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'Enhancing Service Life'

Evaluation of Materials During Outdoor Testing Using a Computer-Controlled Test Apparatus

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Paper 10

Abstract

Ultraviolet radiation, moisture, heat, and cyclic fatigue are some of the stressors that cause materials to degrade outdoors. Considerable research has addressed the effects of ultraviolet radiation and moisture on the rate of this degradation. An often overlooked stressor on materials, during outdoor testing, is the cyclic fatigue. Cyclic fatigue is caused by self-induced dimensional change of a material or by dimensional change of materials in contact with it. For example, changes in the moisture content of wood cause it to shrink and swell, which leads to surface checking; dimensional change of wood may cause paint to crack or sealants to debond. In our research on the service life prediction of sealants, we have developed a computer-controlled test apparatus and accessory instrumentation to subject materials to cyclic loads and to measure their degradation as they are tested. The changes in elastic modulus, temperature dependence of the modulus, plasticizing effect of water above and below freezing, and evaluation of specimen quality at the beginning of the test were made possible using this equipment.

Introduction

As part of ongoing work at the Forest Products Laboratory in Madison, Wisconsin, on the performance of materials used in residential construction, a study of sealants was begun in cooperation with the National Institute of Standards and Technology (NIST) (Gaithersburg, Maryland). This work involves detailed laboratory and field studies using reliability-based service life prediction methods.

Reliability-based service life prediction (SLP) describes tests done rapidly to predict, with reasonable confidence, the performance that can be expected from a material in actual use. Other terms, such as accelerated aging and accelerated and artificial weathering have also been used to describe these types of tests. A critical component of reliability-based SLP is the accurate measurement of the factors causing degradation and the materials response to the degradation factors. In other words, we need accurate dose-response information on the materials under actual use conditions so that accelerated tests can be designed that actually duplicate the critical failure mode, but at an accelerated rate. Reliability-based SLP differs from other accelerated aging tests in that the dose-response of the materials under actual use conditions is compared with the dose-response of the materials during an accelerated test to determine the acceleration factor. The time to failure in the different tests is replaced by materials response.

During the last 50 years, considerable effort has gone into developing standards and instrumentation for evaluating the effect of ultraviolet (UV) radiation on materials (American Society for Testing and Materials, ASTM D 822, D 5031, G 26, G 53, and D 4587 (ASTM 2001) and ASTM C 1442, C 718 93, C 732 95, C 734 93, C 793 97, C 1257, and D 2249 (ASTM 2000). There is no doubt that UV radiation plays an important role in the degradation of many materials, but other factors, such as temperature, moisture, and cyclic fatigue and their interactions may be important and in some cases, more important than UV radiation.

Sealants (caulking compounds) have become widely used in commercial and residential structures to help seal their exterior envelope against water intrusion. Sealants are formulated to accommodate cyclic stress and strain, but they may undergo cyclic fatigue in combination with other degrading factors. A standard that combines cyclic stress (fatigue), water immersion, and temperature change was initially developed by A. Hockman at NIST (ASTM C 719 93, Adhesion and Cohesion of Elastomeric Joint Sealants Under Cyclic Movement (ASTM 2000); the so-called Hockman Cycle). Several devices have been used to induce cyclic movement (fatigue) of sealants during exposure. These devices generally use thermally induced dimensional change to generate fatigue in a sealant. For example, Onuoha (1999) used unplasticized polyvinyl chloride (PVC) pipe to produce fatigue in one-part polyurethane and polyurethane-hybrid sealants. Racks have also been built using dissimilar materials such as wood and aluminum (Brown 1965), concrete and aluminum (Burstrom 1980), and steel and aluminum (Karpati et al. 1977, 1978) to develop fatigue stresses. Manually operated devices have also been used to create cycling effects (Lacasse 1994 and Lacasse *et al.* 1996, 1999). Lacasse and Margeson (1996) cycled sealants during cure. Bolte *et al,* (2000) also reported on cyclic movement of sealants during cure in natural and artificial weathering. Liu and Wang (2006) used cyclic freeze-thaw cycles to test sealants used for horizontal joints in concrete. Al-Qadi *et al.* (1994, 1999) also evaluated sealants used for concrete slabs using cyclic shear and static horizontal deflection. Using the RILEM TC139-DBS test method, Miyauchi *et al.* (2004) conducted durability tests that included cyclic fatigue in combination with exposure to UV radiation in a xenon-arc weathering device. Sharman *et al.* (1983) evaluated sealants in outdoor exposure using a cyclic movement test apparatus. Koike *et al.* (1982) cycled sealants in laboratory tests at temperatures of 0-80° C and calculated modulus and loss tangent. Marechal and Kalifa (1996) used cyclic movement during artificial weathering to evaluate sealant performance under three different simulated climate conditions. Beech (1985) reviewed test methods for sealants. Wolf also (19961999) reviewed the correlation of long-term artificial aging and outdoor exposure of sealants. Wolf and Seneffe (2002) reported on work within IS0 TC 59/SC8 and RILEM TC139-DBS committees since 1990 that dealt with developing meaningful tests for sealants. In previous reported research, there was no attempt to correlate the dose of the degrading factors with a quantifiable change in the chemical or physical properties as the test proceeded. Evaluations were usually visual and were primarily concerned with cohesive or adhesive failure of the sealant.

In reviewing the work done in our laboratory and similar work reported by others who developed accelerated test methods, two problems became obvious. First, weather is not consistent from day to day, season-to-season, year-to-year, and century-to-century. (Martin 2001 a, b). Second, weather data have not been used in any meaningful way during outdoor exposure. That is, there has been no link between specific weather events and response of materials to these events. Our approach to these problems has been to develop instruments and evaluation methods that can be used in both accelerated laboratory tests and outdoor exposure tests. The materials response and the conditions in the laboratory test can then be compared with the weather data and its corresponding materials response obtained during that exact weather event. The Forest Products Laboratory field site, which is five km west of Madison, Wisconsin, has been fully instrumented to collect weather data during outdoor exposure (temperature, relative humidity, precipitation, UV radiation and wind velocity). Our earlier studies employed custom-built apparatus that used the movement of wood to fatigue specimens. We previously reported the materials response of seven different sealant compounds after two months (Williams *et al.* 2002) and after 18 months of weathering. (Williams *et al.* 2004 a, b) The data from outdoor tests is being merged with accelerated tests to develop reliability based protocols for service life prediction (White *et al.* 2002) and to characterize the physical and chemical changes in sealants as they weather. (Hunston *et al.* 2003 a, b, White *et al.* 2003) Test apparatus have also been developed for accelerated weathering of sealants under laboratory conditions. (White *et al.* 2004)

This report describes the analysis of data from sealant formulations exposed for two years in a cyclic fatigue apparatus that was capable of conducting controlled non-destructive tests periodically during the exposure. The methods used to evaluate the data are described and the difficulties encountered in analyzing the data are discussed. It is important to stress that our objective is to describe the analytical methods, not to report the actual performance of various sealants used in this work. We are attempting to determine the dose-damage relationship for sealants as they weather and undergo cyclic fatigue. If subtle changes in material properties, such as modulus, can be determined early in the exposure period, these changes could give early indications of subsequent failure of specimens. Early indications of changes in material properties can greatly decrease the time in test, give service-life prediction estimates from early data, and save time and money in bringing new products to market.

Experimental

Weather Station, Test Apparatus, and Data Acquisition

The weather station, test apparatus, and data acquisition system have been described in detail in previous publications (Williams *et al.* 2002, 2004, Lacher *et al.* 2004). We measured temperature wind velocity, relative humidity, rainfall, and UV irradiance at 18 different wavelengths in the range of 290 to 324 nm. Data were stored locally in a database as hourly averages. Sealant specimens were mounted on a computer-controlled test apparatus (CCTA) capable of holding up to 20 specimens **(Figure 1)**.

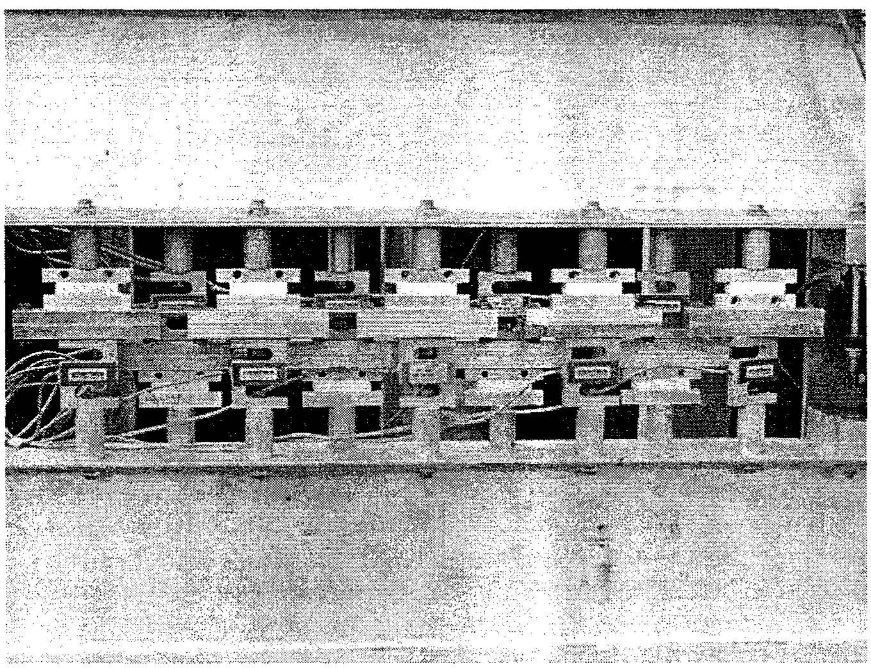

Figure 1. Nine sealant specimens and load cells mounted on the Computer-Controlled Test Apparatus.

Cyclic motion, caused by the natural cyclic dimensional change of a material or combination of materials, can be used to apply a cyclic fatigue to specimens. In our previous studies, cyclic fatigue was caused by the moisture-induced change in dimension of oak *(Quercus rubra)* blocks. In this study, the cyclic motion was obtained from thermally induced changes in dimension of an aluminum bar painted black **(Figure 2).**

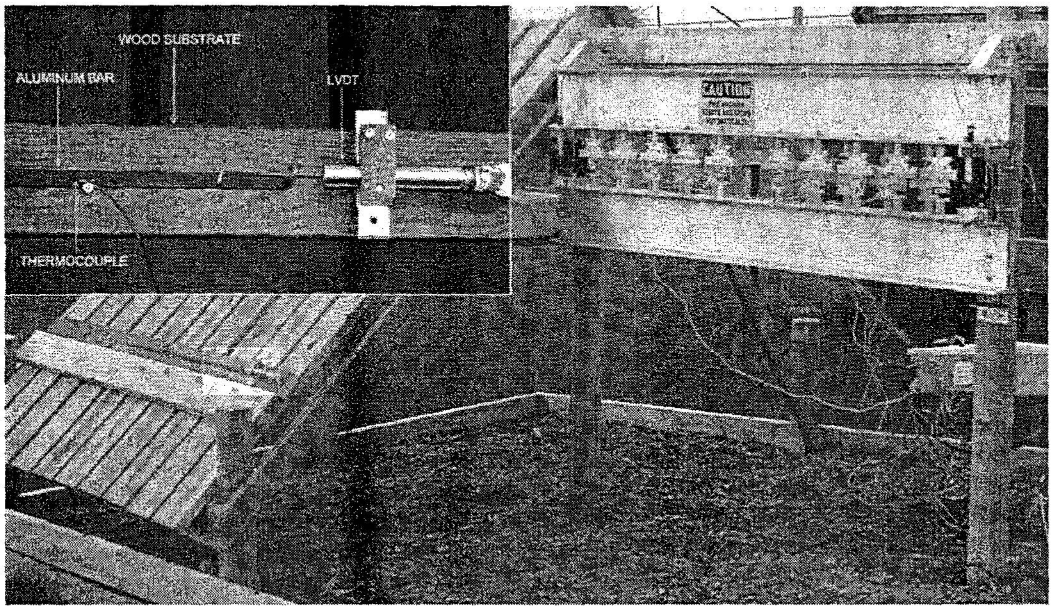

Figure 2. Computer-Controlled Test Apparatus (CCTA) with 18 sealant specimens and load cells mounted. Inset – Close up of aluminum bar and Linear Variable Differential Transformer that provides input to the CCTA.

As the bar changed length, the measurement was fed to a computer. The computer multiplied the measured dimensional changes to meet the target deflections on the specimens. Limits were placed on the maximum movement to ensure the strains did not exceed ± 25% **(Figure 3).**

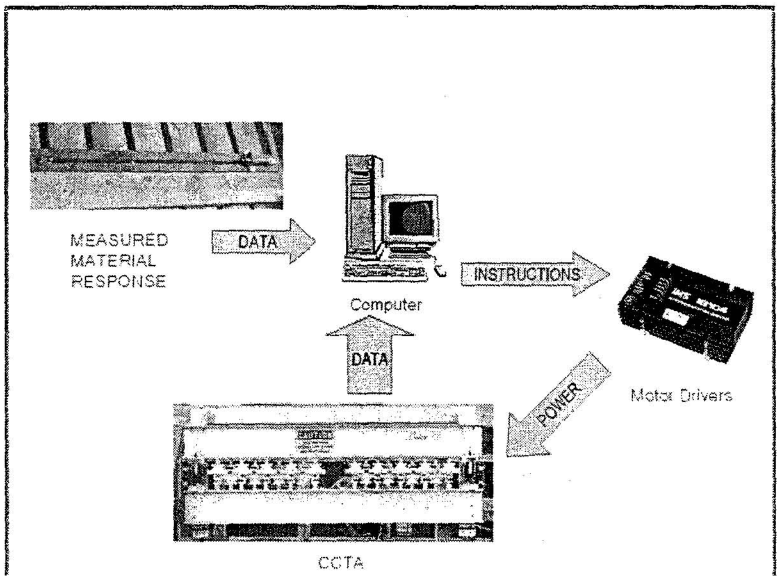

Figure 3. Control schematic for Computer-Controlled Test Apparatus.

The modified signal drove linear actuators (stepper motors with jack screws) on the apparatus to move one of the two parallel beams, thus applying a deflection to the specimens. A feedback loop to the computer ensured that the deflection on the specimen was correct. That is, if the linear actuator failed to apply the proper deflection, the feedback loop corrected this discrepancy. The load on each specimen was measured and the deflection was either measured directly or calculated from the measured movement of the apparatus **(Figure 4).**

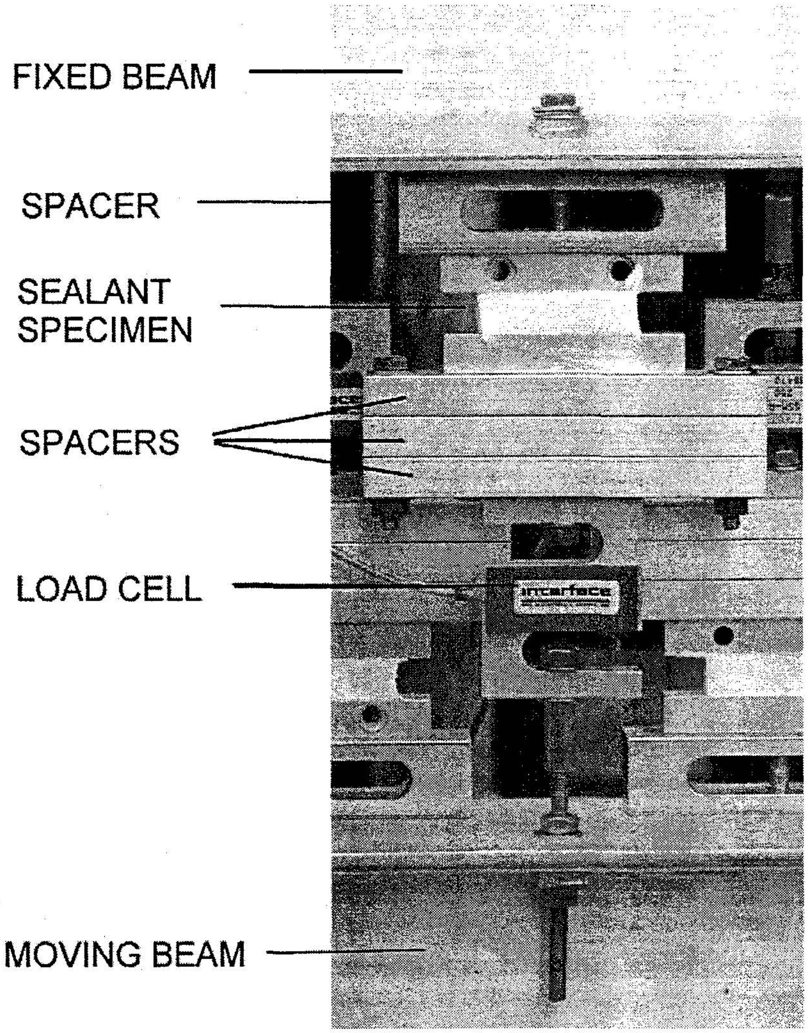

Figure 4. Detail showing sealant specimen, load cell, spacers, and the upper and lower beams of the test apparatus.

All specimens were subjected to a standard strain test every four hours during the exposure to determine temperature effects, strain history, and ensure specimen quality. The standard strain test is used to determine the elastic modulus of specimens by imposing a specific strain profile and measuring the resulting stress **(Figure 5).** Each standard strain test consisted of first bringing all specimens to 0 strain for 60 seconds, then imposing the strain profile consisting of a constant rate ramp up to 10% tensile strain, a 10 second hold, a constant rate ramp down to 10% compressive strain, a 10 second hold, and a constant rate ramp back to zero strain.

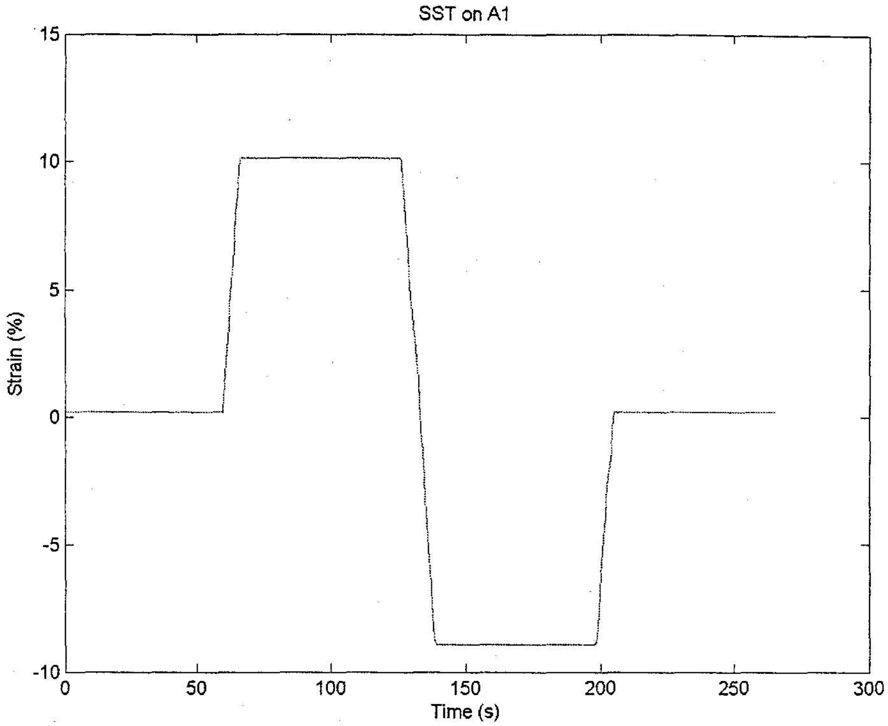

Figure 5. An example ofthe strain profile imposed on specimens during the Standard Strain Test.

Sealants

Two sealants, one low modulus and one high modulus, were selected from the seven different experimental sealants formulated for these studies. The formulations were designed to have a range of properties because the intent of this research is to establish a protocol for future work. The sealants were selected to give different load deflection characteristics and have short service lives. (Williams *et al.* 2002, 2004 a, b) For the study reported here, six specimens from the A-formulation and seven specimens from the B-formulation were evaluated periodically during two years of outdoor exposure using our standard strain test as described above. The specimens for the two formulations are labeled as A1—A6 and B1—B7.

Results and Discussion

When we began measuring dimensional changes and loads on specimens, we thought we could determine changes in “apparent modulus,” adhesive and cohesive failures, and the effect of temperature, strain, and strain rate by analyzing the vast amount of data that we obtained. The. best-fit linear slope of stress/strain plots calculated from the load/deflection data give an “apparent elastic modulus” (henceforth referred to as elastic modulus). It is an apparent modulus because we did not take into account the change in the cross-sectional area or the effect of cohesive or adhesive failure of the specimens as they degraded. Cohesive and adhesive failures were easy to observe, and this was reported earlier for previous studies **(Figure 6)** (Williams *et al.* 2002, 2004 a, b).

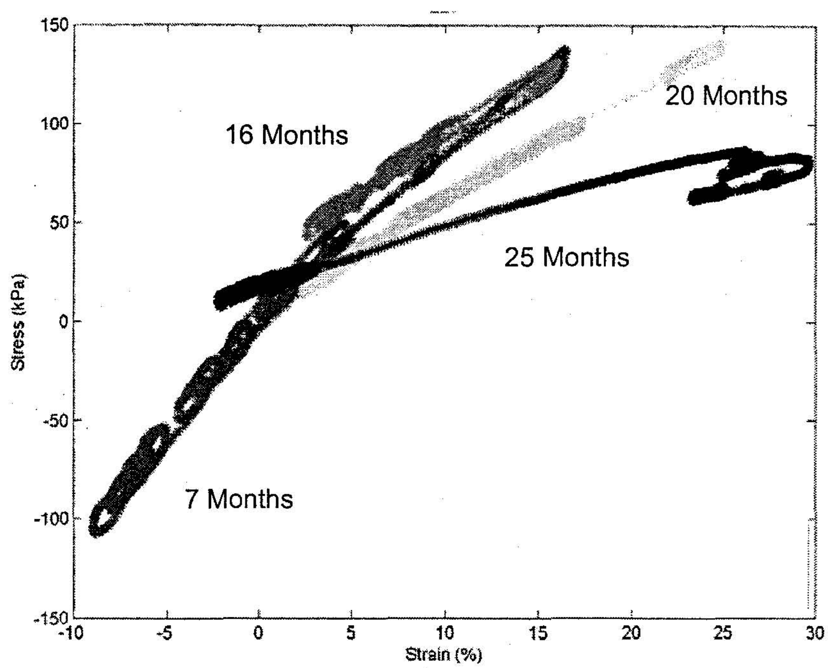

Figure 6. Plot of stress versus strain for sealant specimen showing decreasing apparent elastic modulus (Slopes of the curves on this plot) as specimen failed over a 25 month period. The observed failure was a combination of cohesive and adhesive failure that gradually decreased the effective cross-sectional area of the specimen that, in turn, decreased the force with which the specimen resisted deformation.

Determining modulus proved to be much more difficult. Determination of the modulus from wood driven data required selecting data on an equivalent basis of temperature, RH, and strain and calculating modulus from the relatively small number of data points that were taken under similar environmental conditions. Analysis of more than three years of data from previous work measuring load/deflection response to moisture-driven wood-actuated cyclic fatigue showed no two times when the temperature, strain, and strain rates on the specimens were the same. During three years, the weather never repeated itself so the specimens were never at the same condition more than one time in three years. Therefore, it was impossible to separate specimen degradation from the condition of the specimens as controlled by the weather at the time of the measurement. The data was too variable to detect modulus changes with adequate certainty. We were aware that the data scatter could result from the sealant's sensitivity to strain history. Selecting the data for similar environmental factors and strain history decreased some of the scatter in the data, but also decreased the number of data points available for analysis causing the uncertainty to be unacceptably high.

This shortcoming of the original uncontrolled cyclic fatigue experiments led to the development of the computer-controlled test apparatus (CCTA). The CCTA made it possible to conduct controlled measurements at the beginning of the exposure test to determine specimen quality and determine properties at various temperatures, strains, and strain rates as the specimens aged. Greater control of the experiment enabled us to discover material properties that were obscured in previous work. The powered apparatus is capable of temporarily suspending routine exposure testing and performing a precisely controlled stress/strain test (henceforth referred to as "standard strain test") to measure the elastic modulus.

To determine chemical changes (additional cross-linking or bond cleavage) in sealants during exposure, we are attempting to measure changes in the elastic modulus as they age. Changes in modulus are likely to be obscured by scatter in the measurement data; therefore, all other sources of experimental variability must be identified and accounted for. Possible sources of variability include, but are not limited to, temperature, water content, and strain history of the specimens as well as imposed strain rate, measurement errors, and electronic noise.

Although temperature, water content, and strain history of the specimens was controlled by environmental conditions and varied with the weather, the temperature and strain history were measured and recorded. Currently, there are no means of measuring water content, though it is believed to depend on the recent relative humidity and strain history. We minimized measurement and signal errors by selecting force transducers sensitive to ± 1.25 N (0.3 lb.), LVDTs sensitive to ± 0.2 mm (0.0007 in.), shielding all signal cables, and calibrating all instrumentation. We decreased experimental error by holding controllable factors such as short-term strain history and strain rate constant. The standard strain test always used the same strain rate. We measured all specimens prior to exposure to determine specimen-to-specimen variation.

The strain versus time profile of the standard strain test is shown in **Figure 5** and stress response versus time for nine B-formulation specimens measured at the beginning of the exposure is shown in **Figure 7.**

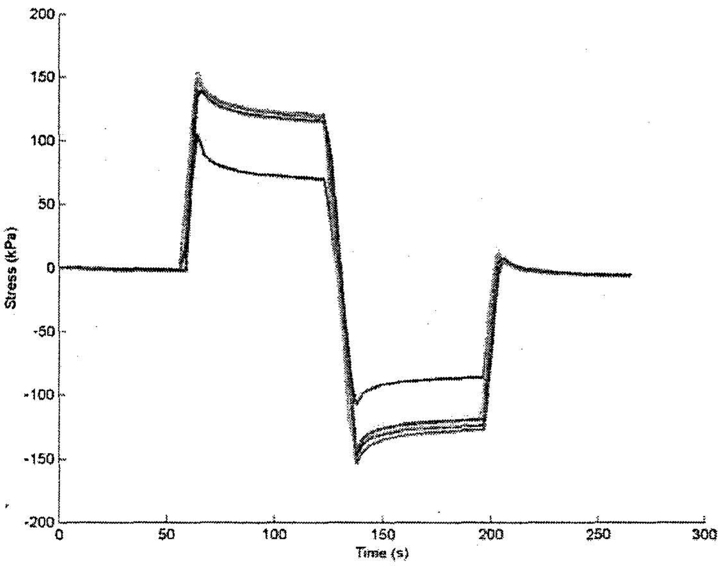

Figure 7. Stress response versus time of B-formulation specimens to the Standard Test strain profile. Test was performed at the beginning of outdoor exposure.

There is considerable overlap of the plots for eight of the specimens, but one is much different. Data from these two time series (stress versus time and strain versus time) were combined to create a stress versus strain plot for the specimens.

Figure 8 shows the plot for specimen B7. The slope of the stress versus strain plot gives the apparent elastic modulus. This plot shows a fairly constant slope during the initial tension phase of the standard test **(Figure 8).** A linear regression of this portion of the stress versus strain plot was used to compute apparent elastic modulus. Similar analyses were completed for all specimens and results for elastic modulus from these standard tests were less variable than the results obtained from previous studies using data obtained from long-term exposure tests where initial strain and strain rate were not controlled. (Williams *et al.* 2002, 2004, a, b) However, there was still too much scatter to give us much confidence in the elastic moduli that were being extracted from the data or to detect differences caused by weather factors, such as temperature and RH. Variation in measured load that occurred because of dissimilar strain histories prior to the standard tests could cause misleading measurements. This behavior (Mullins Effect) is well known to occur with viscoelastic materials such as sealants and was previously shown to occur with these sealants. (White and Hunston 2004). We investigated Mullins Effect on the standard strain test by conducting four standard tests (one right after the other). Large changes between the first and second test and small additional changes between the second and third tests were observed.

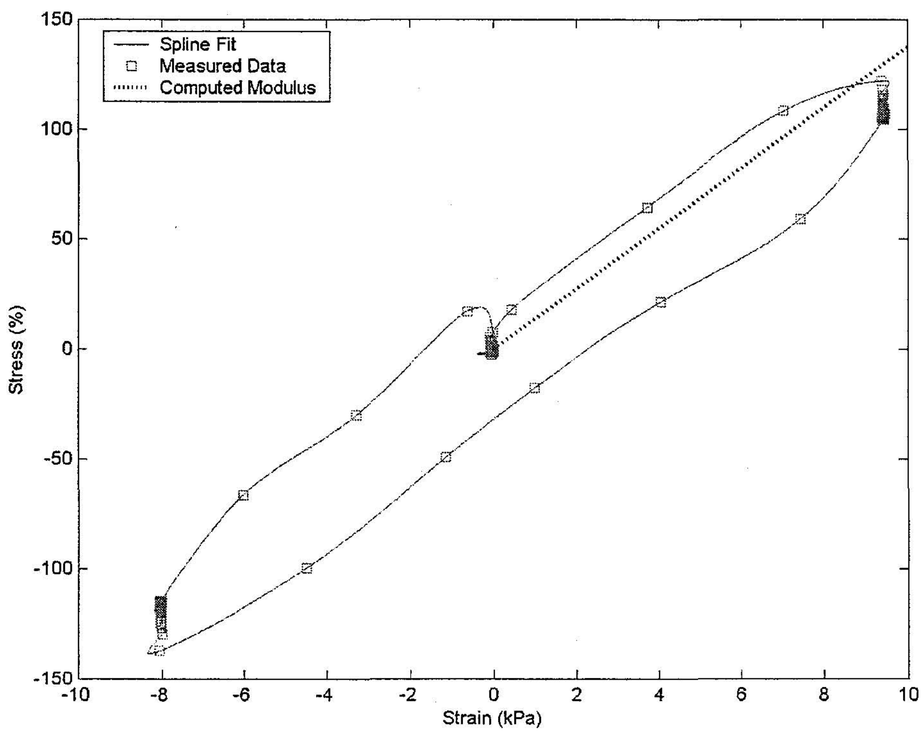

Figure 8. Stress versus strain for sealant specimen B7 for a Standard Test showing linear portion of the curve used in calculating the apparent elastic modulus. Dashed line is a computed best-fit estimate of the slope.

There was no change detected between the third and fourth lest. A plot of four successive standard tests is shown in **Figure 9.**

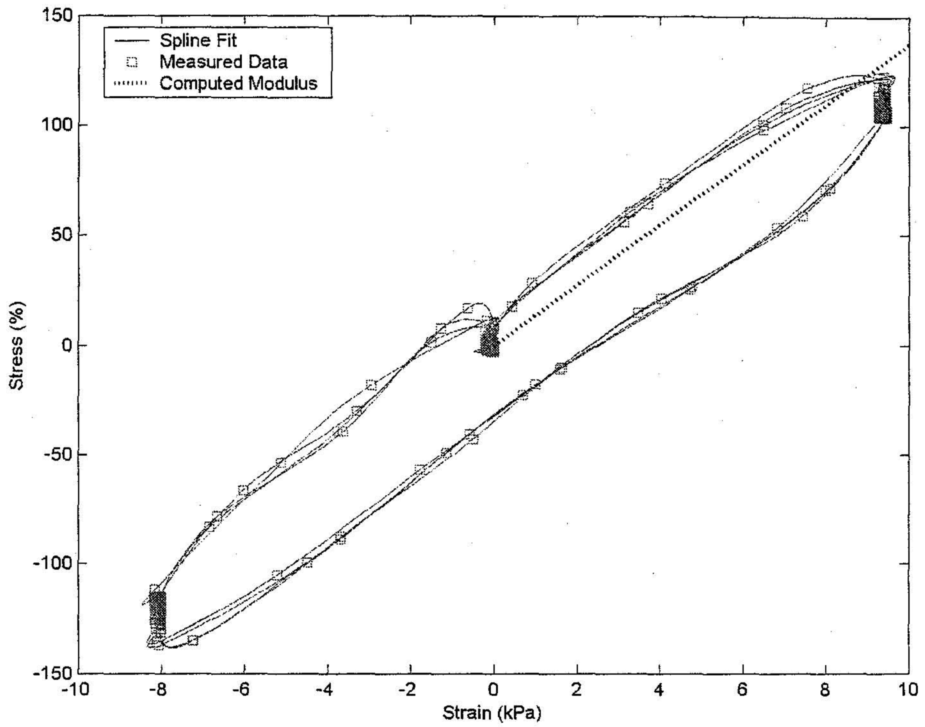

Figure 9. Stress versus strain for sealant specimen B7 showing four consecutive Standard Tests. The first curve shows a slightly higher maximum stress, while the next three curves are similar to each other. Dashed line is a computed best-fit estimate of the slope.

The moduli extracted from the linear portions of the plots were different for successive tests. Plots of the modulus of the second test versus the modulus of the first test (E_2 versus E_1) and third test versus second test (E_3 versus E_2) were used to show these differences **(Figure 10 a, b).** Comparison of the elastic modulus on the first and second cycles of the standard strain test show points scattered above and below the diagonal line **(Figure 10 a).** Points that fall on the diagonal line indicate exact replication. Points above the line indicate stiffening and below the line softening of the specimen between tests. The cluster of points to the lower left of the figure is the A-formulation and the cluster of points on the upper right is the B-formulation. Comparison of the elastic modulus of the second and third standard strain test shows a tighter grouping of points about the diagonal line **(Figure 10 b).** There also appears to be more points below the line, indicating softening of some specimens, which is what would be expected from the Mullins Effect (White and Hunston 2004). Histograms of this comparison show slightly decreased scatter in the data **(Figure 11 a, b).**

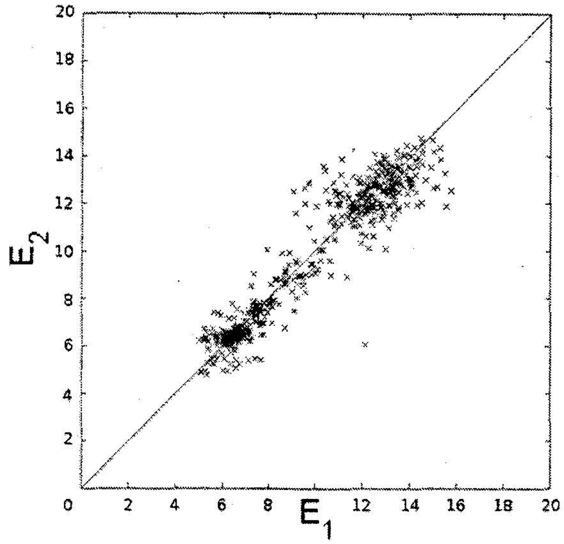

Figure 10a

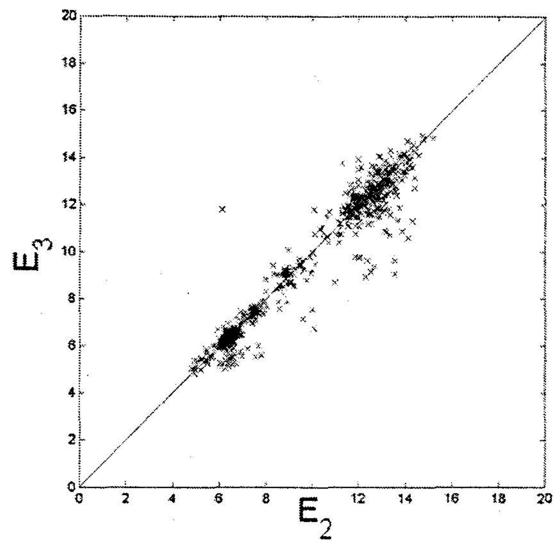

Figure 10b

Figure 10. Apparent elastic modulus calculated from (a) Second standard test versus first standard test. (b) Third standard test versus second standard test. Data points indicating perfect experimental replication lie along a line having slope equal 1. Plot b shows a tighter grouping than plot a (especially in the higher modulus B specimens), indicating better replication.

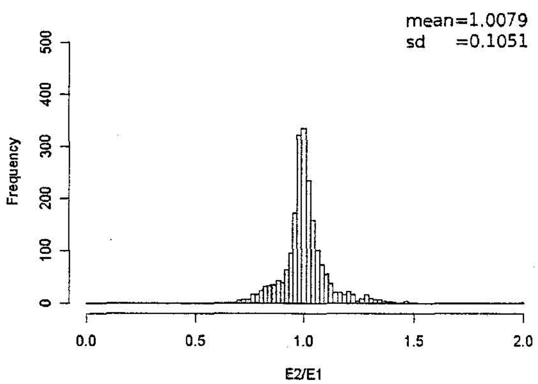

Figure 11a

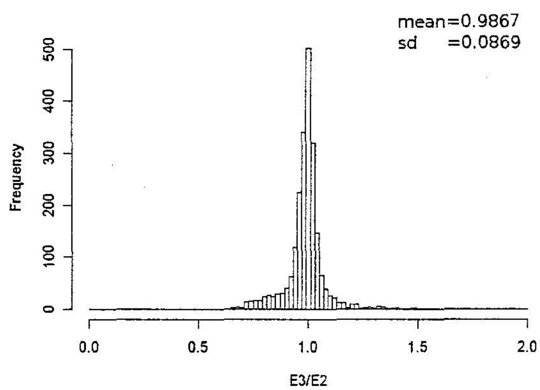

Figure 11b

Figure 11. Histograms of (a) E_2/E_1 and (b) E_3/E_2. A value of 1.0 indicates perfect experimental replication. As in Figure 10, the data indicates that tests 2 and 3 are better replicates than tests 1 and 2.

It became apparent as we developed test methods that took into account the Mullins Effect that there were considerable differences among the specimens within the same formulations. The standard strain test that was done shortly after the specimens were placed in the test showed distinct differences among the specimens. The plot of the B specimens **(Figure 7)** clearly shows that one of the specimens is different. We have no explanation for this, but it indicates that we may have considerable specimen-to-specimen variability. This high variability in the specimens may make it difficult to average the data for each formulation to calculate a material property such as modulus. To determine if specimens were statistically distinct, we performed an analysis of variance (ANOVA), and plotted confidence intervals for all pairwise differences between specimens.

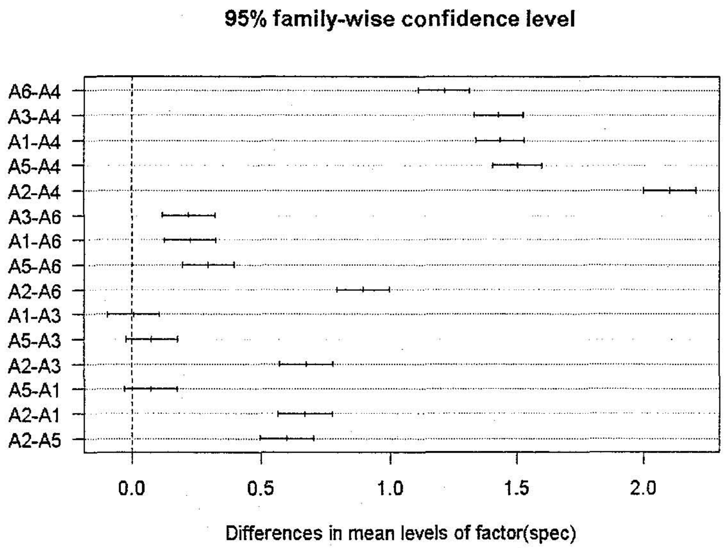

Figure 12a

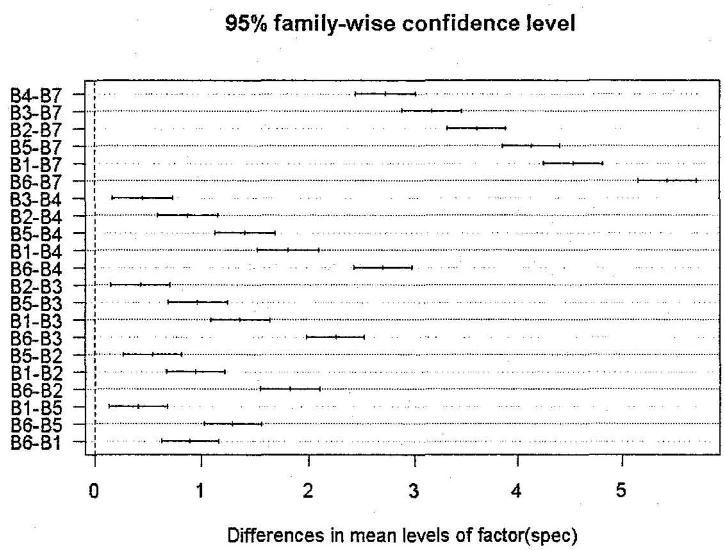

Figure 12b

Figure 12. Results of multiple comparison test used to determine whether individual specimens are statistically different from each other. Horizontal bars indicate 95% confidence intervals of the difference between pairs of specimens. A difference of zero (Dashed line) indicates 95% confidence that two specimens have the same apparent elastic modulus. (a) depicts A-formulation specimens. (b) depicts B-formulation specimens.

The A specimen contrasts are in **(Figure 12a),** and the B specimen contrasts are in **(Figure 12b).** The horizontal lines show a 95% confidence interval for the difference between a pair of specimens. If that line crosses the dotted vertical line toward the left of the plot (difference = 0), then those specimens are not significantly different. The 95% confidence limits were computed taking into account the number of comparisons performed, so the 95% refers to a family-wise error rate, not a test-wise error rate. Among the A-formulation specimens, A1, A3, and A5 are not distinct. All other A specimens are distinct. Among formulation B, all specimens are distinct. Box and whisker plots show the variability in the data for the A and B specimens **(Figure 13 a, b).** Outliers are marked with a circle (determination of outliers was done automatically by the R statistical software). The whiskers extend the full range of the non-outlier data. The box extends from the 25th to the 75th percentile of the non-outlier data. The thick line indicates the mean. Because nearly all specimens were distinct, they were analyzed separately.

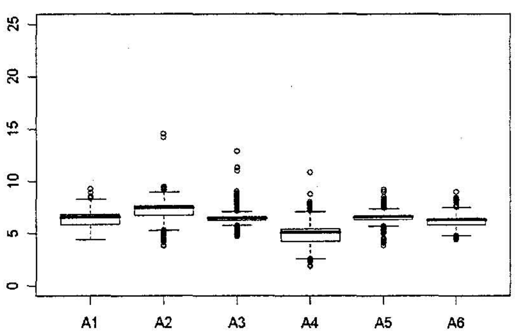

Figure 13a

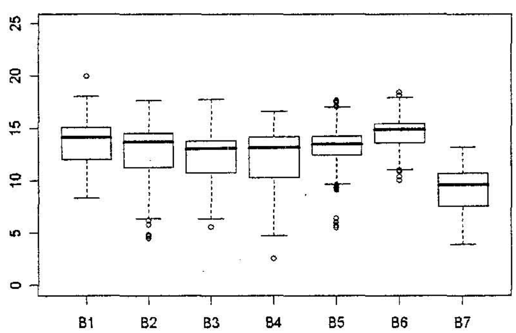

Figure 13b

Figure 13. Box and whisker plots of apparent elastic modulus for all data. (a) A-formulation specimens and (b) B-formulation specimens. The heavy horizontal lines indicate average modulus, the rectangular boxes enclose values falling between the 25th and 75th percentiles and the whiskers indicate the range of the data excluding outliers. Outliers are depicted as circles.

We performed a straightforward analysis involving binning the data such that within each bin, temperature and relative humidity would be similar. We have previously found that temperature and relative humidity do have significant effects on the apparent modulus. **Table 1** shows the number of data points remaining in each bin for specimen B7. All other specimens exhibit similar behavior. Although the data are really quite sparse for some of the bins over the full range of temperature and RH, some of the bins contain enough data to begin our analyses. Determining the modulus for the data in the fullest bin (5 ± 1.25° C, 100% RH) for specimen B7, there is no apparent change **(Figure 14).**

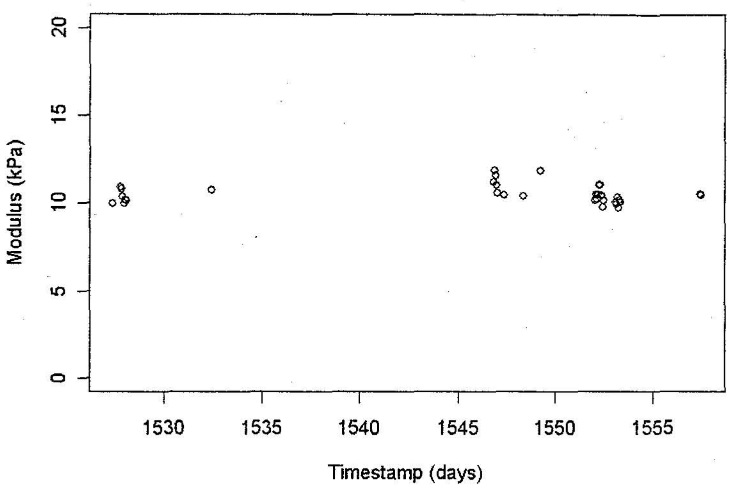

Figure 14. Modulus versus time for specimen B7 selected for 5±1.25° C and 97.5–100% RH. (Note: The 0 on the time axis is the date we brought our weather station on line about 5 years ago.)

The data are clustered closely at about 11 kPa **(Figure 15).** As the time period is only 35 days, there is no trend with time. (Note: The 0 on the time axis is the date we brought our weather station on line about 5 years ago.) Statistical analysis of the data in the plot showed no significant change for a regression of modulus in this bin against time (*p*-value of 0.906, *p*-values less than 0.05 are significant). Our analysis of sample sizes (shown in bold type in **Table 1**) for other bins and other specimens showed the same lack of significant change.

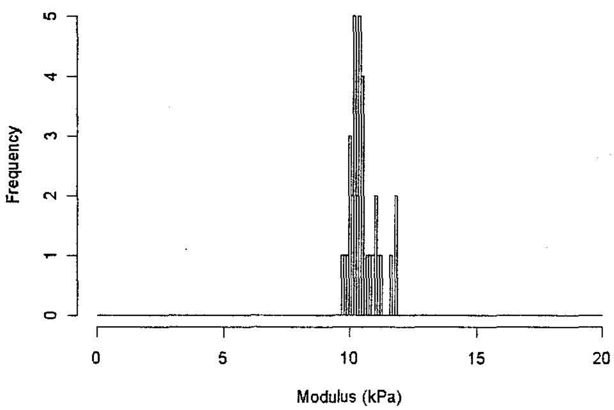

Figure 15. Histogram of modulus for specimen B7 selected for 5±1.25° C and 97.5–100% RH.

Table 1. Number of standard tests binned by environmental factors (Specimen B7). Entries with 10 or more data points are displayed in bold.

		RH (%)														
		30	35	40	45	50	55	60	65	70	75	80	85	90	95	100
Temperature (°C)	-7.5								1		5	5	1	4	1	5
	-5								2	2	4	6	3	8	5	**11**
	-2.5							1	1	3	3	7	9	9	15	8
	0						1	5	5	1	12	11	9	7	16	23
	2.5					1	3	5	1	3	9	4	5	3	4	8
	5					2	6	2	4	9	5	5	9	5	16	35
	7.5					1					1					2
	10		2	3	3	10	9	6	2	5	2	2	8	2		8
	12.5					1			1	1	2			2		
	15			1	2	2	1	4	4	2	1	2		2	1	9
	17.5		1		2	2		4	1	1	3	5	3	2	4	6
	20			1	1			2			1	1	2	2	5	1
	22.5			1	1		1	1		1	2	4	3	3	1	5
	25		1		3	1	4		1	2	4	6	1		1	1
	27.5				2	1	2	2		1	1		2			
	30				1		1	2	3	1	1					
	32.5					1										

The results of this analysis show that our specimens did not change, but we still lack insight into how the specimens react to the weather. As we proceed with this experiment, we will require some understanding of how these materials respond to environmental conditions so that we can separate true degradation of the specimens from environmental responses. Additionally, if we can understand the environmental response of the material before they degrade, we will be able to develop models that can be used to normalize specimen behavior at any temperature/RH to a standard set of conditions. These models will allow us to “factor out” environmental variations and truly observe materials changes in our specimens. Without a model, we are at the mercy of the weather in terms of our ability to observe changes.

Since we have no theory to guide us (at least, not one which spans the range of conditions that the sealants experience during outdoor exposure), the models will need to be pure empirical models (Chambers 1992). The simplest such model to characterize these materials uses a linear combination of independent environmental factors. We recognize that there are interactions among the factors, particularly temperature and RH; however, this model gives a starting point. Future work will need to be directed toward developing an understanding of the non-linear response of these materials to environmental factors, rather than relying on (potentially misleading) assumptions of linearity and independence.

Multiple Linear Regression using ordinary least squares was employed to fit the following model to the data: (Wilkinson and Rogers 1973)

$$sqrt(mod) = b_0 + b_1 \times Cold + temp\_k \times (b_2 + b_3 \times Cold) + RH \times (b_4 + b_5 \times Cold) + N(0,MSE)$$

where

- sqrt (mod) is the square root of the modulus
- bi's represent the regression coefficients
- N (0, MSE) denotes normally distributed error with a constant variance over the range of the data
- Cold is a {0,1} variable, which will be 1 when the ambient air temperature is less than 0°C
- temp_k denotes the ambient temperature measured on the Kelvin scale
- RH denotes the relative humidity.

The model was formulated in terms of sqrt(mod) rather than simply modulus to satisfy the assumptions of the linear model. In particular, using sqrt(mod) rather than modulus stabilizes the variance across a wide range of temperatures. The terms for above and below 0°C are included because we have observed a change in modulus at 0°C for many of the sealants being evaluated in this work. This is discussed below.

This model stipulates that the shape of the response surface for these materials, in terms of relative humidity and temperature is a pair of planes, one above freezing and one below freezing. Stepwise selection was used to reduce these models by removing statistically non-significant terms. Results of this process are summarized for each specimen **(Table 2).** The R^2 values indicate the percentage of the variation in the data that the model explains. The *p*-values indicate how well the model explains that variation (0.05 or lower indicate statistically significant explanatory power). The b_0 and b_1 terms are intercepts at 0° K. They are required for building the model, but have no physical meaning independent of the model. The b_2 term indicates the change in modulus for a 1°K change in temperature when the temperature is above freezing. The sum of b_2 and b_3 indicates the change in modulus for a 1°K change in temperature when the ambient temperature is below freezing. The b_3 term can then be interpreted as the additional effect of temperature below freezing. The b_4 term indicates the change in modulus for a 1% change in RH when the ambient temperature is above freezing. The sum of b_4 and b_5 indicate the change in modulus for a 1% RH change when the ambient temperature is below freezing. The b_5 term is the additional effect of RH below freezing.

Table 2. Estimated model parameters produced by multiple regression

	b0	b 1 (cold)	b2 (temp)	b3 (cold × temp)	b4 (RH)	b5 (cold × RH)	R^2	P
A 1	2.821	–2.568e-02	–8.546e-04				0.02	<0.0001
A2	3.051	-8.574e-01	–8.880e-04	3.019e-03	–5.943e-04		0.16	<0.0001
A3	2.569	–1.882e-02			–2.581e-04		0.13	<0.0001
A4	–0.571	3.419	1.095e-02	-1.245e-02			0.47	<0.0001
A5	2.528	–1.627e-02			–1.914e-04		0.07	<0.0001
A6	3.001	–2.346e-02	–1.610e-03		–3.412e-04		0.10	<0.0001
B1	7.413	3.174	–1.244e-02	–1.168e-02	–1.058e-03		0.74	<0.0001
B2	7.999	3.118	–1.452e-02	–1.223e-02	–1.935e-03	2.249e-03	0.77	<0.0001
B3	7.470	2.626	–1.317e-02	–1.022e-02	–1.380e-03	1.679e-03	0.69	<0.0001
B4	9.365	-0.222	–1.945e-02		–2.439e-03	2.068e-03	0.75	<0.0001
B5	7.531	2.968	–1.339e-02	–1.089e-02	–1.002e-03		0.77	<0.0001
B6	7.526	4.258	–1.275e-02	–1.618e-02	–1.581e-03	1.792e-03	0.70	<0.0001
B7	7.153	2.887	–1.365e-02	–1.102e-02	–1.209e-03	1.273e-03	0.72	<0.0001

Interpretation of these coefficients **(Table 2)** is straightforward and, by using them, a modulus can be calculated for any specimen. Above freezing, the 'base transformed modulus' is b0 = 7.153 sqrt(kPa), it changes b1 = –1.365e-02sqrt(kPa)/(degK) with temperature, and changes –1.209e-03 sqrt(kPa)/(%RH) with humidity. Below freezing, the 'base transformed modulus' is b0+b1 = 7.153+2.887 = 10.04 sqrt(kPa), it changes by (b2+b3) = (–1.365e-02–1.102e-02)= (–2.467e-02)sqrt(kPa)/degK with temperature, and it changes by (b4+b5) = (–1.209e-03 -1.273e-03) = (-2.482e-03) sqrt(kPa)/(% RH) with humidity. Add the effects of temperature and RH to the base transformed modulus to obtain the transformed modulus. Square the transformed modulus to obtain the predicted modulus. **Table 3** shows this calculation of modulus for B7 at 278°K (5°C) and 100% RH. The computed value is 10.48 kPa, which agrees very well with the measured 10.50 kPa.

Table 3. Example calculation of modulus using the model from Table 2 on specimen B7

Coefficients		Terms		Results	
b0	7.153				7.153
b1	2.887	cold	0	b1 × cold	0.000
b2	–1.365e-02	temp	278	b2 × temp	–3.795
b3	–1.102e-02	Cold × temp	0	b3 × (cold × temp)	0.000
b4	–1.209e-03	RH	100	b4 × RH	–0.121
b5	1.273e-03	cold*RH	0	b4 × (cold*RH)	0.000
				sqrt(mod)	3.237
				Modulus (kPa)	**10.48**
				Measured Modulus was	10.50 kPa

To verify that these models were functioning correctly, we checked the model predictions against the mean modulus computed within a number of bins. The results are in **(Table 4).** There is a good correspondence between predicted modulus and measured values. Similar correspondence results were obtained for other specimens at various temperatures and RHs.

Table 4. Comparison of calculated (model output) and measured moduli in selected bins for specimen B7 and specimen A6

Specimen	n	Temp (°C)	RH(%)	Calculated Modulus (kPa)	Measured Modulus (kPa)
B7	16	0	95	10.94	10.86
B7	23	0	100	10.94	11.21
B7	16	5	95	10.51	10.54
B7	15	–2.5	95	11.35	11.06
B7	9	10	55	10.38	10.13
A6	16	0	95	6.277	6.287
A6	23	0	100	6.268	6.339
A6	16	5	95	6.354	6.404
A6	15	–2.5	95	6.397	6.268
A6	10	10	55	6.383	6.364

All of these models had significant *p*-values, indicating that the correlation between our data and the model did not arise simply by chance **(Table 2).** The A specimens are not well characterized (R^2 values range between 0.02 and 0.47). Among the B specimens, R^2-values range from 0.69 to 0.77. These R^2-values indicate that the B specimens are much better characterized by these models. The As appear to be much less sensitive to environmental factors than the Bs.

This modeling effort is meant only as a first pass. We are certain that the true behavior of these materials is non-linear. We are also certain that there are very important non-linear interactions between environmental factors. Future effort will focus on improving the accuracy and increasing the complexity of our models. However, it is interesting to note that the simple model could predict as much as 77% of the behavior of the B specimens. Most of the specimens responded to RH, but not all. Many specimens showed a distinct difference in modulus above and below 0°C. **Figure 16** shows this change in modulus for the B6 specimen. There appears to be a significant interaction between below-freezing temperatures and relative humidity (**Table 2, column b5**).

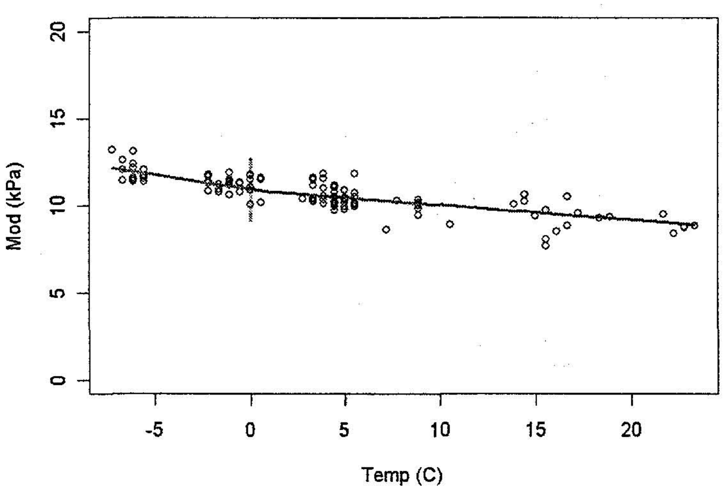

Figure 16. Modulus vs temperature for specimen B7 selected for 97.5-100%RH. With lines showing predicted values above and below freezing. Note that the best-fit slope is not identical above/below 0°C.

The ability to conduct precise standard tests allowed us to identify experimental anomalies and take steps to correct them or to eliminate the data from the data set. Changes in elastic modulus caused by weathering have not yet been detected, but are expected to show up as the specimens continue to age, more standard strain tests are run, improvements are made with our data analysis methods, and more sophisticated models are developed.

Though improvements have been made in our data analysis, further improvement may be possible by increasing the speed of measurement. The current system has a maximum measurement rate of 5.3 measurements/specimen/second for 18 specimens in the apparatus. We plan to install a new faster data acquisition and control system. This system has an accurate electronic pulse generator that will improve the timing of step commands to the motors. This will increase the linearity of the standard test strain ramp-up and improve reproducibility of the tests. The new system will be capable of measuring load and displacement hundreds of times per second. Faster measurement means more data points can be taken during the standard strain test and used for calculating modulus. Together, the fast accurate pulse generator and the high data acquisition rate will allow modification of the standard test to incorporate a higher rate of strain ramp-up. Faster strain application decreases the amount of relaxation during a test resulting in less viscous and more elastic response of the elastomeric specimens. These improvements are expected to decrease variability of the calculated modulus enabling detection of smaller material changes caused by environmental conditions and weathering.

We have shown that data collected from the CCTA could be used to develop models for helping us understand the effects of temperature, RH, and cyclic fatigue on the material properties of sealants and to help us understand the complex changes that occur as they degrade. It was difficult to separate the condition of specimens caused by environmental conditions from actual degradation. Subtle changes were often difficult to measure because of variability of specimens, strain history, and experimental error in collecting data. Statistical analyses were critical for helping to separate these factors. Statistical analyses were of practical value for determining specimen-to-specimen variation prior to beginning the exposure, showing the distribution of properties, and the determining the temperature dependence of the modulus.

The inspiring result from this work is our ability to begin to explain some of the variability that is observed in materials measurement. As we evaluated the data, it was obvious that there were intrinsic problems with the data collection. We also were able to identify an anomaly in the temperature profile. It appears that the small amount of water absorbed into these materials has an effect on the modulus. This would not have been obvious with visual inspection. Binning the data by temperature and RH enabled us to obtained fairly symmetrical narrow distributions of modulus at various temperature and RH. As we collect more data at various temperatures and RHs, it should be possible to refine the model to account for interactions between temperature and RH.

Conclusions

We have demonstrated that the response of sealants and the weather causing the response can be monitored continuously. For the outdoor exposure of the sealants used in this work, weather-induced cyclic fatigue of specimens and the measurement of load and deflection during this cyclic movement were deemed to be critical aspects of the experiment. The data can be analyzed to determine the elastic modulus of the material, however a controlled test (standard strain test) gave much better results. The standard strain test made it possible to show differences in specimens, which meant that it was not prudent to treat specimens as replicates and average the data. The data were used to construct a model to evaluate the effect of temperature and relative humidity on the elastic modulus. As one would expect from these viscoelastic sealant materials, the elastic modulus was dependent on temperature, RH, and strain history, but thus far, we were still unable to detect changes in modulus caused by weathering. A plot of elastic modulus versus temperature showed a change in modulus at 0°C indicating a change in the plasticizing effect of moisture above and below freezing. The development of the computer-controlled apparatus made it possible to gather sufficient data from controlled experiments to construct a series of simple linear models to explain the data.

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