

Kinetics Based Models to Describe Environmental Degradation of Polymeric Sealants

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Introduction

Sealants represent an essential component of modern construction where they prevent unwanted moisture intrusion and subsequent water damage. Although current materials are good, studies have shown that a large percentage will fail within 20 years after installation [1-3]. Consequently, better techniques are needed to estimate/predict lifetimes to ensure timely repair and facilitate the development of improved materials. In this connection, the National Institute of Standards and Technology (NIST) established a government-industry consortium program involving most of the major sealant companies. The goal is to develop the ability to understand and model the degradation behavior of sealant materials. As part of this effort, a wide variety of different sealant chemistries and formulations were exposed to weathering both outdoors and indoors. Any changes in the sealant's properties induced by the exposure were monitored by measuring the stress relaxation modulus using a procedure developed in this program and adopted as ASTM C1735 [4,5].

To date, 18 different sealants have been examined in the program and significant degradation in modulus was observed for 9 of the materials. The most surprising result is that for 8 of the 9 sealants, the exposure produces a downward shift in the stress relaxation curve with relatively little change in shape. In simple elastomers, the rubbery modulus is proportional to the cross-link density in the network structure [6]. Sealants, however, have a complex network structure involving chemical cross-links, entanglements, attachments to various fillers, etc. Consequently, the modulus depends on what might be called an effective density of cross-links and junction points. The exposure induced decrease in modulus, therefore, would be related to a reduction in the effective cross-link density. Eventually, the exposure produces cracks in the sealant which progress to failure but the focus here is on the early phase of the degradation process where damage is at the molecular level.

Theory

As a first simple approach to modelling the behavior, the modulus, E , is assumed to be proportional to the average density of "effective" cross-links and junction

points, α

$$E = C \alpha \quad (1)$$

where C is a proportionality constant. Four different kinetic models were formulated to describe the rate of change of α during exposure. For the particular set of data that will be examined here, however, the best fit was obtained using a first order equation with the added stipulation that not all effective cross-link and junction points were susceptible to degradation. This situation could result from the variety of different cross-link types that are present or, when the degradation is driven by UV radiation, a limited penetration depth. To develop this model, the density of cross-link and junction points is first divided into that part which can be degraded, α , and that part which does not degrade, α_∞ . As a result, eq. (1) is modified by replacing α with $(\alpha + \alpha_\infty)$. The first order rate equation is

$$d\alpha / dt = -k\alpha \quad (2)$$

where k is the rate constant which may depend on temperature, humidity, strain history, and UV exposure. Integrating eq. (2), substituting into the modified version of eq. (1), and rearranging gives

$$E = (E_o - E_\infty)e^{-kt} + E_\infty \quad (3)$$

where E_o is the initial modulus and E_∞ is the limiting value of modulus when all degradation is complete. To facilitate comparisons, the expression can be normalized with the initial value of the modulus: $R = E/E_o$ (similarly for R_o and R_∞ , where $R_o = 1$)

$$R = (R_o - R_\infty)e^{-kt} + R_\infty \quad (4)$$

The analysis above assumes that the exposure conditions are constant, but in an actual application, the conditions are constantly changing. One approach to dealing with this is to divide the exposure into many small steps where the conditions are constant within each step but change between steps. It is then assumed that, if the steps are chosen correctly, the degradation produced in the step process will be approximately the same for that generated by the continuously changing environment. One factor which may help with this assumption is that the exposure conditions in outdoor aging change relatively slowly.

As a first attempt to test this idea, consider an experiment in the NIST SPHERE where the sample is first exposed for a given period of time using one set of envi-

ronmental conditions and then exposed for an additional time period at a different set of conditions. For the model proposed above, the modulus ratio during the first exposure period should follow eq. (4) with parameters corresponding to the initial conditions: $R_{1\infty}$, and k_1 . If the degradation is assumed to be cumulative and eq. (4) is still followed, some algebra shows that during the second exposure period, R will follow this relationship

$$R = (R_1 - R_{2\infty})e^{-k_2(t-t_1)} + R_{2\infty} \quad (5)$$

where R_1 and t_1 are the values of R and t at the end of exposure period 1 while $R_{2\infty}$, and k_2 are the best fit parameters for the second exposure conditions. Moreover, this iterative procedure can be generalized to predict behavior when more than two step exposures are involved.

Experimental[†]

Of the 8 materials that exhibited degradation in the tests to date, the sealant with the most data is based on Kraton-D, a commercial styrene-butadiene-styrene triblock polymer. This material was selected for inclusion in this program because it displays the properties of a sealant, but contains double bonds that are sensitive to UV radiation. As a result, it shows environmental degradation in a relatively short time period which facilitates generating data more quickly. Consequently, results for these tests will be utilized to examine the model proposed above. Specimens were exposed to a controlled environment in the NIST SPHERE (Simulated Photodegradation via High Energy Radiant Exposure). This device is a specially constructed exposure chamber that allows complete control of environment: temperature, humidity, UV radiation, and mechanical strains. Details of the device are given elsewhere [7,8]. For the tests here the relative humidity was held constant at 50 %, and the UV irradiance was 50 W/m². During exposure, the sample is subjected to deformation via a triangle wave going from 0 % strain to a fixed maximum strain and then back to 0 % strain with a period of 28 minutes. The strain cycle is based on the fact that in applications the sealant is generally subjected to strains resulting from expansion and contraction of the structure resulting from temperature variations between day and night. The 28-minute period should be slow enough to minimize any frequency effects. The uncertainties in the experiments were ± 0.5 °C for temperature, ± 2 % for relative humidity, ± 1 % for the strain, and ± 5 W/m² for UV irradiance.

[†] Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology nor does it imply necessarily that the items are the best available for the purpose.

Specimens were characterized before, during, and after exposure by generating stress relaxation curves using ASTM C1735 with a pretreatment strain of 25 % followed by a test strain of 15 %. For the characterizations during exposure, the test was stopped, the sample cooled to room temperature, the characterization performed, and then the exposure test was continued. For each characterization, the results from four specimens were averaged and error bars representing 1 standard deviation were calculated. Figure 1 shows some typical curves for fresh and exposed specimens. The curves are parallel, and the plateau moduli for the analysis were taken by arbitrarily selecting the values at 100 s.

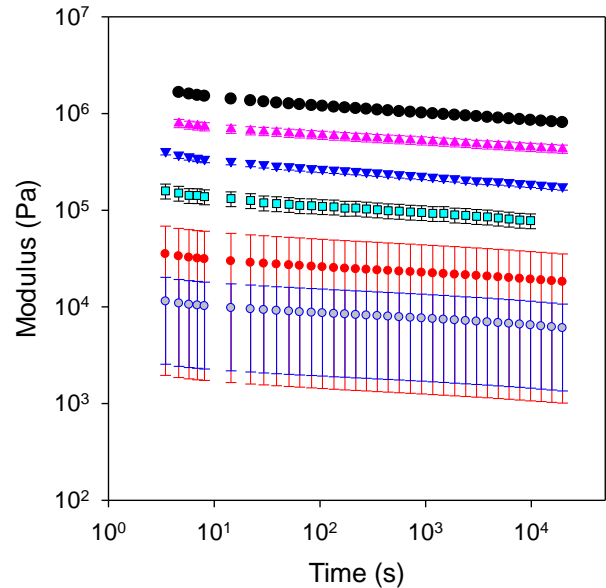


Figure 1: Stress relaxation curves for fresh samples (black) and specimens aged at 51 °C with 21 % maximum strain, for 2 d (pink), 4 d (blue), 8 d (green/black), 20 d (red), and 40 d (gray/blue). Points are average of 4 tests with error bars for 1 standard deviation.

Results and Conclusions

For the initial analysis of the exposure tests, sufficient data were available at 5 conditions: maximum strain of 21 % at temperatures of 31 °C, 41 °C, and 51 °C, and maximum strain of 11 % at 31 °C and 41 °C. Figure 2 shows a plot of the normalized modulus ratio vs exposure time as well as the predictions based on best fits with eq. (4). Again, each point represents the average of four tests with error bars of 1 standard deviation. It is clear that the model captures the trends in the data very well. Tests are now underway using 2 step exposure experiments where two different environments are combined in sequence. Initial results look promising.

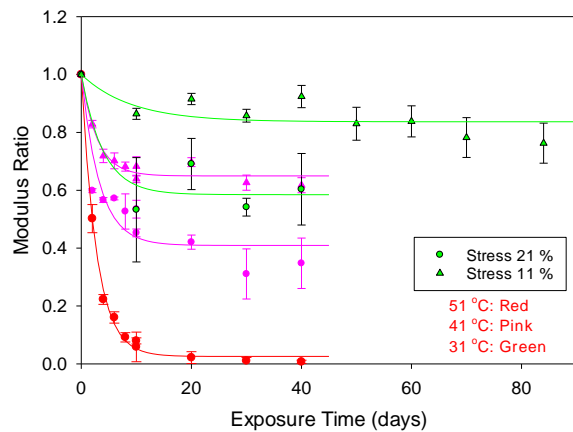


Figure 2: Values for modulus ratio at 100 s for specimens exposed at indicated conditions as a function of exposure time. Points are an average of 4 specimens with error bars of 1 standard deviation. Solid curves are best fit results using eq. (4).

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