

● Development of Reactive Plasticizers for Sealants

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1. Introduction

Building sealants are materials that are used to fill seams and gaps in exterior walls to prevent moisture from entering the indoor areas and to maintain airtightness¹⁾. Non-solvent-type curable liquid compositions (amorphous sealants) consisting of a base resin (curable resin), a plasticizer, inorganic components, etc. are commonly used, and among these, demand for sealants using modified silicone resin (Fig. 1) as the base resin has increased¹⁾.

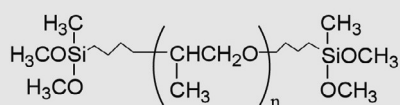


Figure 1: Modified silicone structure

In recent years, with the enforcement of the Act on the Promotion of Housing Quality Assurance, “a 10-year period of warranty against defects regarding prevention of water leakage in housing” has become mandatory, and demand for highly weather-resistant and highly durable sealants has been growing²⁾.

We market acrylic oligomers obtained by the Uniform Functional Oligomer (UFO) process under the trade name “ARUFON.” The UFO process enables molecular weight control through high-temperature continuous polymerization without the use of chain transfer agents, allowing efficient and cost-effective production of solvent-free acrylic oligomers with high weather resistance. We have already launched the non-functional type acrylic oligomers “UP Series” as highly weather-resistant plasticizers for sealants³⁾⁻⁷⁾. We recently developed the “US Series,” reactive plasticizers containing alkoxyethyl groups (moisture-curing crosslinking groups), in response to growing market demand for higher weather resistance and functionality.

2. Issues around sealants

Sealants are required to deliver good workability (low viscosity) during application, and flexibility (low modulus, high elongation) to follow the expansion and contraction of joints due to changes in outside temperature after curing. In general, plasticizers such as phthalic acid esters are added to adjust these properties. However, in recent years, the performance requirements of the market have become higher, and there are cases where conventional plasticizers cannot meet these requirements. For example, ceramic-based siding boards are increasingly used in detached houses because they can easily enhance the design of the building's exterior. Ceramic-based siding boards tend to shrink over time due to drying after installation, which causes the joint width to keep widening (Fig. 2). If the sealant lacks sufficient flexibility, the sealant's bonded interface may peel off or rupture, leading to water leakage.

The conventional solution method has been to increase the amount of plasticizer added to increase the flexibility of the sealant so that it would follow the movement of the joints. However, plasticizers added in large amounts tend to bleed onto the sealant surface, not only failing to prevent peeling and rupture over time but also creating a new issue: surface-only softening that makes the sealant prone to staining.

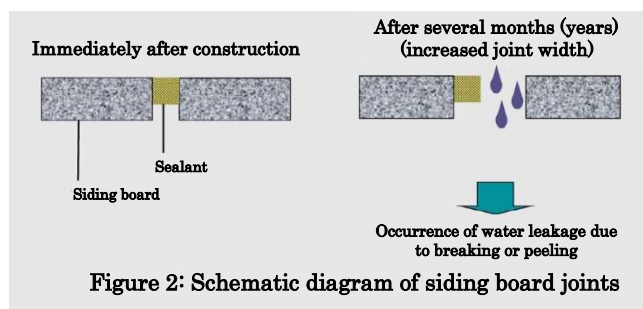


Figure 2: Schematic diagram of siding board joints

Furthermore, elastic adhesives are now being used for interior and exterior tile bonding, etc. in applications similar to sealants. Elastic adhesives are required to have both mechanical properties of higher modulus and relatively lower elongation at break than sealants, as well as low viscosity and good workability.

As described above, the market is seeking a means to enable a wide range of performance designs while maintaining workability.

3. Structure of the US Series

The US Series is a liquid acrylic oligomer containing an alkoxyethyl group as the crosslinking functional group, as shown in Fig. 3. It is capable of co-crosslinking with the base resin such as modified silicone thanks to the moisture curing of the alkoxyethyl group, and can be used as a reactive plasticizer.

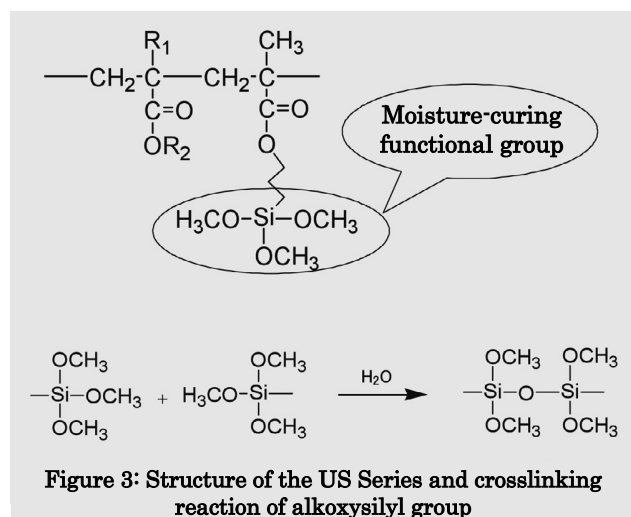


Figure 3: Structure of the US Series and crosslinking reaction of alkoxyethyl group

4. Properties of the US Series

Table 1 summarizes the representative grades of the US Series and their properties. Both are low viscosity liquid resins and can be used as plasticizers. A high-crosslinking grade (US-1) and the low-crosslinking grade (US-2) are available.

Table 1: Properties of the US Series

Grade name	US-1	US-2
Form	Liquid	Liquid
Nonvolatile content [%]	≥ 98	≥ 98
Mw	3200	2500
Viscosity (25°C) [mPa·s]	2500	2300
$f^*)$ [groups/molecule]	0.9	0.1
Compatibility with MS	○	○
Characteristics and uses	High modulus Low elongation Adhesive	Low modulus High elongation Sealant

*) Average number of alkoxyethyl groups per polymer chain

5. Evaluation of sealant physical properties

Table 2 shows examples of sealant formulations using modified silicone (MS) as the base resin. In this study, sealants were evaluated using the formulations listed in **Table 2** unless otherwise noted.

Table 2: Sealant formulation examples

Component	Parts	Example
Base resin	100	Modified silicone (MS), etc.
Plasticity	50	US Series, DOP, etc.
Filler	120	Calcium carbonate
Anti-sagging agent	2	Amide wax
Antioxidant	2	HALS, UVA, etc.
Property modifier	6	Silane coupling agent
Curing catalyst	2	Tin compound

We also used the following three types of non-functional plasticizers for comparison.

Table 3: Non-functional plasticizers for comparison

Plasticizer	Composition	Mw	Viscosity [mPa·s]
UP-1110	Acrylic oligomer	2500	3500
PPG	Polypropylene glycol	3000	450
DOP	Phthalic acid ester	390	50

5.1 Gel fraction

The cured product was obtained by mixing 100 parts of modified silicone resin, 50 parts of plasticizer, and 1 part of dibutyltin diacetylacetonate, then curing the mixture in a temperature-controlled room (23°C, 50% RH) for 1 week. The cured product was extracted with acetone, and the extraction residue was taken as the gel fraction.

As evident in **Table 4**, the US Series exhibited a higher gel fraction compared to existing non-functional plasticizers.

Table 4: Gel fraction test results

Plasticizer	f [groups/molecule]	Gel fraction [%]
US-1	0.9	80
US-2	0.1	64
UP1110	0	60
DOP	0	58
PPG	0	60

Fig. 4 shows the relationship between f value and the amount of non-extracted plasticizer calculated according to the following equation.

Non-extracted fraction = (extraction residue - MS-derived extraction residue) / initial plasticizer amount. While nearly the entire amount of the plasticizer component was extracted with acetone in the case of a non-functional ($f = 0$) plasticizer, the non-extracted fraction of plasticizer increased as the f value increased. This is assumed to be due to the co-crosslinking between the reactive plasticizer and modified silicone, which reduced the low molecular weight components that were easily extracted by acetone.

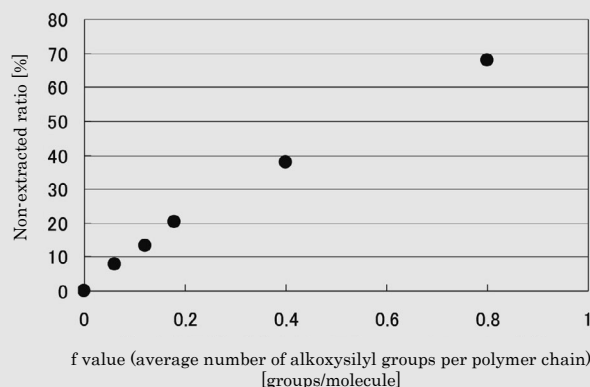


Figure 4: Relationship between f value of reactive plasticizer and amount of non-extracted plasticizer

5.2 Tensile properties

Table 5 shows the tensile test results on the sealant formulations.

Table 5: Sealant tensile properties

Plasticizer	50% modulus [MPa]	Breaking strength [MPa]	Elongation at break [%]
US-1	0.70	1.59	380
US-2	0.22	1.48	890
UP-1110	0.27	1.48	700
DOP	0.27	1.50	720
PPG	0.26	1.52	710

Curing: 23°C, 50% RH, 1 week

Sample: Dumbbell cutting die No. 2, film thickness 2 mm

The non-functional plasticizers all exhibited similar tensile properties. US-2, which has a small f value, resulted in a lower 50% modulus and higher elongation at break compared to the non-functional plasticizers. This demonstrates suitability for applications that require flexibility, such as sealants for ceramic-based siding materials. On the other hand, US-1 with

a large f value has a high modulus and a low elongation at break, making it suitable for applications requiring higher strength, such as adhesive applications. Normally, the amount of plasticizer added is reduced to increase modulus, but this increases the viscosity of the formulation and reduces its workability. With the US Series, tensile properties can be adjusted by the amount of alkoxyethyl groups introduced, and it is possible to achieve the best balance between physical properties without changing the amount of plasticizer added.

Fig. 5 shows the correlation between f value and the tensile properties of the reactive plasticizer with Mw 2400. We found that the minimum 50% modulus and maximum value of elongation at break occurred at $f = 0.1$ to 0.2 . We confirmed that reactive plasticizers containing a small number of alkoxyethyl groups were more effective than non-functional plasticizers at reducing modulus and improving elongation at break.

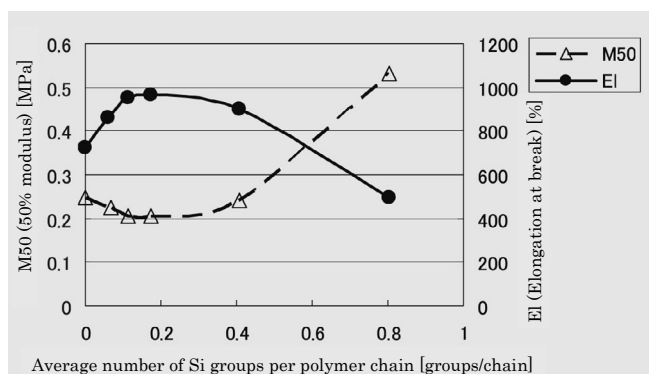


Figure 5: Relationship between f value and tensile properties of reactive plasticizers

We believe that the distribution of alkoxyethyl groups in the reactive plasticizer is related to the existence of minimum values and maximum values of modulus and elongation at break with respect to the f value. **Fig. 6** shows the relationship between the f value and the distribution of alkoxyethyl groups in a polymer of Mw 2400. For example, the polymer with $f = 0.1$ consists of about 20% monofunctional components (one alkoxyethyl group per molecule) and about 80% non-functional components, with almost no multifunctional components.

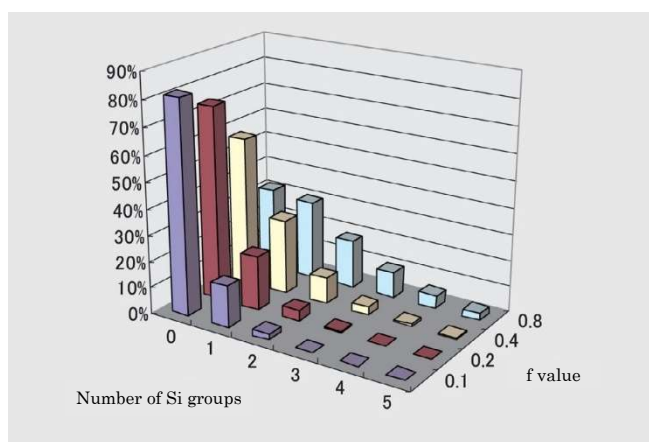


Figure 6: Distribution of f values and alkoxyethyl groups in reactive plasticizers

As the schematic diagram in **Fig. 7** indicates, the monofunctional component is assumed to reduce the crosslink density and contribute to the decrease in modulus and the increase in elongation at break.

Fig. 6 shows that as the f value increases, the proportion of non-functional components decreases and the proportion of monofunctional components increases, but the proportion of bifunctional or multifunctional components also increases. We believe that the increase in the number of multifunctional components led to the decrease in elongation at break, since it increases the crosslink density and results in a higher modulus.

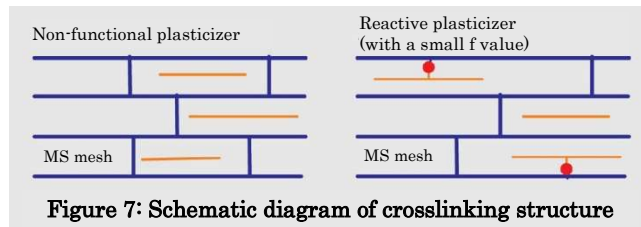


Figure 7: Schematic diagram of crosslinking structure

5.3 Contamination resistance

We evaluated the ΔE value after applying a water-based topcoat on the surface of the cured sealant, letting it stand at 60°C for one week, sprinkling contaminating powder onto the coating, and air blowing. **Fig. 8** shows an outline of the test method. A large color difference ΔE before and after testing is considered to indicate greater plasticizer bleeding and softening of the sealant surface.

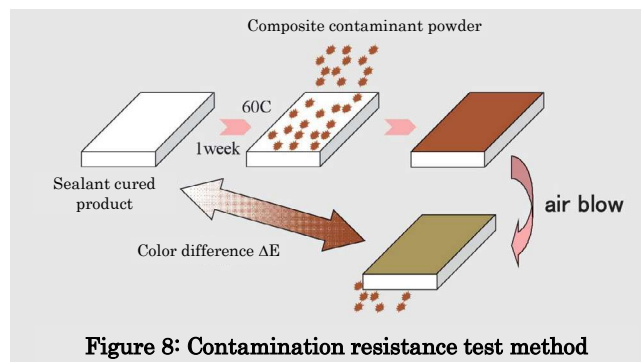


Figure 8: Contamination resistance test method

Fig. 9 shows the test results. UP-1110, a non-functional plasticizer with a large molecular weight, had a smaller ΔE value and less staining on the sealant surface compared to DOP. It is noteworthy that US-2, with only a small number of alkoxyethyl groups introduced ($f = 0.1$), exhibited a substantial decrease in ΔE . This indicates that reactive plasticizers can make sealants more stain-resistant (i.e., the plasticizer itself exhibits better bleeding resistance) compared to non-functional plasticizers. As mentioned earlier, the polymers with $f = 0.1$ contain a non-functional component proportion as high as about 80%. It is assumed that the acrylic component co-crosslinked to the modified silicone also acts as a compatibilizer and effectively suppresses the bleeding of the plasticizer.

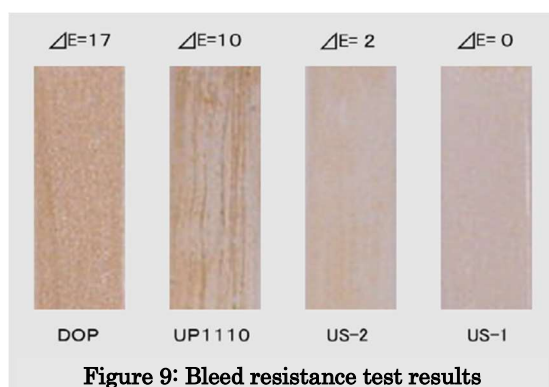


Figure 9: Bleed resistance test results

5.4 Weather resistance

QUV (ultraviolet fluorescent lamp) accelerated weathering resistance tests were carried out on sealants using various plasticizers, and the retention rates of breaking strength and elongation at break were measured. **Fig. 10** shows the results. While sealants using plasticizers such as DOP and PPG showed a decrease in physical property retention over time, the UP Series and US Series showed significantly higher physical property retention even after 1,500 hours.

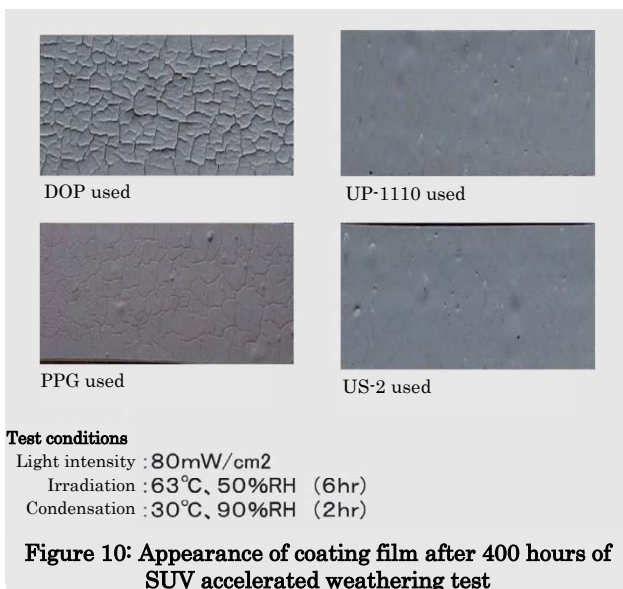
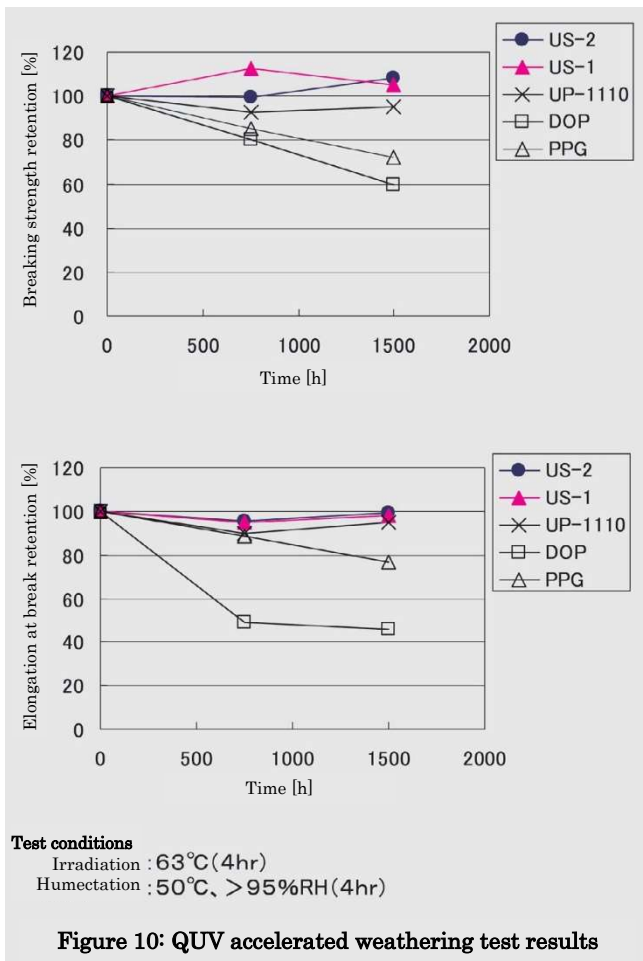


Fig. 11 shows the appearance of the coating films after 400 hours of SUV (metal halide lamp) accelerated weathering testing.

While DOP and PPG showed signs of degradation with cracks on the surface of the coating film, UP-1110 and US-2 showed good weather resistance with no cracks or other abnormalities in appearance.

6. Conclusion

The “US Series” of reactive plasticizers, which contain alkoxyethyl groups, have unique characteristics including the following:

- 1) High weather resistance (common characteristic of UFO polymers)
- 2) High bleed resistance, with stain resistance on the coating film surface
- 3) Adjustable physical properties in a wide range from low modulus to high modulus depending on the amount of silyl groups introduced.

Fortunately, customers have recognized the above characteristics, and the use of the series in sealant and adhesive applications is expanding. We hope to continue to make further improvements and develop new materials that will contribute to the market's need for higher functionality and performance.

Reference

- 1) Japan Sealant Industry Association (ed.), “Sealants for Construction - Basics and Correct Usage -,” Revised Edition, Japan Sealant Industry Association (2002) p147, p166.
- 2) S. Terauchi, The Bousui Journal, 32 (6), 33 (2001).
- 3) S. Kayamori and T. Kimura, Engineering materials, 47 (11), 106 (1999).
- 4) H. Inukai, The Bousui Journal, 33 (6), 64 (2002).
- 5) S. Kayamori, Toagosei Annual Research Report, 3, 42 (2000).
- 6) H. Inukai, Toagosei Annual Research Report, 4, 29 (2001).
- 7) T. Kimura, H. Inukai, S. Kayamori and M. Kawai, Toagosei Annual Research Report, 6, 32 (2003).