Studies on the Effect of Movement During the Cure on the Mechanical Properties of a Silicone Building Joint Sealant

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A novel sealant testing device was used to continuously monitor the mechanical properties of a one-part silicone sealant for movement cycles initiated from 10 to 168 h after sample creation. These cure times fall between the proposed RILEM TC-139 technical recommendation of 5 min and the ASTM C719 standard of 21 days. At 10 h of cure, enough crosslinking occurred before testing such that neither the overall movement history of the sample nor the deformation step shapes affected subsequent curing of the sealant. A critical parameter for sealant performance appears to be the extent of cure at the onset of movement. POLYM. ENG. SCI., 50:113–119, 2010. © 2009 Society of Plastics Engineers*

INTRODUCTION

Current test methods used to evaluate materials designed for use in outdoor environments do not yield predictions of the in-service performance and lead to excessively long product development, evaluation, and introduction times. The current experimental protocol involves multi-year outdoor exposures for which a typical single exposure period is 26 months. As a result product development cycles for materials such as sealant and coatings are typically greater than 10 years. For the past 100 years, laboratory testing has been used to "accelerate" this weathering through the use of laboratory ultra violet light sources. These tests have had mixed success in product development, because seldom does one obtain a high correlation between the indoor and outdoor exposure results.

Possible explanations for this lack of fidelity between laboratory and field exposure are product dependent. For building joint sealant, one of the major questions has been the effect of the joint movement on performance during the initial curing period. In field testing, the sealant experiences movement of the joint after application, but in the corresponding laboratory testing methods, such as ASTM C719, the sealant is allowed to cure for 21 days without any movement before the testing protocol begins. Recently, International Union of Laboratories and Experts in Construction Materials, Systems, and Structures, Technical Committee 139 on Durability of Building Sealants (RILEM TC-139-DBS) has developed a technical recommendation, which provides an option to include movement immediately after a sealant joint is cast. In this testing option, the sealant sample is subjected to a $\pm 7.5\%$ strain during a 2.5 h cycle initiated within 5 min after a specimen is cast. This cycle is repeated once in every 24 h for the first 12 days.

The onset of early movement during cure and its effect on the physical properties of a sealant has been documented in the literature [1–9]. Early movement of sealant degrades performance [3–5, 7] as measured by reductions in modulus [4, 7] and/or causes visible failure of a sealant joint [3–5]. In other studies, no loss of performance was observed [8]. However, important differences exist in these studies, as summarized in Table 1, making definitive conclusions difficult. For example, in the study that showed no loss of performance [8], the sealant was allowed to cure for 24 h before movement. In other studies, movement was applied within 2 h of casting [4, 7, 9]. There has been discussion that 1-part chemistries appear to be more tolerant of movement during cure than 2-part chemistries [1, 2]. In another study, base sealant chemistry played a role, but all samples showed some loss of performance [3]. Certainly, the time of movement onset, testing speed, the strain level, waveform shape are all important relative to the curing speed of the sealant. Extracting the relative importance of these factors from the sealant literature is difficult because of the heterogeneity between the studies as indicated in Table 1. Additional understanding of the potential relative importance of these

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TABLE 1. Summary of the existing sealant literature that has studied movement during cure.

Reference	Curing time before movement	Cyclic or constant extension	Strain range	Testing speed	Sealant type	Comments
[1]	5 min	Cyclic	±7.5%	2.4 h/cycle	Many	Decreased performance for some, increased for others
[3]	Six different protocols spanning 10 h–2 weeks	Varied	±10%	1 cycle/d	Five different chemistries	Backer rod contributed to failure
[1]	1 h	Cyclic	±5%, ±10%, ±15%, ±25%	0.5 mm/min and 0.05 mm/min	Silicone	Premature failure at 15% and 25%, decreased performance at all other strains
[10]	Immediate testing	Cyclic			Four chemistries, four depths of sealant	Observed four failure modes, all exhibited decreased performance
[2]	2 h, 15 min	Continuous cycling	±10%, +25%	0.053 mm/min	Oxime-cure silicones	Observed reduced performance
[3]	2d to 100 d	Cyclic movement		0.211 mm/min, 0.053 mm/min	Water based and chemically cured	No degradation of water based materials
[11]	Immediate testing	Cyclic movement	±7.5%, +12%	1 or 10 cycles/day	Many chemistries	One part chemistries show significant performance decrease, two part are not as affected

effects on the curing sealant can be obtained by examining the elastomer or rubber literature. Behavior and properties of elastomers have been well-documented in the literature for more than 50 years. Rubber is an especially useful system to use in comparing the effect of movement during cure in sealant. This comparison is based on two properties, first, the ability to control the rate and extent of cure of the rubber, and second, the virtually identical physical properties between cured sealant and crosslinked rubber. The major difference between these two classes of materials is the development of substrate adhesion during the curing of the sealant.

Tobolsky [12] outlined a framework to explain strain softening behavior in rubber, proposing an explanation based on multiple networks formed at different points of physical deformation. In a classic experiment, rubber is first cured in compression, followed by a second cure while the same rubber is in tension. The equilibrium state of this rubber was modeled as the sum of the contributions of the first network in tension and the second network in compression. Rolland and coworkers [13–18] have provided the most recent experimental verification of this model. To relieve the internal stress, specific crosslink will break and reform in a different location, thus forming a different network configuration. This phenomenon, termed strain softening, has been well documented in the literature [12].

Understanding strain softening is still an active area of research [13–50]. The formation of multiple networks has been shown to result in significantly different behavior than for single network formation in materials of same type. The process of formation of multiple networks has significant implication for understanding the effect of movement during cure on the performance of a sealant. If the rate of cure is on the same timescale as the movement, a curing sealant will establish crosslinks at different levels of extension. In the Tobolsky framework, this curing can be modeled as a series of networks each with a different equilibrium extension point. At different points during the deformation cycle, each of these networks is assumed to contribute to the overall internal stress within the sealant. The magnitude of the internal stress is directly related to the contribution to the overall stress from these multiple networks.

In this article, the effects of changing movement onset at intermediate times between the two proposed extremes, 5 min (proposed RILEM standard) and 21 days (ASTM C719 standard) will be examined for a single component silicone sealant. Joint movement is continuously monitored using a novel hybrid testing device. Additionally, the effect of the rate of movement on the sealant modulus is examined.

EXPERIMENTAL

Instrumentation

Previous studies have focused on visual inspection of the sealant in evaluating its performance. However, a more quantitative approach is to continuously monitor the elastic modulus of the sealant. This can be accomplished by recording the load and displacement in-situ during the mechanical cycling. In addition, these measurements can be used to calculate changes in the crosslink density or the molecular weight between crosslinks, M_c, which is directly related to stress, σ, and the extension ratio or strain, α, by [51]:

$$\sigma = \frac{\rho}{M_C} RT(\alpha - 1/\alpha^2) \quad (1)$$

where σ (stress) = force/area; ρ is the density of the sealant; R is the gas constant; T is the temperature in K; and $\alpha = L/L_o$, where L_o is the original length, and L is the instantaneous length. It is important to note that this calculation assumes a homogeneous crosslink density. Previous work in the area have demonstrated that there are compositional gradients in cured sealant [10, 11]. Thus the M_c, value calculated from *Eq. 1* is actually an average crosslink density integrated over an inhomogeneous network.

Measurements of the applied strain and resulting stress are made with a hybrid sealant-testing device described elsewhere [52]. The relevant features of this hybrid device are the ability to measure precisely movement and load, the ability to simultaneously evaluate five samples, and the potential for autonomous operation. A schematic of the device is shown in Fig. 1.

The deformation cycle selected was movement of ±7.5% of the 1.27 cm joint width or 0.9524 ± 0.0003 mm deformation in both the positive and negative direction resulting in a triangular shaped waveform. This cyclic deformation is consistent with the International Union of Laboratories and Experts in Construction Materials, Systems, and Structures (RILEM) recommendation and previous studies which have identified this movement as a "typical" deformation occurring during a diurnal building cycle [1]. The deformation cycle was divided into 0.0152 ± 0.0003 mm discrete steps or 200 data points. The relative standard uncertainty estimate for displacement was calculated from the lead screw error (±250 nm per mm of travel) combined with the precision of the stepper motor (±25 nm per step). After each step was completed, the load was measured on each of the five load cells. The relative standard uncertainty on the load measurement is estimated to be ±0.02%, primarily due to the nonlinearity of the load cell. This device can measure the mechanical properties of a standard sealant joint with 0.045% relative standard uncertainty. This value is a combination of the relative movement uncertainty of ±0.025% combined with the non-linearity of the load cells ±0.02% for a 7.5% expansion of a standard sealant joint.

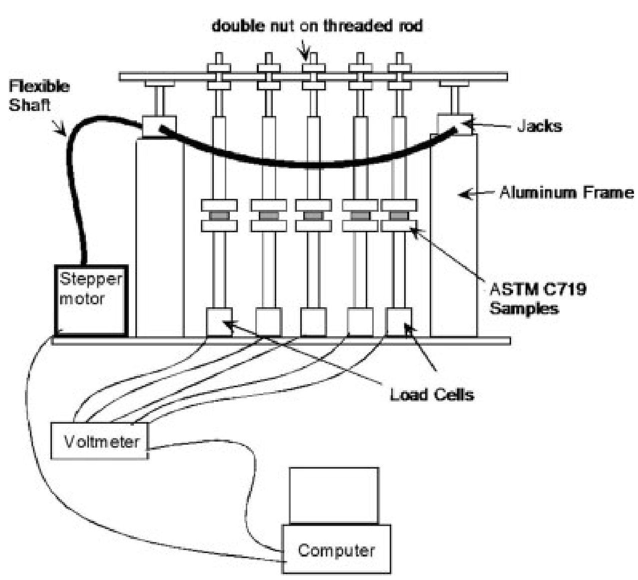

FIG. 1. A schematic illustration of the hybrid sealant testing device. Note that the load cells are located on the fixed side of the frame.

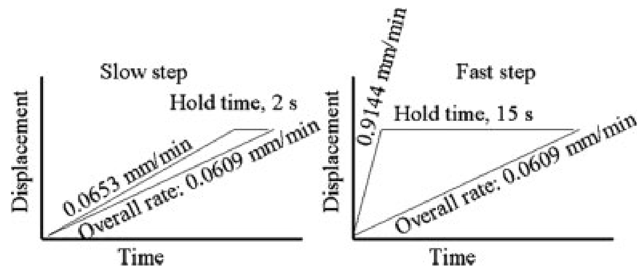

FIG. 2. Illustration of the two step profiles used in the experiments. The slow step profile was designed for a continuous movement with a minimal hold time to record the force reading. The fast step profile produces the motion in a minimum amount of time while keeping the overall rate constant.

The two step profiles tested in this experiment are shown in Fig. 2. These two step profiles were selected to examine influence of step shape on the resulting properties while holding the overall rate fixed. For the slow or continuous step profile, the velocity of the motor was 0.0653 mm/min with a fixed hold time of 2 s, the minimum time required to obtain the force readings. For the step or sudden profile, the motor velocity was 0.9144 mm/min with a 15 s total step. This gives both profiles an average rate of movement of 0.0609 mm/min. This overall rate is similar to that typically used to evaluate sealants [53].

Materials

A precompetitive silicone sealant formulation was supplied by Dow Corning Corporation (Identification of a commercial product is made only to facilitate experimental reproducibility and to describe adequately experimental procedure. In no case does it imply endorsement by NIST or imply that it is necessarily the best product for the experiment). The exact details of the formulation were not given, but this polydimethylsiloxane (PDMS) formulation is representative of a typical silicone product that cures in the presence of moisture, albeit with no additives. The sealant samples were prepared by extruding the seal-

TABLE 2. Relative time and movement histories for the three samples sets tested with the slow or continuous step shape.

Sample set	10 to 101 h	96 to 172 h	168 to 245 h
A	7.5% movement	Static	Static
B	Static	7.5% movement	Static
C	Static	Static	7.5% movement

ant from a cartridge into a 5.08 cm × 1.27 cm × 1.27 cm sample cavity composed of 7.62 cm × 1.27 cm × 1.27 cm aluminum supports on each side, a polytetrafluoroethylene (PTFE) film on the bottom and 1.27 cm × 1.27 cm PTFE spacers on each end. This is a typical sample size ASTM C719 testing. The samples were cured in this fixture for 5 h and then removed, keeping the PTFE spacers and the aluminum substrates intact. After removal from the fixture, the samples were allowed to cure for another 5 h of cure (10 h total) before the loading cycles were applied. The fixture used to prepare the samples can simultaneously accommodate 10 samples at a time. The samples were tested in a rotating fashion according to the schedule shown in Table 2 for the slower step speed and Table 3 for the faster step speed. For example, samples in set D were tested between 10 and 101 h after they were cast (zero time point) using the fast step profile, followed by 97 h of a static period and then cycled again from 198 to 242 h. Samples in set E were allowed to cure statically for 96 h after casting and were then cycled for 173 h. The overlap in time for the samples present in Tables 2 and 3 is designed to directly compare samples with different movement histories.

RESULTS

Typical results for a single sealant sample from three deformation cycles are shown in Fig. 3 for cycle numbers 1, 30, and 70. In this figure, the 200 points that comprise the data cycle are plotted along the *x*-axis and the voltage from a single load cell is plotted along the *y*-axis. A small feature caused by the endplay in the screw threads, used to produce the deformation (see Fig. 1), is clearly visible after the peak load is reached in either compression or tension on Fig. 3. After a change in direction into either compression or tension, a short period of nonlinear response was observed in the load curves before the load cell data again becomes linear with each deformation

TABLE 3. Relative time and movement histories for the three sample sets tested with the fast or steep step shape.

Sample set	10 to 101 h	96 to 173 h	168 to 217 h	198 to 242 h
D	7.5% movement	Static	Static	7.5% movement
E	Static	7.5% movement	Static	Static
F	Static	Static	7.5% movement	Static

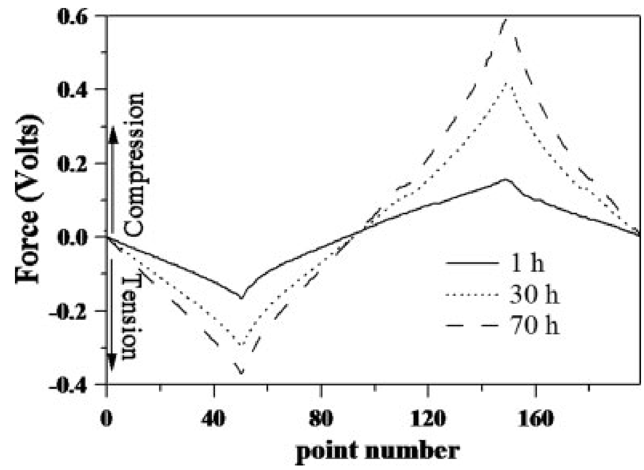

FIG. 3. Plot of the force recorded for one of the samples as a function of deformation cycles. A smooth line has been drawn between the 200 data points for each deformation cycle. The data from cycles 1, 30, 70 are plotted. The end play in the screw is clearly evident in the 1 cycle data.

step. Because the data of interest is the initial stress–strain response the endplay of the jack threads does not significantly affect the measurement since it occurs after the data acquisition is completed for each cycle.

The calculation procedure used to determine M_c is presented in Fig. 4 for the three deformation cycles from Fig. 3 (see also *Eq. 1*). The 1, 30, and 70 cycle deformation data for a single sample are shown; there is a clear increase in the number of crosslinks indicated by a decrease in M_c or increasing slope in these curves. The relationships plotted are linear which validates the implicit linear elastic assumption of *Eq. 1*.

In Fig. 5, the change in M_c data versus time is shown for five samples as a function of cycle number. The calculated values from Fig. 4 are indicated with arrows. The

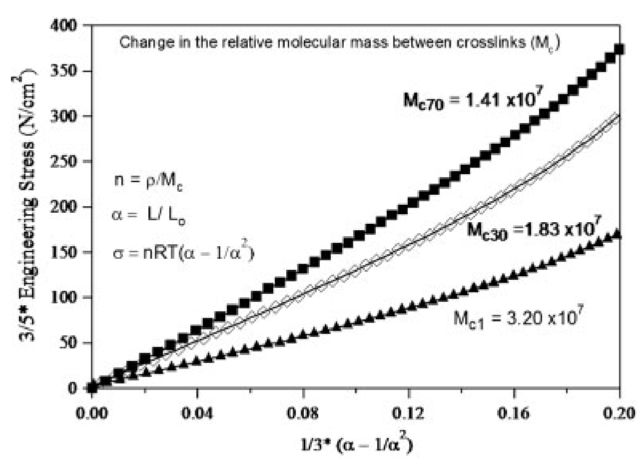

FIG. 4. Plot of stress as a function of (α − 1/α^2) where α = l/l_o, showing the procedure for calculation of the molecular weight between cross links, M_c for the three deformation cycles depicted in Fig. 3. M_c is inversely proportional to the slope of the curves as given by *Eq. 1* (also pictured on left).

M_c values decreased with time, indicating an increase in the number of crosslinks formed as expected. Also the sample-to-sample variability was small for both the individual time points and the time dependence of the M_c data.

In Fig. 6, the master plot of the M_c data versus time is shown for all of the experiments listed in Tables 2 and 3. For each letter identified, five replicate samples were used to determine M_c versus time. The A, B, and C samples were tested first, and then testing was repeated with the steeper step speed D, E, and F samples. Sample A exhibits a higher degree of scatter in the early stages of cure when compared with the other samples.

The measured M_c trend shows considerable agreement over the range of movement histories. For the three slow step speed samples (A, B, and C) good agreement is observed for overlapping values of time. A smooth curve fit to all of the data from A, B, and C would yield a reasonable description of the progress of the curing reaction.

For the samples tested with the rapid step speed (D, E, and F), a similar degree of agreement is observed. Again, a smooth curve fit to the M_c values versus time for all of the D, E, F, and 2nd D values would yield a good description of the curing process. Additionally, though some discrepancy exists between the two different step speeds at early times, for times greater than 70 h, the data is indistinguishable within uncertainty for the calculated M_c values. This demonstrates that for the range of step speeds studied, the response of the sealant does not appear to be dependent on the shape of the step deformation at longer cure times.

Initially for sample sets B and F, the modulus increased over the first few cycles before it developed a plateau. This result may be due to noncrosslink entanglements of the polymer chains [20]. For the first few cycles, the imposed strain may be physically changing the nature of these entanglements. After these noncross link structural features have been changed by the imposed strain,

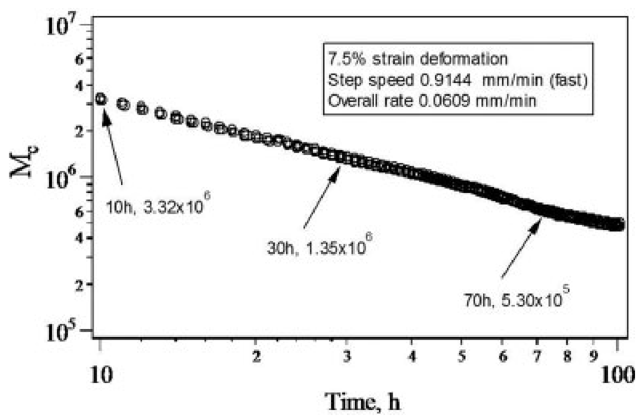

FIG. 5. Logarithmic plot of M_c versus time for five sealant samples. The values calculated in Fig. 3 are depicted with arrows. The decrease of the M_c with time is due to increasing cure or cross link density.

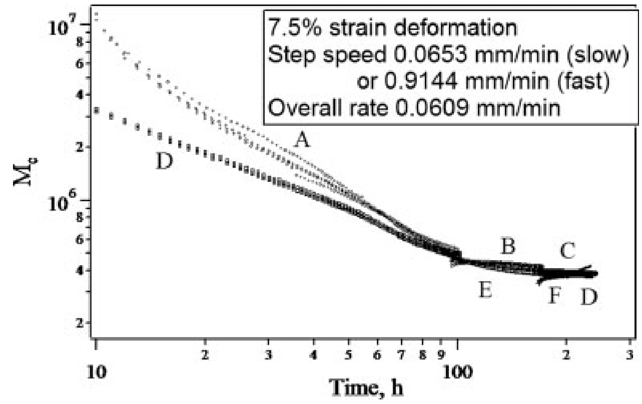

FIG. 6. Logarithmic plot of M_c versus time for all the sample sets described in Tables 2 and 3. Five time points are plotted for each time point of each sample set.

the modified crosslink structure becomes stable and dominates physical performance.

DISCUSSION

Following the work by Tolbolsky and others previously presented, allowing the sealant to cure for 10 h likely resulted in the formation of a dominant single network structure. Movement of the joint after this initial curing could have caused the formation of subsequent networks for which the equilibrium extension was not zero, thus movement caused some internal stress. However, the initially cured primary network dominated the overall properties, as evident in the measured M_c values, which were identical at long times for all the samples. The primary network continues to cure, but the rate of that cure does not seem to be affected by the movement or lack of movement of the sealant joint. This observation is consistent with the idea that this sealant cures by moisture diffusion. After the first several minutes the sealant crosslinks and forms a skin, and the moisture transport through that skin determines the rate of cure for the rest of the sealant bead.

Brower [6] proposed that the speed of movement relative to the speed of cure was an important factor in determining the degradation of joint performance. Because the initial 10 h of cure allowed a primary network to form, little or no degradation of the properties was observed, which is consistent with the results of Matsumoto [5] and Lacasse and Margeson [8]. Initiating movement without letting the sealant form a primary network is the likely cause of degraded performance found in other studies [1–3, 7, 9].

In this study, the step shape did not appear to affect the observed M_c values. For all the other sample sets, the agreement between the sample sets is within the observed experimental scatter of the five replicate samples. The areas of overlap of the data reinforce this point. Changes in the extent or rate of deformation may have a larger effect than changes in the step shape, a point to be considered in future studies.

Additionally, the cure of the silicone sealant is limited by moisture diffusion and the diffusion of that moisture is strongly affected by the ambient relative humidity and temperature. In this study, the two sets of sealant, set one (A, B, and C) and set two (D, E, and F) were prepared over a 3 week period. Although the conditions were held relatively constant, no effort was made to control the ambient temperature or humidity. The initial phases of the curing are the phases where the ambient conditions will have the strongest effect, potentially accounting for the observed differences between A and D. However, these differences might also have been due to changes in step strain shape and not changes in ambient conditions. Thus, future studies should be performed where the temperature and humidity are strictly controlled.

SUMMARY

Mechanical properties from a prototype silicone sealant allowed to statically cure for 10–168 h and then subjected to tension/compression cycles have been presented. These cure times are longer than the proposed RILEM TC-139 technical recommendation of 5 min, but shorter than the ASTM C719 standard of 21 days. Neither the movement history of the sample nor the step shape affected subsequent curing of the sealant as monitored by the mechanical properties.

This study is the first in which continuous monitoring of a sealant subjected to deformation has been performed. The device used was a novel sealant-testing device. The deformation cycle was divided into 200 discrete strain steps and the resulting force measured. The data was then used to calculate the molecular weight between crosslinks or M_c.

Two step shapes were investigated: one in which the deformation was continuously changed over the fifteen sec cycle, and another where the entire deformation was imposed in one sec followed by 14 s of rest. The M_c data showed no dependence on the step shape with the possible exception of the very earliest stages of cure. The data obtained in this study indicates that if the sealant is allowed to form a primary network before the onset of movement subsequent movement does not seem to affect the rate or extent of cure as monitored by the mechanical properties.

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