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Preparation and Adhesion of One Part Room Temperature Curable Alkoxy Type Silicone Sealant

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일액형 알코올형 실리콘 실란트의 제조 및 접착 물성

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요 약

실리콘 실란트는 실리콘폴리머, 가소제(plasticizer), 가교제(crosslinker), 충전제(filler), 촉매(catalyst), 첨가제(additive) 등으로 제조할 수 있으며, 실란트의 실용특성에는 각 제조변수의 종류와 혼합비율이 크게 영향한다. 알코올형 실리콘 실란트는 최근들어 환경적인 이점 때문에 그 사용이 늘고 있다. 본 연구에서는 상온경화형 일액형 알코올형 실리콘 실란트를 PDMS(polydimethylsiloxane)의 점도를 달리하여 제조한 후 그 접착특성을 평가하였다. 또한 점도 20000과 80000 cps의 PDMS를 혼합 사용하고 가교제, 가소제, 촉매 등의 함량을 변화시켜가면서 실란트를 제조하고 접착특성을 평가하였다. 또한 각 실란트의 제조과정 중의 반응온도 변화를 기록하여 적절한 제조조건을 얻도록 하였다.

실란트 제조시 혼합물의 온도가 40℃ 이하가 되도록 제조변수의 조성을 조절하여 적합한 물성의 실란트를 제조할 수 있었다. 피착재에 따라 접착력이 달라졌으며, 유리/유리 > 유리/알루미늄 > 알루미늄/알루미늄 순으로 나타났다. 실란트의 신장률은 폴리머 점도와 가소제의 함량 증가에 따라 증가하였으며, 강도는 가교제와 가소제 함량 감소와 촉매함량 증가에 따라 증가하였다.

ABSTRACT

Silicone sealants are composed of polymer, plasticizer, crosslinker, catalyst and filler. Types and compositions of components are effected on sealant performances. In recent, use of alkoxy type silicone sealant increased due to environmental advantage. In this study, we investigated effects of component types and ratios on one-part room temperature curable alkoxy type silicone sealant preparation and adhesion properties. Alkoxy type silicone sealants were prepared with various PDMS (polydimethylsiloxane) viscosities. In addition,

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the effect of plasticizer, crosslinkers, and catalyst on sealant obtained from by mixture of PDMS viscosities of 20000 and 80000 was investigated. Reaction temperature on change of mixing time was observed, and then proper crosslinking systems were found. Adhesion (properties) of silicone sealants were measured.

In the sealants preparation, stable reaction was achieved by adjusting composition variance ratio in the sealant mixture temperature below 40℃. The adhesion properties of sealant differ from substrate composition. The order of adhesion strength was glass/glass > glass/aluminum > aluminum/aluminum system. The elongation of sealant was increased as polymer viscosity and plasticizer content increased. The strength was increased as crosslinker and plasticizer decreased, while catalyst increased.

KEYWORDS : SILICONE SEALANT, ALKOXY TYPE, POLYMER VISCOSITY, CROSSLINKER, PLASTICIZER, CATALYST

INTRODUCTION

Structural glazing is becoming increasingly popular as a means of finishing building facades.[1] This method involves bonding of glass, aluminum or other materials to the supporting curtain wall structure by silicone sealants. Silicone construction sealants designed for structural glazing applications are of the medium- to high-modulus range. This medium- to higher-strength sealant, which has excellent bonding properties to nonporous substrates such as glass, aluminum, and various types of coated metals, is necessary because it becomes an integral part of the structural support design. This type of silicone sealant is utilized in a glazing system where it bonds the glass to the structural framing of a building. Dynamic wind loads are then transferred from the glass to the perimeter support by the cured elastomeric sealant. However, they should not be too stiff as to not allow movement, because the presence or absence of thermal movement is an important factor in this sealing application. Only silicone sealants are allowed in structural glazing applications.[1,2] Comparative between conventional glazing and structural glazing is shown in Figure 1.

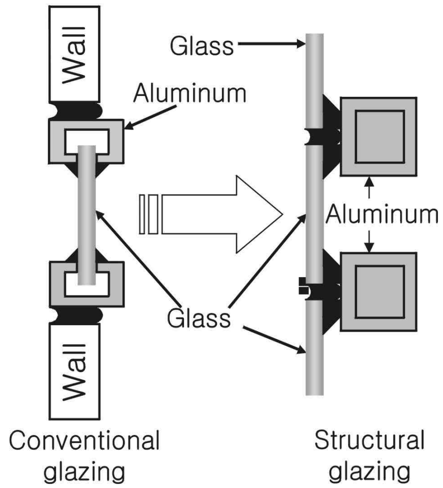


Figure 1. Comparative between conventional glazing and structural glazing.

Silicone sealants are composed of polymer, plasticizer, crosslinker, catalyst, and filler. Types and compositions of components are effected on sealant performance. Silicone sealants are distinguished into acetoxy, oxime, or alkoxy types, according to the crosslinkers.

Acetoxy type silicon sealant is one of the most widely used in silicone sealant industry. However, it has a drawback in that it easily corrodes on some metals and alkaline substrates. Also, acetic cure sealants are not popular owing to the odor of the acetic acid generated during cure.[3,4]

Oxime type silicone sealant has acceptable cure rates and is non-corrosive by acid/base reactions. However, the methylethylketoxime by-product can complex with some metals such as copper to generate unwanted colors, and if allowed to accumulate, the ketoxime vapor can induce crazing on certain plastics such as polycarbonate. This makes it unsuitable in certain applications.[3,4]

Thus, alkoxy types are readily available. It releases methanol as a by-product, which is non-corrosive to most substrates and its odor is not particularly offensive. But, it is much less reactive and requires specialized catalyst systems to achieve adequate cure rates.[3,4]

In this study, we investigated the effects of component types and ratios on one-part room temperature curable alkoxy type silicone sealant preparation and adhesion properties. Alkoxy type silicone sealants were prepared with various PDMS (polydimethylsiloxane) viscosities. Reaction temperature on change of mixing time was observed, and then proper crosslinking systems were found. In addition, the effect of plasticizer, crosslinker, and catalyst on silicone sealant obtained from mixture of PDMS viscosities of 20000 and 80000 was investigated. Adhesion (properties) of silicone sealants were measured.

EXPERIMENTAL

Materials

One part room temperature curable alkoxy type silicone sealants were prepared with various compositions. The silicone polymer was silanol terminated PDMS (polydimethylsiloxane) with viscosities of 20000, 50000, and 80000 cps (Shinetsu Co.), respectively. The molecular weights (M_w) of PDMS were 61500, 106000, and 120500 as viscosities of 20000 (20k), 50000 (50k), and 80000 (80k) cps, respectively.

The crosslinker was TSL-8113 (Thoshiba Co.), a alkytriacetoxysilane with 2, 4, 6, and 8 wt.% based on PDMS. The plasticizers were silicone plasticizer with 100 and 1000cts viscosities or organic plasticizer with 5, 15, 25, and 35 wt.% based on PDMS. The catalysts were D-10, T-12 (Hance Co.) or TIPT, TBT (Dupon Co.), titanate type catalysts with 1.5, 1.9, 2.3, and 2.7 wt.% based on PDMS and crosslinker. In addition, filler and additives (chain extender, adhesion promoter, pigment slurry, fungicide) were used.

Preparation of Alkoxy Type Sealants

One part room temperature curable alkoxy type silicone sealants were prepared in Hermann Linden LPMD10, high disperser mixer with cooling apparatus. The compounding mixer and preparation procedure are shown in Figures 2 and 3, respectively.

During preparation of alkoxy type silicone sealants, reaction temperature changes were observed.

Adhesion Properties

Adhesion properties were measured by H-type specimens according to KS F 4910 (Figure 4). The substrates used in adhesion test were glass, aluminum, and specimens of glass/sealant/glass, glass/sealant/aluminum, and aluminum/sealant/aluminum were prepared.

Bead of silicone sealants 12 mm by 12 mm by 50 mm were applied in parallel 50 mm by 50 mm faces of glass or aluminum. Using appropriate spacer blocks, proper size of the bead was formed. The specimens were cured at 25℃ and 50% RH in

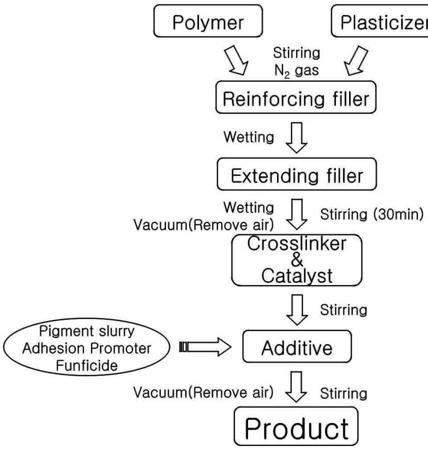


Figure 2. Method of silicone sealant blending.

Figure 3. Compounding mixer.

four weeks, and then adhesion properties were measured. The crosshead speed during the tensile strength and elongation was 50 mm/min.

RESULTS AND DISCUSSION

Reaction Temperature Change During Silicone Sealant Preparation

Reaction temperature changes during alkoxy type silicone sealants preparation with various compositions are shown in

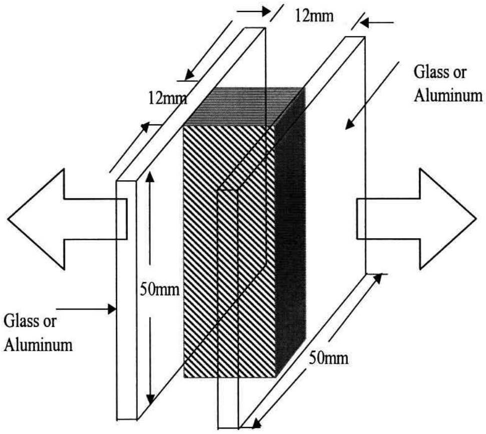


Figure 4. Sample for adhesion force measurement (KS F 4910).

Figure 5. As shown in Figure 5, reaction temperature increased with an increasing in PDMS viscosities. In the alkoxy type silicone sealants preparation, stable reaction was achieved by adjusting composition variance ratio in the sealant mixture below 40℃. Above 45℃ of reaction temperature, gelation of sealant mixture was observed. Cooling system with cooling water could be used to prevent gelation.

Although the increase of plasticizer content based on PDMS in the rage from 5 wt.% to 25 wt.%, reaction temperature change has similar tendency. While, reaction temperatures in plasticizer content of 25% were decreased rapidly. Similar tendency was observed in result of reaction temperature change as catalyst content increased. Gelation was observed in 2% of crosslinker content.

Adhesion Properties

Adhesion Properties as a Function of PDMS Viscosity

The stress-strain curves and adhesion properties of alkoxy type silicone sealant as a function of PDMS viscosity are shown in Figures 6 and 7, respectively. And also,

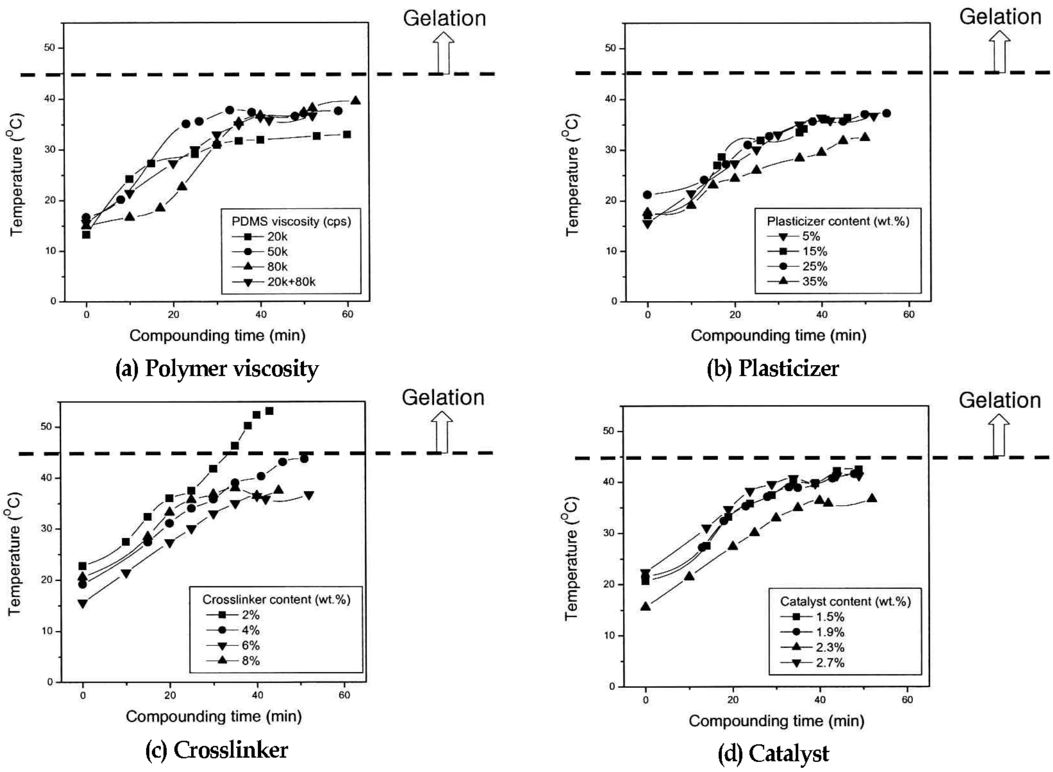


Figure 5. Reaction temperature and manufacturing process.

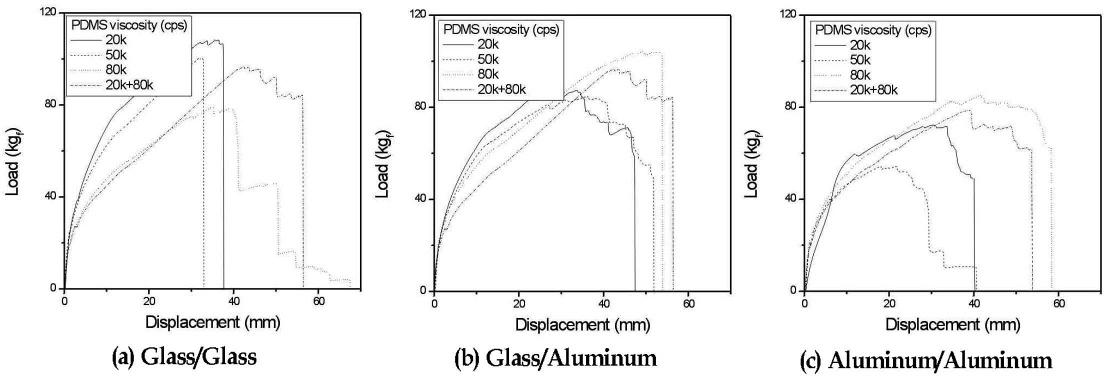


Figure 6. Adhesion force by substrate as a function of PDMS viscosity.

failure mode are shown in Table 1.

The stress-strain curves of sealant differ from substrate composition. As shown in Figure 6, the order of S-S curve slope was glass/glass 〉 glass/aluminum 〉 aluminum/aluminum system. This result indicates that glass substrate has higher stress than aluminum substrate. In glass/glass systems, adhesion failure was 0% (totally cohesive failure) and glass substrate failed due to the strength of sealant. Adhesion failure occurred partly in aluminum/aluminum and glass/aluminum system.

The joining of ceramics and glasses to other ceramic and glass parts and to

Table 1. Failure Mode of Silicone Sealant by PDMS Viscosity

Substrate	PDMS viscosity(cps)	Failure mode
Aluminum/ Aluminum	20000 50000 80000 20000+80000*[1]	20% AF*[2] 30% AF 30% AF 10% AF
Glass/ Aluminum	20000 50000 80000 20000+80000	10% AF 20% AF 0% AF 0% AF
Glass /Glass	20000 50000 80000 20000+80000	0% AF 0% AF 0% AF 0% AF

*[1] : 50:50 wt. of mixture
*[2] : AF represents adhesive failure

metallic structures requires an understanding of the features distinguishing ceramics from metals and polymers. Ceramics and glasses usually show strong covalent/ionic bonding.[5] Interfacial or material failure may result because of the difference between the elastic modulus of a ceramic and that of a metal. Typically, ceramics show greater stiffness than metals. If the ceramic must follow the deformation of the metal because the metal is the larger member in an assembly, a relatively low stress in the metal (α_m) will result in a high stress (α_c) incurred on the ceramic at the ceramic-metal interface. This is because the strain must be compatible ($\varepsilon_{m,c}$) across the interface. Even if the ceramic is much stronger than the metal, the fracture stress may be exceeded. Failure will occurr in the ceramic or at the bond interface.[5,6]

As shown in Figure 6, S-S curve slope was decreased as polymer viscosity increased (e.g., polymer weight increased). As polymer viscosity increased, elongation was increased and maximum strength was decreased. The tendencies were shown in Figure 7.

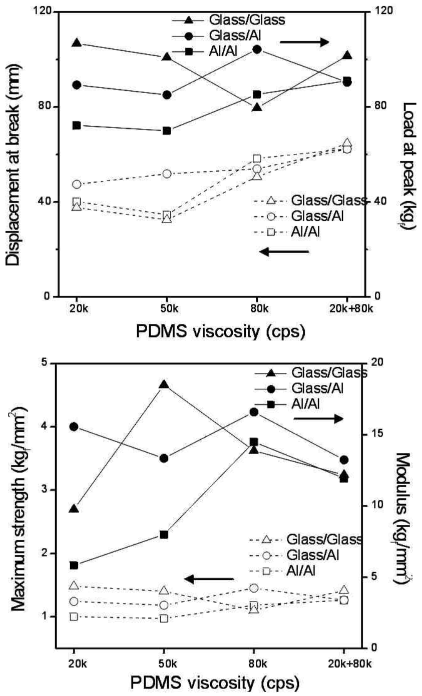
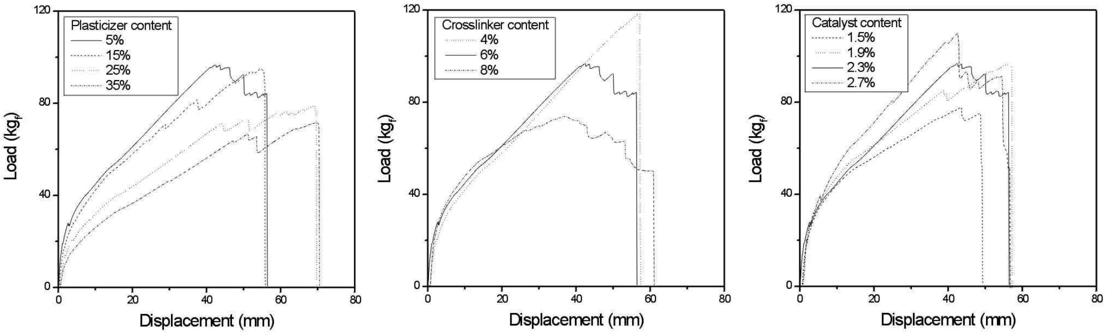


Figure 7. Adhesion properties of silicone sealant as a function of polymer viscosity.

According to earlier studies, the increase in viscosity of PDMS associated with an increase in molecular weight of PDMS. Molecular weight of the PDMS matrix influence the properties of the sealant in which it is used. In general, an increase in molecular weight causes a decrease in the modulus of the cured sealant, and increase in the ultimate elongation.[2-4]

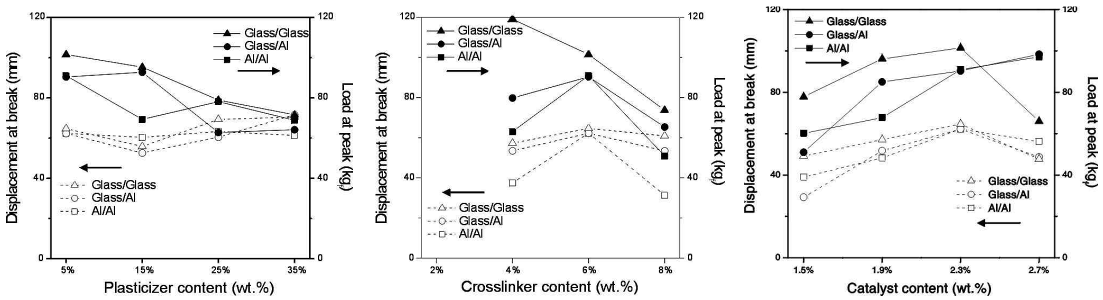
Adhesion Properties as a Function Component Variance Change

The effects of plasticizer, crosslinkers, and catalyst on sealant made by mixture of PDMS viscosities of 20000 and 80000 were investigated and are shown in Figures 8 and 9, and Tables 2, 3 and 4. The stress-strain curves of sealant for glass/glass system is shown in Figure 7.



(a) Plasticizer (b) Crosslinker (c) Catalyst

Figure 8. Effects of composition variance on adhesion force for glass/glass system.



(a) Plasticizer (b) Crosslinker (c) Catalyst content

Figure 9. Effects of composition variance on displacement and load at peak.

As shown in Figure 7, S-S curve slope was decreased as plasticizer content increased and catalyst content decreased. In crosslinker content change, S-S curve slopes are similar in all range but load of break point was increased as crosslinker content decreased.

Due to plasticizer, the strength was decreased and elongation was increased as plasticizer content increased up to 25%. Adhesion (properties) are almost similar between 25% and 35% of plasticizer content. As shown in Table 2, adhesion failure occurred conspicuously above 15% of plasticizer content.

Plasticizer increase ultimate elongation and reduce hardness in the cured sealant. They modify the rheology of uncured sealant. The use of a low viscosity plasticizer makes the sealant more mobile and easier to extrude although at high loadings the yield point can reduce to the point where the material begins to flow.[4]

Table 2. Failure Mode of Silicone Sealant by Plasticizer

Substrate	Plasticizer content*1(wt.%)	Failure mode
Aluminum/ Aluminum	5	10% AF*2
	15	20% AF
	25	0% AF
	35	30% AF
Glass/ Aluminum	5	0% AF
	15	0% AF
	25	5% AF
	35	10% AF
Glass/ Glass	5	0% AF
	15	0% AF
	25	0% AF
	35	0% AF

*1 : Weight fraction based on PDMS

*2 : AF represents adhesive failure

The degree of crosslinking in elastomers is directly related to the modulus of material.[7] In silicone sealant, excess crosslinker is generally used to avoid multiple reactions of PDMS chains with a single crosslinker molecule which would lead to premature gelling and also to provide the compounded sealant with a degree of protection from adventitious moisture.[4,8]

As shown in Table 3, up to above 8% of crosslinker content, adhesion failure of 70% and 40% occurred in aluminum/aluminum and glass/aluminum systems, respectively. Generally, low-modulus materials tend to be slightly crosslinked, while higher-modulus materials have greater crosslink densities in their structures.[7] In this study, proper adhesive properties were obtained in the range from 4% to 6%. Cochrane and Lin[9] studied the effect of fumed silica in RTV one part silicone sealant including the effect of crosslinker level. In their paper, they reported that as the crosslinker level increased from 2 to 12 parts, the rheological properties of the formulations changed with a general increase in yield stress value and viscosity and with decreases in penetration and extrusion rate values.

Due to the catalyst, strength and elongation was increased as catalyst content increased up to 2.3%. Generally, increasing the catalyst concentration increases

Table 3. Failure Mode of Silicone Sealant by Crosslinker Content

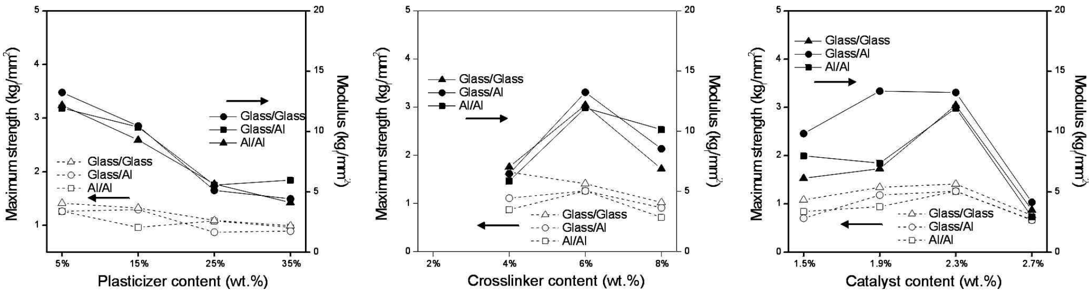
Substrate	Crosslinker content*1(wt.%)	Failure mode
Aluminum/ Aluminum	4 6 8	60% AF*2 10% AF 70% AF
Glass/ Aluminum	4 6 8	30% AF 0% AF 40% AF
Glass/ Glass	4 6 8	0% AF 0% AF 0% AF

*1 : Weight fraction based on PMDS
*2 : AF represents adhesive failure

Table 4. Failure Mode of Silicone Sealant by Catalyst Content

Substrate	Catalyst content*1(wt.%)	Failure mode
Aluminum/ Aluminum	1.5 1.9 2.3	30% AF*2 30% AF 10% AF
Glass/ Aluminum	1.5 1.9 2.3	50% AF 30% AF 0% AF
Glass/ Glass	1.5 1.9 2.3	0% AF 0% AF 0% AF

*1 : weight fraction based on PMDS and crosslinker
*2 : AF represents adhesive failure



(a) Plasticizer (b) Crosslinker (c) Catalyst

Figure 10. Effects of composition variance on maximum strength and modulus.

the reaction rate, but limits unique to each catalyst. Above these concentration limits the intrinsic stability of the silicone sealant, and especially the thermal stability, is reduced. Catalysts provide an effective means of controlling cure rate, but they must be used judiciously.[3]

CONCLUSION

In the sealants preparation, stable reaction was achieved by adjusting composition variance ratio in the sealant mixture temperature below 40℃. Above 45℃ of reaction temperature, gelation of sealant mixture was observed. Cooling system with cooling water could be used to prevent gelation.

The adhesion (properties) of sealant differed from substrate composition. The order of adhesion strength was glass/glass 〉 glass/aluminum 〉 aluminum/aluminum system. The elongation of sealant was increased as polymer viscosity and plasticizer content increased. The strength was increased as crosslinker and plasticizer decreased, while catalyst increased. In this study, proper adhesive properties were obtained in the range from 4% to 6% of crosslinker content.

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