One-Component Moisture Curing Methoxysilane Sealants

Introduction

CRAYVALLAC SLX and CRAYVALLAC SL are micronised amide wax rheology modifiers specifically developed to meet the high performance requirements of the one-component moisture curing methoxysilane sealant market. Their function is to provide a shear thinning rheology sufficient to prevent slump and sag during application, and this performance is demonstrated for CRAYVALLAC SL in Figure 1.

Figure 1: Cured one-component methoxysilane sealants. The sealant on the left contains no rheology modifier while that on the right was prepared using 3.5% CRAYVALLAC SL

The roles of CRAYVALLAC SLX and CRAYVALLAC SL are differentiated in the following manner:

- CRAYVALLAC SLX is designed for the low temperature manufacturing process i.e. 60 - 90°C (140 - 194°F).
- CRAYVALLAC SL is designed for the high temperature manufacturing process i.e. 80 - 115°C (176 - 239°F).

The high temperature process is that traditionally associated with moisture curing methoxysilane based sealants. Here the use of high temperatures and vacuum essentially provides the formulator with a greater control over moisture content, especially when lower grade fillers are used. Compared to this, the low temperature process demands the use of the higher grade low moisture content fillers and a greater reliance on chemical drying. This is because the temperatures involved are insufficient for the effective removal of moisture under vacuum.

The primary advantage of the low temperature process is improved productivity through reduced cycle times. However, irrespective of the process used, CRAYVALLAC SLX and CRAYVALLAC SL both provide the following benefits:

- 100% active
- Good cost to performance ratio
- Impart excellent shear thinning rheology
- Very good extrusion characteristics
- Excellent slump and sag resistance

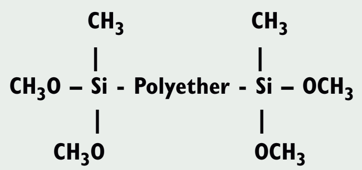
When CRAYVALLAC SLX and CRAYVALLAC SL are used in the place of fumed silica the following additional advantages are often obtained:

- Minimal effect on modulus
- Excellent stability on storage
- Very good resistance to UV-degradation
- Ease of handling due to their higher bulk densities

For one-component moisture curing methoxysilane sealants, excellent slump and sag control will generally be obtained when CRAYVALLAC SLX and CRAYVALLAC SL are used at a level of 1 – 5% by mass on total formulation.

One-Component Methoxysilane Sealants

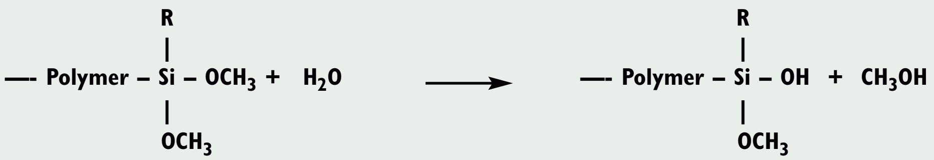
The base polymers used in these sealants are composed of polyethers end-capped with the potentially cross-linkable methoxysilane group e.g. KANEKA MS POLYMER ex. Kaneka Corporation.



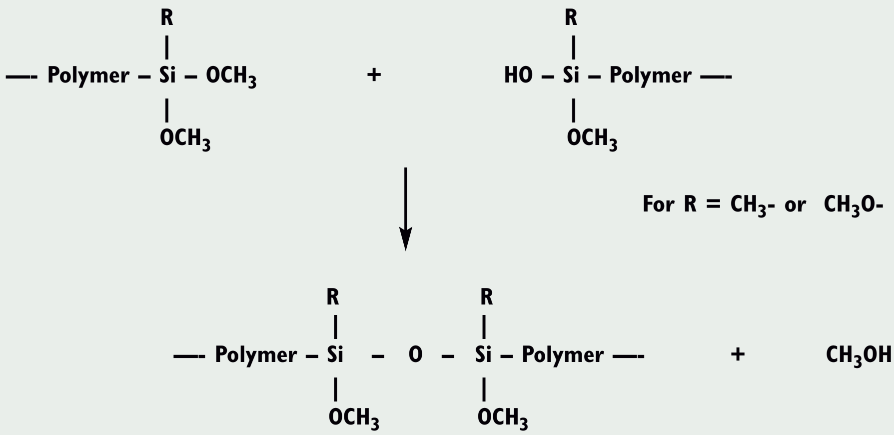
There are also similar proprietary systems available based on a polyurethane backbone. Their preparation involves the end-capping of an isocyanate functional polyurethane with an amine functional methoxysilane.

With methoxysilane based sealants, the cross-linking mechanism involves the direct reaction with atmospheric moisture. This process proceeds in two steps:

Step 1: Hydrolytic conversion of a methoxysilane group to silanol.



Step 2: Condensation of a silanol and methoxysilane group to form the siloxane cross-link.



As a consequence of the direct involvement of moisture, the successful manufacture of these one-component sealants requires that moisture be strictly controlled at all stages of production and during storage.

Incorporation Method and Processing Instructions

The following outlines the typical processing conditions and controls required when manufacturing one-component methoxysilane based sealants:

Stage 1: Pre-Drying of Fillers and Pigments

The fillers and pigments are often a major source of moisture. Therefore it is normal practice to pre-dry these prior to dispersion with the methoxysilane polymers, plasticiser and rheology modifier. This is often achieved by heating to 80 - 100°C (176 - 212°F) under vacuum in the dispersion vessel prior to the addition of the base polymer and plasticiser. Alternatively, higher grades of low moisture content raw materials may be used.

Stage 2: Rheology Modifier Activation

The rheology modifier, CRAYVALLAC SLX or CRAYVALLAC SL, is added to the pre-dried pigments and fillers along with the base polymer and plasticiser. If required, other additives such as anti-oxidants and UV-stabilisers may also be added at this point. With the dispersion vessel sealed under vacuum, the temperature is raised to between 60°C (140°F) and 115°C (239°F) depending on the choice of rheology modifier. The sealant is then processed until the rheology modifier is fully activated and sufficient dispersion has been obtained. Full activation is generally obtained after 30 – 60 minutes at 60 – 80°C (140 – 176°F) for CRAYVALLAC SLX and 90 – 115°C (194 – 239°F) with CRAYVALLAC SL.

Stage 3: Water Content Reduction

When the desired level of dispersion and activation has been obtained, agitation under vacuum is maintained in order to reduce the moisture content to less than 800ppm. Water content is conveniently monitored using the Karl-Fischer technique. However, if chemical drying were employed at Stage 1, this additional drying step may not be necessary. The sealant is then cooled to below 60°C (140°F) under vacuum.

Note: With the low temperature process, moisture removal by vacuum is often very inefficient. Consequently a greater emphasis is placed on chemical drying and the selection of higher grade low moisture content raw materials.

Stage 4: Performance Promoters

Once cooled to less than 60°C (140°F), the vacuum is released and performance enhancing additives such as moisture scavengers and adhesion promoters are added and thoroughly mixed in, followed by the curing catalyst. With all the components added and thoroughly mixed, the sealant is de-aerated by applying vacuum for a few minutes prior to discharge and packaging. It is recommended that a good quality packaging be used to enhance the shelf-life of the sealant.

Rheology Modifier Activation Mechanism.

The activation process for CRAYVALLAC SLX and CRAYVALLAC SL constitutes the conversion of the micronised amide wax particles into an interacting network of crystalline fibres. It is this network that gives rise to the finished sealant's excellent shear thinning rheology.

During application, the shear forces resulting from extrusion cause the crystalline fibres to align one with another, a condition leading to a decrease in viscosity and ease of application. Once the sealant has been applied, low shear conditions again prevail and the fibrous network rapidly rebuilds itself as the fibres reorientate in a random manner. This results in a well formed fibrous network with an associated very high viscosity, and this is what prevents slump and sag. Activation at too low a temperature, or for too short a time, will result in the formation of an inefficient interacting network and consequently poor sag and slump resistance.

Rheology Modifier Performance

The following data highlights the excellent performance of methoxysilane based sealants prepared using CRAYVALLAC SLX and CRAYVALLAC SL as the rheology control agents.

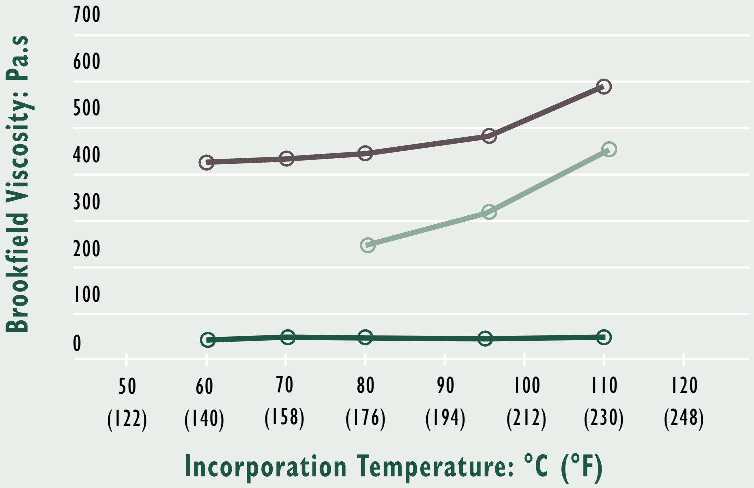


Figure 2: Brookfield viscosity data for methoxysilane sealants prepared at various temperatures using CRAYVALLAC SLX (Grey) and CRAYVALLAC SL (Light Green) at 3.5% by weight on total formulation. Reference (Green): No rheology modifier added. This data was collected at 23°C (74°F) using a Brookfield Helipath Viscometer: Spindle E at 5 rpm.

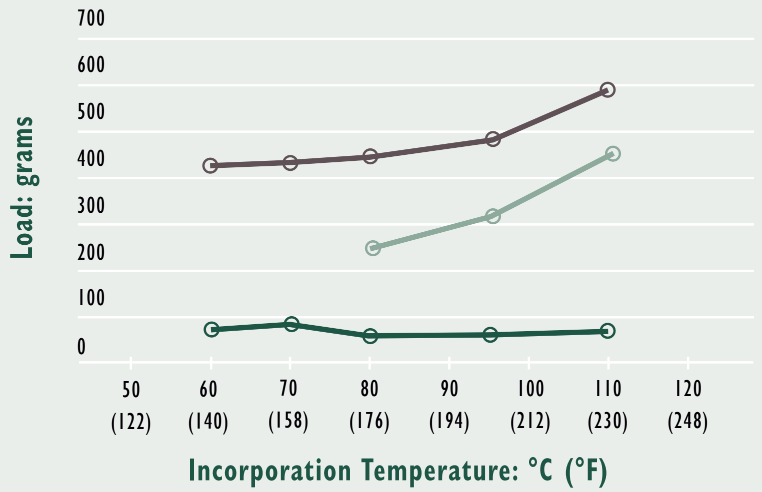


Figure 3: Mechtric Stevens structure data for methoxysilane sealants prepared at various temperatures using CRAYVALLAC SLX (Grey) and CRAYVALLAC SL (Light Green) at 3.5% by weight on total formulation. Reference (Green): No rheology modifier added. This data was collected at 23°C (74°F) using a Stevens L.F.R.A. Texture Analyser (speed 0.5mm/sec; distance 40mm; 35mm cylindrical probe).

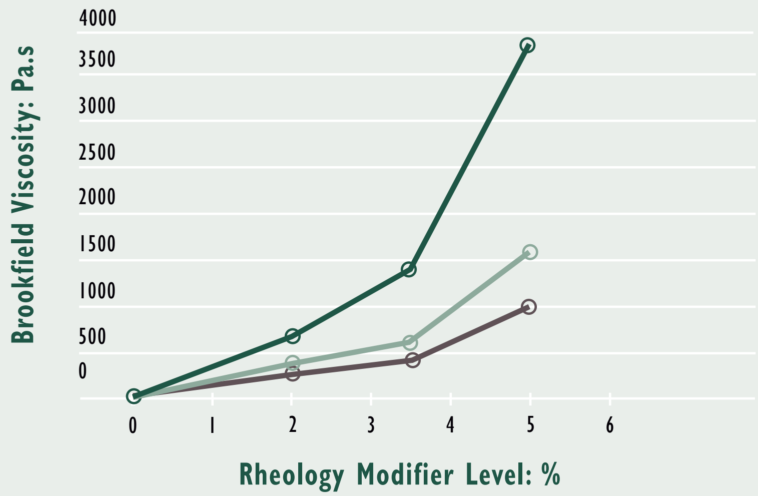


Figure 4: Brookfield viscosity data for methoxysilane sealants processed at 80°C (176°F) using CRAYVALLAC SLX at various levels by weight on total formulation. This data was collected at 23°C (74°F) using a Brookfield Helipath Viscometer fitted with Spindle E: Green = 1 rpm, Light Green = 5 rpm and Grey = 10 rpm.

The data presented in Figures 2 and 3 clearly shows that the use of CRAYVALLAC SLX and CRAYVALLAC SL results in an excellent increase in the sealants body-structure. From Figure 4 it is obvious that this structure development is shear thinning in character. It is also demonstrated that CRAYVALLAC SLX provides an enhanced performance when used at lower temperatures. Although it may appear that CRAYVALLAC SLX is superior to CRAYVALLAC SL at all processing temperatures, it has been demonstrated by some end-users that in certain methoxysilane formulations the use of CRAYVALLAC SL enables a slightly greater elasticity to be obtained from sealants manufactured at higher temperatures.

Summary

The use of CRAYVALLAC SLX and CRAYVALLAC SL in methoxysilane sealants provide excellent shear thinning rheology. This characteristic provides for ease of sealant application and excellent slump and sag resistance. For manufacturing processes at temperatures less than 80 – 90°C (176 – 194°F) CRAYVALLAC SLX is the obvious choice of rheology modifier. However, at higher temperatures the choice is not clear cut and the final choice will require a more detailed study of the final cured sealant properties e.g. elasticity.

Experimental

The experimental data presented in this technical paper was obtained from methoxysilane sealants prepared using the following recipe:

Components	Parts: w/w
Calcium Carbonate[1]	50
Titanium Dioxide	3
Methoxysilane Polymer[2]	25
Plasticiser[3]	17
Rheology Modifier[4]	3.5
Dehydrating Agent[5]	0.7
Adhesion Promoter[6]	0.5
Curing Catalyst[7]	0.3

(1) CARBITAL 110S ex. Imerys
(2) KANEKA MS POLYMER ex. Kaneka Corporation: S203H and S303H 60:40.
(3) JAYFLEX DIUP ex. ExxonMobil Chemical
(4) CRAYVALLAC SLX or CRAYVALLAC SL.
(5) DYNASYLAN VTMO ex. Degussa.
(6) DYNASYLAN DAMO -T ex. Degussa.
(7) METATIN CATALYST 740 ex Acima

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