of chemicals in the formulation that:
    - May be toxic to life
    - Contribute to ozone depletion, greenhouse gas formation, acid rain, or water pollution, and
    - Cause safety and health issues
- Reduce releases of such harmful materials in the workplace, during application, and after the sealant installation
- Use fewer non-renewable resources (e.g., petroleum-based chemicals)
- Decrease energy consumption required for manufacture, use, and disposal
- Use non-migrating additives to prolong the sealant’s useful life
- Reduce maintenance or replacement costs

Here, we will review how silane modified polymer (SMP) sealant formulations can be optimized to reach sustainability goals without diminishing properties. SMP sealants are also known as “hybrid” sealants since they have properties comparable to both polyurethane and silicone sealants. Let’s see how to maximize the sustainability of these products.

Sustainability as a Sealant Value Proposition

Sustainable sealants are those that reduce harm to the environment throughout its entire life cycle. Environmental responsibility must be exerted not only during the manufacture of raw materials but also during formulation, application, end-use, service life, and disposal at end of life. The environmental concerns do not stop at the formulator or end-user of **construction sealants**. Once it is applied and cured, the sealant may require **“indoor” environmental properties** such as **low toxicity and odor**.

In the building construction industry, several certification programs have been developed to show the builder’s commitment to sustainability. In addition to promoting environment and health perceptions, the motivation for certification of a building as “**sustainable**” is to achieve higher value for the building.

The procedure is to collect points by fulfilling "**credits**" for proper consideration of environmental aspects (e.g., indoor air quality, saving of energy and of resources, and more). Standards and certifications that meet sustainable building criteria have emerged globally. Some of these standards are listed in the table below.

Country/Region	Standard
United States	LEED (Green Building Council’s Leadership in Energy and Environmental Design)
United Kingdom	BREEAM (Building Research Establishment’s Environmental Assessment Method)
France	French Démarche HQE certification
Germany	German DGNB (Deutsche Gesellschaft für Nachhaltiges Bauen)

Global Standards and Certifications Affecting Selection of Sealants

The motivation of sealant manufacturers is that they can offer products to contractors who want to maximize sustainability credits for their building. Sustainable building projects are gaining importance in the market. **Low VOC and high bio-content sealants** contribute to the rating of a building as "sustainable".

What Makes Silyl Modified Polymers (SMPs) so Popular?

Silane modified polymers, also known as silyl modified polymers (SMPs), are obtained by combining reacting polymers with a silyl group. The products are differentiated by backbone (generally polyether or polyurethane) and in number and nature of groups attached to the backbone. All of the polymer backbones are terminating with a silyl group. They have closely associated chemistry and many common features. The most common SMP polymers are known as:

- MS polymers (polyether backbone)
- SPUR polymers (polyurethane backbone)

The global SMP market was valued at USD 3.5 billion in 2019 and is expected to grow at 7.3% CAGR during the 2019-2024 period.[1] The growth is driven mainly by the **increasing use in the construction of modern and energy-efficient buildings**.

Advances are also expected in bonding / sealing of lightweight materials in the transportation and wind power industries. A **broad range of SMP polymers** are available. Key players in the market include:

- Kaneka Corporation
- Risun Polymer International Co., Ltd.,
- PCC Group
- Evonik Industries
- Wacker Chemie AG, and
- Momentive

SMPs as Base Polymer in Sealant Formulations

SMP single-component sealants cure via **reaction with environmental moisture**. Curing entails crosslinking by the hydrolysis and generation of siloxane linkages. A catalyst is required to accelerate this process.

SMPs have become important base polymers for sealant formulations due to their:

- High-performance properties, and
- Sustainable characteristics.

Performance comparisons between SMP, polyurethane and silicone sealants are provided in the table below. SMPs offer superior properties which makes them suitable for use in numerous sealant applications.

Property	SMPs	Polyurethane	Silicone
Environmental friendliness	10	5	9
Non-bubbling	10	6	10
Low temperature gunnability	10	8	10
Slump resistance	10	10	10
Quick cure	10	7	10
Storage stability	10	7	9
Body (tooling capability)	9	10	8
Weather resistance	8	6	10
Adhesion to various substrates	10	5	8
Mechanical properties	10	10	10
Heat resistance, mechanical stability	9	8	10
Non-dirt pickup	10	10	5
Stain resistance	8	8	5
Paintability with water-based paint	10	10	3

Performance Property Comparison of SMP, Polyurethane, and Silicone Sealants

(Based on 10 Point Rating with 10 being the highest performance)

Environmental Benefits of SMPs

Sustainability has also become a key value proposition in the demand for SMP sealants. Formulators benefit by **using less energy** during the manufacturing process due to the low viscosity, and SMP properties can be easily modified with additives. End-users benefit from the:

- Reduced application cost (less need for primers, increased storage stability, low temperature gunnability), and
- Reduced maintenance cost (improved paintability, less dirt pick up, longer life) of these higher performing sealants.

But perhaps the major sustainable benefit is that SMPs offer a **safer, environmentally acceptable solution**. Unlike many other high-performance sealants, SMP formulations are both solvent-free and isocyanate-free. Although some SMPs generate methanol during cure, new formulations have been developed that generate ethanol, a less harmful byproduct. As a result, SMPs are a good first-choice for sustainable sealant formulation. However, there are pathways to boost sustainability even further.

The improved sustainability helps both formulators and end-users as indicated in the table below.

Formulator Benefits	End-User Benefits
• No solvent • Reduced VOCs • No free isocyanate • Increased bio-content • Reduced energy usage (easier mixing, less heating) • Elimination or reduction of plasticizer content • Improved storage stability	• No solvent • Reduced VOCs (before and after cure) • No free isocyanate • Increased bio-content • Improved storage stability • Improved gunnability • Lower maintenance costs (dirt and stain resistance, easy paintability) • Longer life (excellent weather resistance, no cracking or splitting, improved adhesion)

Benefits of Sustainable SMP Sealant Formulations

Additives in SMPs – Roadblock in Sustainability Journey

Conventional sealants, including SMP formulations, have several additives that can contribute to health, safety, and environmental issues. The most important of these are:

- Rheology modifiers / fillers: Fine thixotropic fillers such as silica and titanium dioxide are suspected health hazards.
- Plasticizers: Reproductive harm and asthma are known to come from phthalate plasticizers. Plasticizers can eventually migrate out of the sealant creating environmental concerns and degraded properties.
- Catalysts: Tin-based catalysts are a suspected bioaccumulation toxin and endocrine disruptor. These catalysts are commonly used in silane crosslinking mechanisms.

New rheology modifiers and non-tin catalysts have the potential to alleviate these issues.

New Renewable Rheology Modifiers Supporting SMP Sealants Sustainability

New rheology modifiers from **Elementis** (THIXATROL® product line) have the potential of alleviating some of the concerns related to both **fillers** and **plasticizers**.[2] THIXATROL® is a diamide-based organic thixotrope that is produced from renewable raw materials (>75% bio-content). In addition to having a high bio-content, the **THIXATROL® products** provide other properties and benefits, as listed below, that can indirectly increase the sustainability of SMP sealants.

- Up to 50% higher efficiency than thixotropic fillers resulting in excellent slump / sag resistance
- Easy extrudability by virtue of its low yield point
- Easy compounding and much less energy, dust, and frothing compared to fumed silica
- Twenty times the density of fumed silica allowing less volume in transportation and storage space
- Free of hazardous or special labeling
- Improved sealant elongation without the need of plasticizers

THIXATROL® is an easily handled powder (5 µm max) that must be heat activated as do all amide wax thixotropes. Good rheological performance is achieved at an **activation temperature of 40°-60°C** which is lower than other amide waxes and is generally accomplished during mixing.

The thixotrope operates by forming a three-dimensional network. Once fully activated, the molecules orient themselves to each other forming a fibrillar structure due to the nature of the amide functionality. **Intermolecular interactions** (e.g., hydrogen bonding and Van der Waals forces) are responsible for the thixotropic structure.

Being a non-associative rheology modifier, THIXATROL® does not require the presence of pigments or fillers to function. As a result, it can be used in both non-pigmented and pigmented systems and allows the formulator to achieve thixotropy without the safety and health issues of particulate fillers as indicated above.

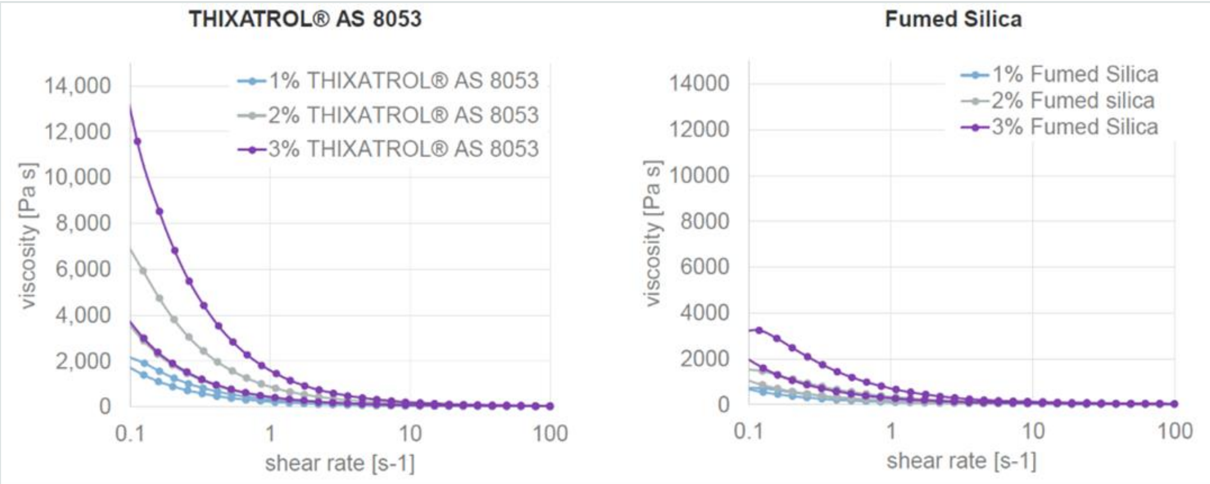
Examples of SMP formulations (SPUR base polymer) using both fumed silica and diamide-based thixotropes are provided in the table below. Similar formulations are possible for sealants using other SMP base polymers. Modification of this formulation to achieve greater sustainable value will be discussed in the following sections.

Component	Pigmented Concentration (%)	Non-pigmented Concentration (%)
Silylated polyurethane prepolymer (SPUR)	23.0	58.0
Plasticizer	18.0	31.5
Calcium carbonate	54.3	-
Titanium dioxide	0.7	-
Moisture scavenger	0.3	1.5
Rheology additive	3.0 / various*	7.5 / various*
Adhesion promoter	0.6	1.0
Catalyst	0.1	0.5
Total	100	100
**Concentration of fumed silica and diamide-based thixotrope varied as 1.0, 2.0, 3.0% by weight for pigmented formulation, and 5.5, 6.5, and 7.5% for non-pigmented formulation.*		

Starting Formulations for Pigmented and Non-Pigmented SPUR-Based Sealant

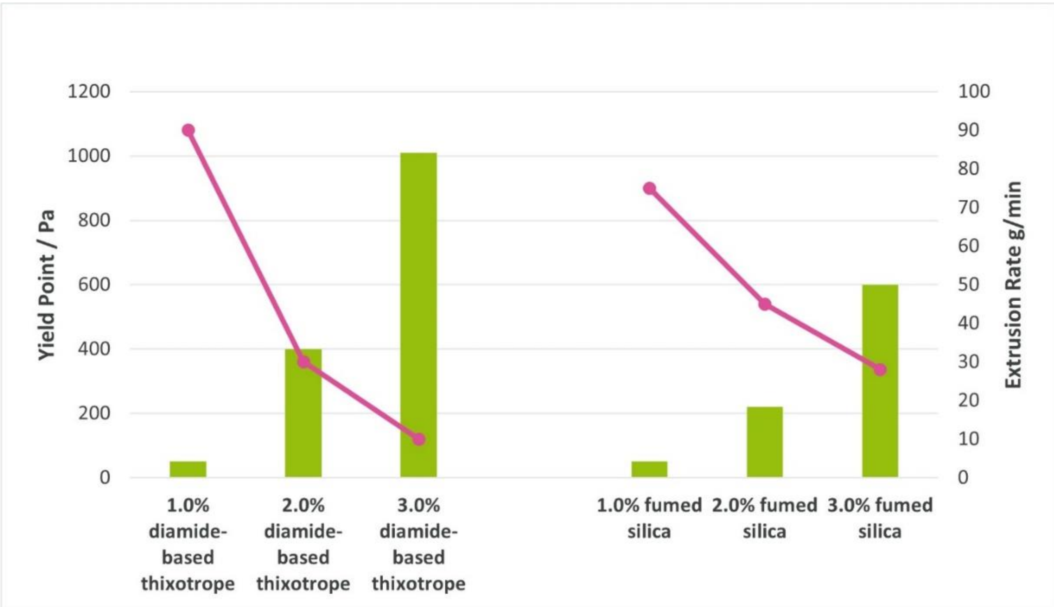
Improved Rheological Performance

When activated at 50°C, THIXATROL® AS 8053 demonstrates excellent results at concentrations from only **1% and a significantly higher viscosity** when compared to fumed silica (see figure below).



Diamide thixotrope provides significantly higher rheological performance in a SMP when compared to fumed silica.

As the loading level of the diamide-based thixotrope is increased to 2.0%, an ideal extrusion rate of about 30 g/min is achieved; 3.0% of fumed silica is required to achieve a similar extrusion rate. However, the **yield point achieved with 3.0% fumed silica** is higher than the diamide-based thixotrope at an almost equal extrusion rate, which implies that one needs to apply 30% more force to extrude the same amount of material. The influence of THIXATROL® and fumed silica on yield point and extrusion rate is shown below.



Influence of Rheology Modifiers on Yield Point and Extrusion Rate in SPUR Sealants.

Fumed silica with 1.0% loading showed no sag stability; the sample completely runs out of the channel (Figure below). However, at a similar loading level, the diamide-based thixotrope showed no sagging. Subsequent increases in the loading level of both modifiers improved the rheological and **anti-sag** properties.

Improved Sag Properties with the Diamide-based Thixotrope (right) compared to Fumed Silica at Equal Loading of 1.0%.

At all loading levels, the diamide-based thixotrope showed significantly higher efficiency in comparison to fumed silica. It is apparent that the diamide-based thixotrope outperforms fumed silica at all loading levels and provides better performance.

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[Gain production efficiency and easily meet end user performance requirements with a new generation of organic thixotropes.]

Eliminating Plasticizers – Get Higher Elongation in SMP with THIXATROL®

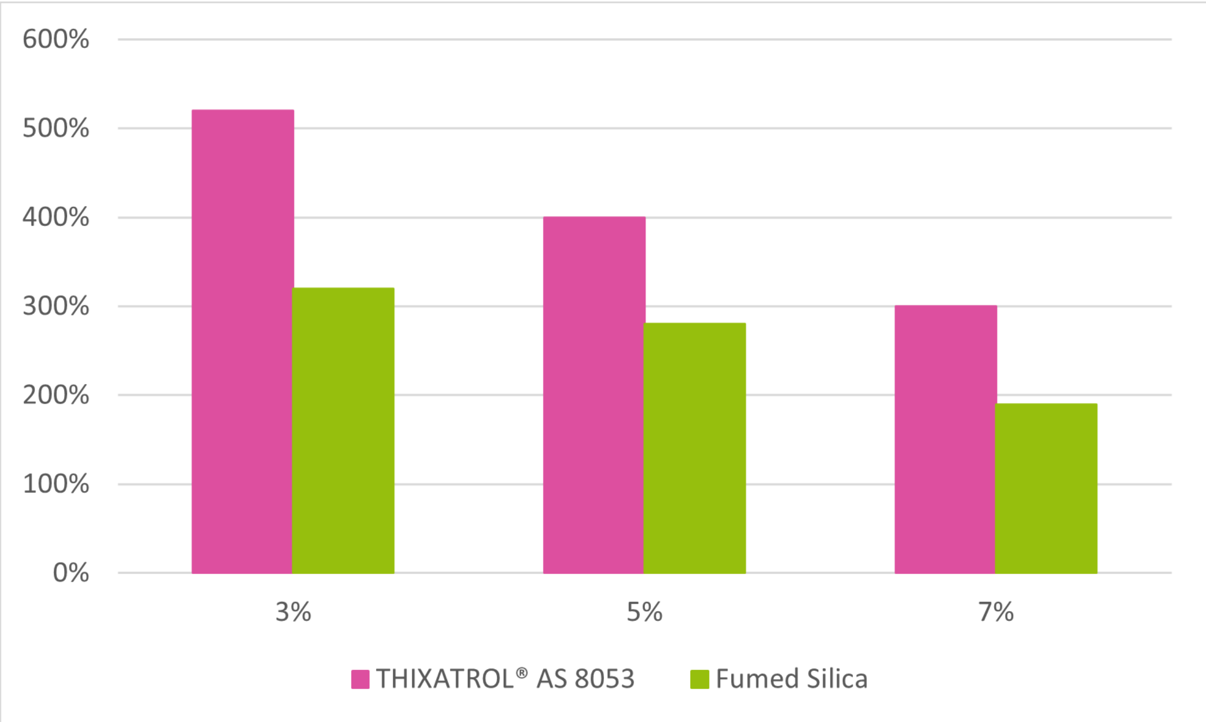
Plasticizers are an important component of many sealants including SMP formulations. A plasticizer is an additive used to increase elongation of a polymer system. Plasticizers also typically affect the viscosity, lower the glass transition temperature, and lower the elastic modulus of a product.

In most sealant selection processes, movement capability is the key parameter (ASTM C719). High performance adhesives are those that have a movement capability in extension or compression of at least 25%. As a result, plasticizers are used to **achieve higher elongation and movement capability**.

Many of the effects of plasticizer incorporation are unwanted in sealants. As a result, efforts have been made at developing phthalate alternative plasticizers, reducing the plasticizer content, or even eliminating the plasticizer via replacement with reactive diluents.

The main problem resulting from the use of plasticizers is **potential migration out of the sealant with time**. This causes negative environmental effects, loss of elongation with time, dirt and particle adhesion to the sealant's surface, reduced paint adhesion, etc. Many government agencies are seeking to limit the amount of certain plasticizers, such as phthalates, that enter the environment.[5]

THIXATROL® rheology modifiers provide higher elongation in SMP sealant when compared to fumed silica (Figure below). This provides the formulator with a tool other than plasticizer to provide higher degrees of movement capability and improved properties.



Elongation of SMP Sealant Based on THIXATROL® AS 8053 are Significantly Higher vs Fumed Silica Sealants.

Get Comparable Mechanical Properties with Tin-free Catalysts

Regulatory restrictions on the use of tin catalysts can create difficulties for formulators of SMP systems.[6] Tin compounds are commonly used to **catalyze the crosslinking of SMP systems**. Compounds that efficiently catalyze these crosslinking reactions include dioctyl tin diacetyl acetonate and dibutyltin dilaurate. Concerns about toxicity of tin compounds have driven formulators to explore other catalyst options.

The level of tin required to achieve sufficient cure of moisture-cured SMP systems is typically very close to the ≤ 0.1% limit established in REACH Annex XVII, Entry 20. Therefore, tin replacement is an issue for industries that use **moisture-cured organosilane sealants**.

Several studies regarding tin-free organometallic catalysts have shown that these new catalysts can be non-toxic and also provide good mechanical properties with similar cure times.[7,8] It has been found that along with the regulatory benefits of being tin-free, an important benefit of using these catalysts (e.g., **K-KAT® 670, a catalyst from King Industries**) is its activity in ethoxy silane SMP systems.

Ethoxylated silane polymers produce ethanol on cure, a less harmful chemical than methanol which is produced in methoxy silane systems. However, catalysis of the ethoxy silane crosslinking reaction is challenging. Tin compounds have proved to be inefficient for these reactions. The K-KAT® 670 catalyst does not contain tin and provides mechanic properties and cure rate that are comparable with tin-based catalysts for all silane systems. Typical dosage ranges from 0.4 to 2.0% on total formulation weight.

Conclusion

New raw materials are being developed that are finding their way into sustainable building sealants. These include additives that are biobased and safer to use. New SMP sealant formulations have been motivated by the green building movement. SMP polymers are already free of VOCs and solvent. New rheology modifiers and catalysts such as described in this article will even further contribute to their sustainability by eliminating potentially hazardous particulate fillers, plasticizers, and tin-based catalysts.

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The rheological properties of an adhesive or sealant are vital to its success in the market. A well formulated adhesive or sealant has balanced rheological properties, easy but controlled application, high sag or slump resistance with good storage stability. Selecting the right thickener in the adhesive or sealant formulation allows the manufacturer the ability to design the right characteristics that are needed for a specific end use.

Presented By: Carlos Feito

Length: 60 min