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Impact of Humidity on Structural Silicone Rubber Sealants in Window Glazing

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Abstract Exposure to moisture can lead to various detrimental effects on structural sealants, resulting in their degradation. The extent of this degradation is influenced by several factors, including the type of sealant and the curing period. Silicone sealants are commonly used in structural glazing due to their excellent resistance to weather conditions. This research investigates the impact of moisture on commercial silicone sealants by tracking changes in their physical properties. Moisture exposure was simulated using a water spray with a pH range of 4 to 10. These pH levels reflect typical conditions from mildly acidic rain (pH 4) to alkaline cleaning solutions (pH 10). The laboratory assessment of degradation focused on alterations in tensile tangential modulus, percentage elongation, and ultimate tensile strength.

Index Terms moisture resistance, silicone sealants, tensile modulus, outdoor exposure, crosslinking mechanism

I. Introduction

Silicone sealants were first introduced in the mid-1970s and quickly gained popularity in the construction industry due to their superior physical properties compared to other organic sealants. These sealants are renowned for their high flexibility, excellent resistance to UV radiation, and low water absorption. However, during service, silicone sealants can be subjected to a variety of factors that can significantly impact their performance. For instance, the exposure conditions for sealants can vary from minimal to extensive contact with moisture [1].

This study presents the outcomes of laboratory experiments aimed at evaluating the effects of moisture on structural silicone sealants across four different pH levels. The performance of three distinct sealant formulations was assessed based on changes in their tangential tensile modulus, percentage elongation, and ultimate tensile strength.

II. Mechanism of Collapse

When a partially cured silicone sealant is exposed to moisture, it absorbs the moisture and continues to undergo crosslinking. This increase in crosslink density typically results in a higher modulus of the material. From the initial mixing of components in the sealants (such as polymer, fillers, and stabilizers) to well after their application, silicone sealants generally experience an increase in modulus or crosslink density. Additionally, both our findings and those of other researchers have observed that some further curing occurs during service. However, prolonged exposure to moisture eventually causes the modulus of the sealant to decrease. This decline is due to the halt in crosslinking and the beginning of degradation (chain scission) caused by hydrolysis. This degradation is quantifiable through changes in the material's modulus [1].

III. Experimental Procedure

Test specimens were fabricated from cast sheets of three commercially available silicone structural sealants. The low-modulus structural sealant (a one-part sealant) is composed of polydimethylsiloxane, a hydroxyl-terminated polymer, which undergoes chain extension with methyl vinyl bis(n-methylacetamido) silane and crosslinking with dimethyl, methylethyl-N-hydroxyethamine silicone. The medium-modulus structural sealant (also a one-part sealant) consists of a proprietary polysiloxane polymer crosslinked with methyltrimethoxysilane in the presence of a catalyst. The high-modulus structural sealant (a two-part sealant) comprises polydimethylsiloxane, a hydroxyl-terminated polymer, crosslinked with n-propylorthosilicate in the presence of a catalyst. The manufacturers provided these sealants in sheet form, and they were initially cured before testing [2].

IV. Mechanical Properties in Tension

The methodology employed to correlate the physical properties of the silicone sealants was based on the ideal elastomer concept. This theory, developed by early researchers, posits that elastomeric materials stretch quickly without energy loss and

Property	Low-Modulus Sealant	Medium-Modulus Sealant	High-Modulus Sealant
Young's Tensile Modulus (MPa)	Increase after initial exposure	Similar degradation pattern	45% to 70% drop after exposure
Elongation at Break (%)	Additional 30% before decrease	Greater resistance compared to low-modulus	Decrease below initial levels
Ultimate Tensile Stress (MPa)	More than 70% increase after exposure	Similar trend as low-modulus	Below control levels

Table 1: Summary of experimental results for silicone sealants

subsequently retract to their original length. However, when silicone elastomers are subjected to a uniaxial tensile test at less than rapid extension rates, the stress response is complex and depends on the extension, indicating that elastomers do not exhibit a linear stress-strain (Hookean) relationship across the full range of extension. Nonetheless, the ideal elastomer concept does explain some of the non-Hookean behavior [3]. A simplified expression for the behavior of an ideal elastomer under stretch can be written as follows:

$$\alpha = DCT(\beta - \frac{1}{\beta^2}) \quad (1)$$

α =tensile stress (Pa)
D =crosslink density (mol m 3)
C = gas constant
T =absolute temperature for the test conditions (K)
β =extension ratio (L/Lo) =e + I, where e is the strain

Here, stress is considered a function of extension rather than strain. By applying the concept that the elastic modulus is the derivative of the stress-strain relationship, and expressing extension as a function of strain, the tangent modulus of an elastomer can be determined in terms of the extension ratio:

$$E = DCT(\beta + \frac{2}{\beta^3}) \quad (2)$$

Equation (2) shows that for isothermal testing, the modulus of the elastomer depends on both the crosslink density and the extension. In this study, the experimental stress-strain data were analyzed using Equation (1) to determine an appropriate value for the crosslink density, D. This value of D was then applied in Equation (2) to calculate the tangential modulus at various levels of strain, ranging from 10% to 40% (i.e., e=40%,β=1.4).

V. Tensile Test Procedures

During uniaxial tension tests on TA joints, the glass plate failed before any adhesive or cohesive failure was observed in the sealant. The impact of the sealant quantity in the joint on performance was consistent with findings from our previous study. Test sheets were cut into dumbbell-shaped tensile specimens following ASTM Standard D-412 for elastomers, with each sample measuring 14 centimeters in length. An Instron testing machine conducted the uniaxial tensile tests on these specimens, with maximum elongation kept below 40% of the gauge length. This limit was set because the forces from wind and other loads are not expected to elongate the sealants beyond 40%. The specimens were tested to failure at the end of the monitoring period, with an extension rate fixed at 5.18 cm/min, closely matching the loading rate experienced during wind conditions. Although ASTM Standard D-412 specifies an extension rate of 50 cm/min, such a high rate is impractical for actual service conditions [4].

The outdoor experimental setup for moisture exposure is illustrated. Each set of coupons was sprayed once daily in the morning with one of the pH solutions, then left to dry outdoors in air and sunlight. This process of applying moisture and then drying was termed a weathering event. Test specimens were periodically removed from the layout after drying and tested at room temperature for changes in their Young's tensile modulus (tangential). The same samples were reinstalled in the layout after testing. It was assumed and later confirmed through experimentation that the short-duration tests did not alter the crosslinking mechanism. For each type of sealant, five subsample tests and three sample replications were conducted per specimen. Several coupons were also maintained under ambient laboratory conditions as controls. All testing occurred at ambient room temperature and pressure (30 ± 5°C, 1 atm, and 60% or less relative humidity) [5].

VI. Results and Discussion

The three key physical properties examined in this study are Young's tensile modulus, elongation at break, and ultimate tensile stress. As previously mentioned, the actual TA joints did not exhibit adhesive or cohesive failure under uniaxial tension. Therefore, the study focused on monitoring the failure of the sealant under different weathering conditions. An increase in the modulus indicates that the sealant has hardened due to crosslinking or loss of plasticizer, while a decrease in the modulus suggests softening as a result of increased moisture content. Chain scission from UV radiation exposure also leads to a decrease in modulus (Table 1) [6].

The variation in Young's tensile modulus with the number of exposure events for low-modulus coupons. Initially, the low-modulus formulation, though very compliant, exhibited a significant increase in modulus after exposure, indicating ongoing curing. Coupons exposed to lower pH levels (3 to 4) showed an accelerated initial increase in modulus compared to those exposed to other pH levels, suggesting that additional crosslinking sites facilitated rapid curing in acidic conditions. However, after seven exposure events at low pH, chain scission became more dominant than crosslinking. Coupons exposed to other pH levels continued to cure slowly through 19 exposure events, with their modulus doubling compared to those exposed to lower pH levels. After reaching a maximum, all coupons began to soften, continuing for 70 events, after which the modulus was slightly less than the initial value. This moisture-induced degradation was irreversible, as the test coupons did not return to their initial modulus after a 30-day period (less than 5% change).

The medium-modulus and high-modulus sealants showed similar behavior to the low-modulus formulation. Despite following a similar degradation pattern, the medium-modulus coupons did not exhibit any degradation effects after 70 exposure events, indicating better resistance compared to the other formulations. In contrast, the high-modulus formulation experienced a 45% to 70% drop in modulus compared to the initial value before exposure, indicating a substantial impact from moisture [7].

The percentage elongation at break for control and test coupons. Over 254 days of curing, all control coupons showed an increase in elongation at break. Silicone rubber sealants are known to cure slowly through crosslinking over extended periods under actual service conditions. Low-modulus sealants exposed to alkaline moisture for 354 events showed an additional 30% elongation before failure compared to those exposed for 75 events. Initially, after 75 exposure events, coupons exposed to acidic conditions (pH 3 to 4) exhibited greater elongation at break compared to other pH levels. However, prolonged exposure to low-pH moisture resulted in decreased elongation. After 350 events, elongation at break fell below the levels observed for all four pH levels at 75 events, indicating reduced crosslink density due to moisture. Despite this, elongation remained above control levels. This behavior, similar to that observed in natural rubber, likely results from reduced active crosslink sites.

Changes in ultimate tensile stress due to weathering for the three formulations. For low-modulus material, specimens exposed for 354 events showed a more than 75% increase in tensile strength compared to controls (zero events). This increase in tensile strength over time has been documented for many rubber materials. Similar behavior was observed in the other two silicone formulations. However, ultimate tensile stress remained below the level obtained for control coupons.

VII. Conclusions

This study demonstrated that the ideal elastomer concept effectively correlates the tensile modulus and other physical properties to evaluate the moisture resistance of silicone sealants. The outdoor exposure tests were straightforward to perform and offered a realistic approach to accelerated testing. Although the total monitoring period was relatively short (152 events), it was sufficient to reveal performance changes that might be anticipated in actual service conditions. Based on the experimental data, the authors have shown that the life expectancy of the sealants can be estimated using the developed models for the crosslinking mechanism.

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