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State-of-the-Art Methods for Testing Materials

Outdoors

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Abstract

In recent years, computers, sensors, microelectronics, and communication technologies have made it possible to automate the way materials are tested in the field. It is now possible to purchase monitoring equipment to measure weather and materials properties. The measurement of materials response often requires innovative approaches and added expense, but the instrumentation vastly improves the quantity and quality of the data that can be obtained. Data on weather and materials can be linked to a computer system, either at the field site or through a communications link back to the laboratory. Collecting materials response and weather data every few minutes during exposure gives a complete history of specimens during the exposure. As a specimen degrades, the degradation can be linked to the conditions causing the degradation. The ways in which field tests are automated are probably limited more by tradition and lack of imagination than by technology to do the measurements.

Introduction

Lengthy outdoor tests of materials, components, and products have been conducted for many reasons: to increase consumer confidence, maintain company image, get a larger market share, and avoid litigation, for example. People in many organizations invest considerable resources in testing. But testing is expensive, whether in the form of an accelerated laboratory test or an outdoor exposure test. Are we getting the return on the testing investment that we should? I believe that we are not. In this paper, I will explore methods for increasing the return on our testing investment, focusing primarily on outdoor testing of materials.

Until recently, outdoor testing involved placing specimens on test fences and periodically evaluating changes. For paints and other finishes, degradation was usually estimated from visual ratings of erosion (ASTM D 662), cracking (ASTM D 661), peeling (ASTM D 772), mold growth (ASTM D 3274), and general appearance (ASTM 2001). Panels could remain on the fence for these evaluations, but the analysis of gloss, color, and chemical changes had to be conducted in the laboratory. All of these evaluations were done manually, and, if the measurements were entered into a database, this too was done manually. Equipment is now available to automate much of this data collection. As tests for materials are automated, we need to design experiments that give us information on the underlying principles causing the degradation. We need to show that

- the data collected is relevant to the service life in actual use,
- outdoor test results correlate with accelerated tests,
- accelerated tests can predict service life, and
- the test can detect juvenile failures.

What we really want to know is, How long will the material or product last? But how long it will last (its service life) depends on exposure conditions. Accelerated tests have predicted that data on a compact disc (CD) should last 400 years if the CD is kept in a cool dark place. If it is placed on a car dashboard on a hot sunny day, the data will be destroyed within a few minutes. Automotive finishes last well beyond 10 years under “normal conditions,” but can be completely eroded by driving through a sandstorm. House paint should last 20 years, but often fails prematurely because of moisture intrusion. We need to design tests that stress materials in ways typical of normal in-service stress and determine the mechanism for the observed physical and chemical changes.

What are “normal” service conditions? Normal conditions must take into consideration deviation from average. For example, finishes on vehicles used in the desert are normally subjected to windblown sand and abrasion resistance should be an important part of the test protocol for finishes for this use. Normal weather conditions (weathering factors) at one outdoor exposure site are not the same as those at another, so the choice of site can be critical for getting realistic information on the test materials. There is no such thing as normal or average weather, but rather a series of diurnal cycles superimposed on seasonal variations that often contain extreme conditions (hailstorms, typhoons, drought, etc). We need to know what the extreme conditions are during outdoor testing. It is often the extreme weather conditions that cause rapid damage to materials.

Weathering Factors

Weathering factors are solar radiation, abrasion, pollutants, changes in temperature and relative humidity, and wet/dry and freeze/thaw cycles. All of these factors can be approximated in laboratory tests. Different materials will be vulnerable to different factors and combinations of factors. Therefore the choice of a field site for testing can be important. Many materials are vulnerable to moisture and ultraviolet (UV) light; data obtained from tropical sites can be valuable for predicting service life for these materials. But if the material is sensitive to freeze/thaw cycles, a test at a tropical location would give misleading results. One should keep in mind that outdoor field tests are still a form of artificial test and may not represent the conditions experienced in service. If a material is to be used in a wide range of conditions, it is important to test it in a wide range of conditions. If the material is used as a component in different systems, it may perform quite differently depending on the system. For example, if an architectural coating is tested on a wood board, this would probably give a good indication of its service life on wood siding because both are similar uses. However if the same finish is used on a window unit or a deck, its performance could be quite different. The conditions are completely different.

Often in materials testing, there is quite a large difference between the time of failure of the first of several replicates and the last, as was observed in a series of 12 boards after 16 years of exposure (Figure 1). The lumber was carefully selected to have almost the same grain angle and growth rate. All boards were weathered for 16 weeks prior to painting. After weathering they were rinsed with distilled water, allowed to dry, and painted with the same amount of the same paint. These boards could be considered replicates, but their performance was quite different. After 16 years, two boards were in almost perfect condition whereas all the others had failed. On some boards, the paint began to fail after 3 years; on others, the paint was in almost perfect condition after 16 years.

The question is, Are these boards really replicates? Do we assume they are replicates because they had the same treatment? At the time these panels were prepared, we did not conduct any type of quality control prior to painting other than visual inspection. Nor did we do any type of quality control after the panels were painted. It is unknown whether the differences in time to failure were caused by differences in the weathering of the boards prior to being painted or by intrinsic differences in the boards. The boards were evaluated once per year, not tracked continuously. The weather conditions during the exposure were unknown. Figure 1 illustrates the importance of using many replicates, establishing better methods for quality control when preparing specimens, and tracking the conditions during exposure.

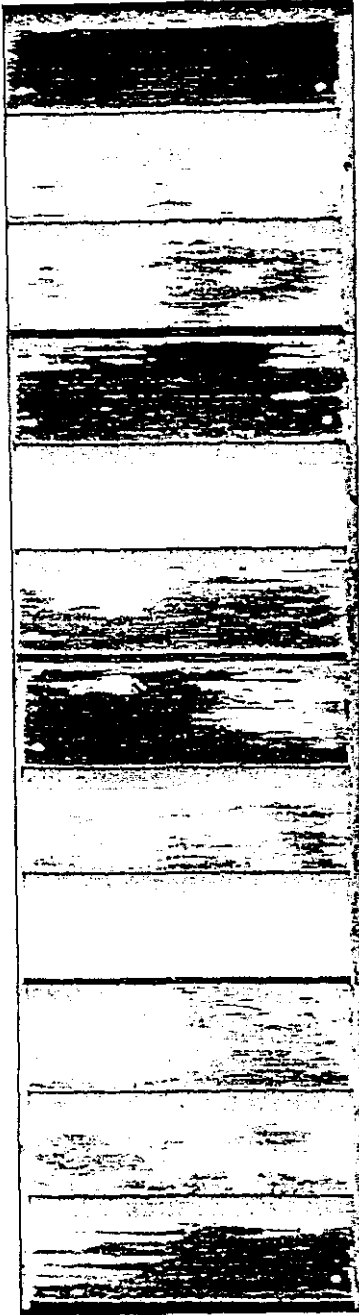


Figure 1. Effect of 16 years of outdoor exposure near Madison, Wisconsin, on panels painted with primer and one topcoat.

only once per year. In a 10-year test, this gives only 10 data points per specimen—~~not~~ very much information. In addition, there is no way of knowing what caused the degradation. It is

really what we really want are quick tests to predict service life. In other words, service life prediction (SLP) describes a test 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, accelerated weathering, and artificial weathering, have also been used to describe this type of test. The test is intended to simulate the normal failure mode of a material, but at an accelerated rate. Whether or not the test accomplishes this objective is a matter of concern—and probably a lot more research.

For more than 50 years, researchers have understood the importance of the link between accelerated weathering and the outdoor environment. However, it has not been possible to establish an acceptable acceleration factor for many materials, primarily because the important factors that cause degradation outdoors were not known or could not be duplicated in the accelerated tests. It is through outdoor tests that we determine the important degrading factors. Once this is determined, a laboratory test can be designed to test for these factors.

Link Between Outdoor and Laboratory Tests

In reviewing the work in our laboratory and similar work reported by others who have 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 and Bauer 2001). 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 the response of materials to these events. Thus, a variety of weathering events that may have had a dramatic influence on degradation have been averaged out. There has been no way of knowing what the conditions were when the specimens degraded. The specimens may have degraded more or less at the same rate since the previous evaluation, or all the degradation could have occurred during a single weather event, like a

hailstorm. Periodic evaluations—the standard method used in accelerated tests—show only the change since the previous evaluation, not the conditions that caused the change. Results have often been misleading because critical factors causing the degradation were either not known or not measured.

Traditional methods for linking outdoor weathering tests with laboratory accelerated tests usually involve a weathering device programmed with a wet/dry and UV radiation cycle to approximate the outdoor weather. W radiation from a carbon arc (ASTM D 822, ASTM 2001) was used in early weathering devices; to a great extent, this source was later replaced by a xenon-arc source (ASTM D 5031 and G 26, ASTM 2001). Other devices use UV fluorescence light sources (ASTM G 53 and D 4587, ASTM 2001). Considerable effort has been made to develop a light source that duplicates natural sunlight. Researchers continue to search for the correct cycle that replicates outdoor conditions. Researchers want accelerated tests that predict the degradation that occurs in actual use, but they seldom attempt to discover the degradation mechanism. If the mechanism of degradation is not the same in the two tests, there is little chance that the accelerated test will give reliable results. Tests often gave false positive and false negative results. In the schematic in Figure 2, note that the conventional SLP procedure includes a materials response from both the laboratory and outdoor components of the test, but not a measure of the conditions that cause the response. It is not possible to integrate the various components of the exposure conditions to get the dose (e.g., the cumulative dose of UV radiation at a particular wavelength). In addition, the materials response has usually been determined from a qualitative visual evaluation. There has been no attempt to measure chemical changes to discover the degradation mechanism.

Reliability-Based Service Life Prediction

Reliability-based SLP depends on accurate and precise measurement of specimen response during weathering, measurement of weathering factors, and integration of the factors to obtain the dose. Field data can then be compared with accelerated laboratory tests using dose and response rather

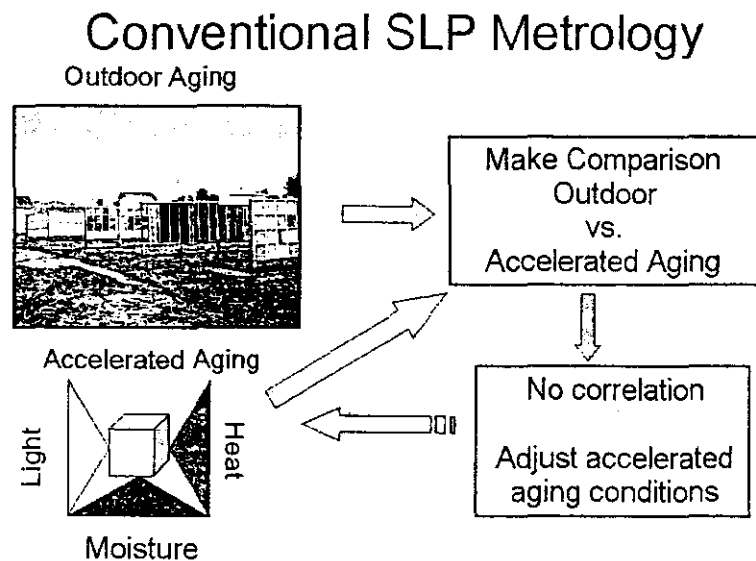


Figure 2. Conventional service life prediction (SLP) methodology.

Reliability-Based SLP Methodology

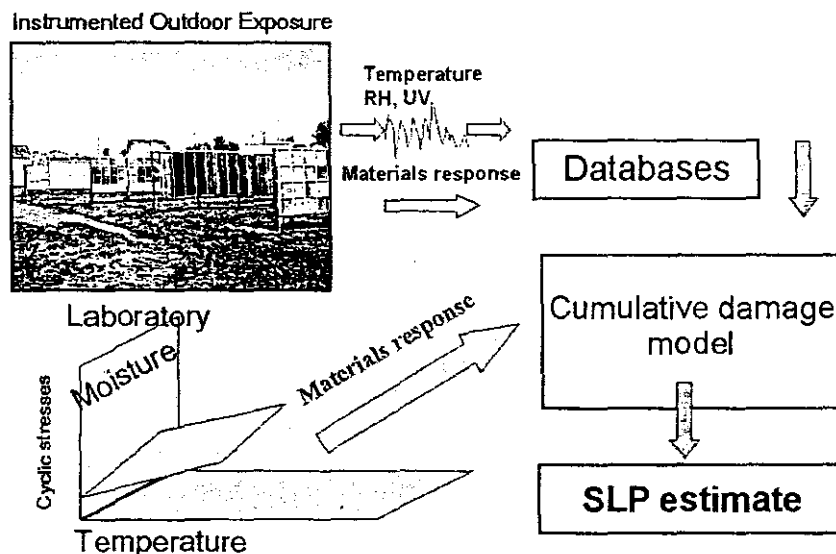


Figure 3. Reliability-based service life methods.

than some response versus time (Figure 3). The materials response and the conditions in the laboratory test can then be compared with the weather data and the materials response obtained from the outdoor exposure.

Specimen Response

For reliability-based SLP, specimen response must be measured frequently. This can be accomplished through in situ measurements by placing sensors in/on specimens or by removing specimens for measurements at closely spaced intervals. A variety of sensors are available for monitoring specimens during outdoor exposure. Changes in specimen temperature, moisture content, and dimension can be easily measured in situ every few minutes. However at present, some measurements, such as chemical change, gloss, color, cracking, and peeling, cannot be made continuously during exposure. For these measurements, the intervals may vary, depending on the exposure and material. In some cases, it may be necessary to analyze specimens every few hours. As researchers recognize the value of continuous measurements, the innovation of new sensors, instrumentation, and procedures to automate data collection will likely follow.

As a material degrades, chemical change occurs. The most useful measurement of degradation is this change in the chemistry of the system. It is the best link between the field and laboratory. The chemical change can occur through hydrolysis, photochemical reactions, cyclic fatigue, corrosion, and combinations of these factors. The following sections will elaborate on two of these (photochemical degradation and cyclic fatigue) and show how these types of chemical change can be measured using reliability-based SLP.

Table 1. Total spectral irradiance for ultraviolet, visible, and infrared radiation

| Radiation | Wavelength range | Total irradiance (%) |
|---------------|------------------|----------------------|
| UV | 295-400 nm | 6.8 |
| Visible light | 400-800 nm | 55.4 |
| Infrared | 800–2450 nm | 37.8 |

Photochemical Degradation

For polymers, chemical changes are often caused by photochemical reactions catalyzed by UV radiation. The UV and visible solar radiation that reaches the earth's surface is limited to the range between 295 and 800 nm. Wavelengths from 800 to 2450 are infrared radiation. The radiation from

295 to 2450 nm comprises a distinct range that affects weathering: UV radiation, visible light, and infrared radiation (IR) radiation (Table 1). The energy from the sun that reaches the earth's surface as discrete bundles of energy called photons and their energy can be calculated from the following equation:

$$E = hv = hc/\lambda \quad (1)$$

where h = Planck's constant,

v = frequency,

c = velocity of radiation, and

λ = wavelength of radiation.

From this equation, the photon energy is inversely proportional to the wavelength of the radiation (Figure 4). The energy of the photon is an important factor in the photochemical reactions that this radiation can initiate. Several terms need to be defined before continuing the discussion of solar energy: *irradiance*, the radiant flux per surface area (Watts/m^2 (W/m^2)); *spectral irradiance*, irradiance measured at a wavelength ($\text{W/m}^2/\text{nm}$); *radiant exposure*, irradiance integrated over time (Joules/m^2 (J/m^2)); and *spectral radiant exposure*, radiant exposure measured at a wavelength ($\text{J/m}^2/\text{nm}$).

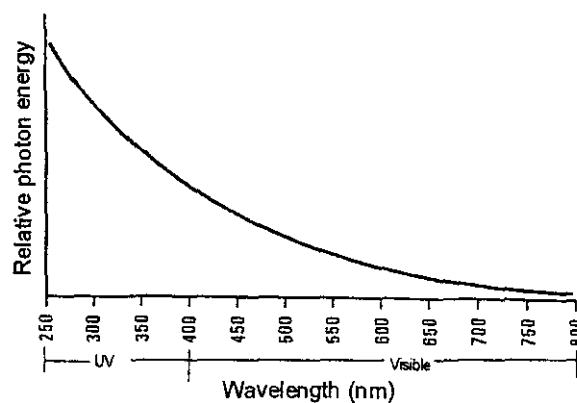


Figure 4. Relative photon energy for visible light and ultraviolet radiation.

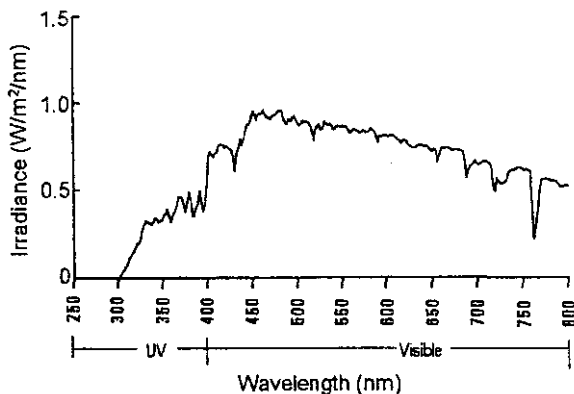


Figure 5. Spectral power distribution.

When using the term irradiance, it is necessary to define the spectral range (e.g., the total solar irradiance (295–3000nm) or the total UV irradiance (295-400 nm). For exposure or measurement at a particular wavelength (e.g., 340 nm), the spectral irradiance would be expressed as W/m^2 at 340 nm. The radiant exposure and spectral radiant exposure are irradiance and spectral irradiance integrated over time.

The spectral power distribution is obtained by plotting the spectral irradiance ($W/m^2/nm$) as a function of wavelength (Figure 5). The plot gives the spectral irradiance at each wavelength. By integrating the areas under the curve for UV radiation (295-400 nm), visible light (400-800 nm), and IR radiation (not shown in the figure), the percentage of total irradiance for each component can be calculated (Table 1).

From Figure 5 and Table 1, the energy in the W portion of the spectral power distribution is quite low compared to the total energy in the spectral power distribution. This means that although the energy for photons at 300 nm is quite high, these photons are few in number, so the spectral irradiance is quite low. As the wavelength increases to 400 nm, the spectral irradiance increases (lower energy photons, but more of them). This becomes important as we design experiments to assess chemical change. The experiment can be designed to have the same number of photons or the same energy at different wavelengths, but it's not possible to have both. For comparing chemical changes at different wavelength ranges, the band-width or time of exposure should be adjusted to achieve the same energy.

For a photochemical reaction to occur, energy at a sufficient energy to disrupt a chemical bond must be absorbed by some chemical moiety in the system. This is the first law of photochemistry (the Grotthus–Draper Principle). In addition, a particular moiety in the polymer can absorb only one quantum of radiation (the Stark–Einstein Principle) (McKellar and Allen 1979) The energy required to break chemical bonds depends on the type of chemical bond (Table 2). The bond dissociation energy available for radiation in the W and visible range and photon energy per wavelength are shown in Figure 6. Using Equation (1), the energy for W radiation at a wavelength of 295 nm is about 97 Kcal/mole and that for 400 nm about 71.5 Kcal/mole. As Table 2 shows, the bond dissociation energies for many carbon–oxygen moieties commonly found

Table 2. Bond dissociation energies and radiation wavelengths ^a

| Bond | Bond dissociation energy (Kcal/mol) | Wavelength (nm) |
|--------------------------------------|--|--------------------|
| C-C (Aromatic) | 124 | 231 |
| C-H (Aromatic) | 103 | 278 |
| C-H (Methane) | 102 | 280 |
| O-H (Methanol) | 100 | 286 |
| C-O (Ethanol) | 92 | 311 |
| C-O (Methanol) | 89 | 321 |
| CH ₃ COO-C (Methyl ester) | 86 | 333 |
| C-C (Ethane) | 84 | 340 |
| C-Cl (Methyl chloride) | 82 | 349 |
| C-COCH ₃ (Acetone) | 79 | 362 |
| C-O (Methyl ether) | 76 | 376 |
| CH ₃ -SH (Thiol) | 73 | 391 |
| C-Br (Methyl bromide) | 67 | 427 |
| N-N (Hydrazine) | 57 | 502 |
| C-I (Methyl iodide) | 53 | 540 |

^a Bond energies abstracted from table 2.1 in Rånby and Rabek 1975.

in polymers fall within the UV radiation range (295-400 nm). Several of these chemical moieties have bond dissociation energies well above the energy of terrestrial UV radiation and therefore cannot be affected by natural UV radiation. However, by comparing the energy available from the photons in the UV range of the spectrum, it is apparent that there is sufficient energy to break bonds in the chemicals that comprise many coatings systems. Energy must be absorbed by some component of the polymer, but the absorbed energy may not result in a degrading chemical reaction. The absorbed energy puts the molecule in a higher energy state (excited state) that can be dissipated through a number of paths. The most benign would be a return to the ground state through dissipation of heat. Other alternatives would involve chemical reactions.

In traditional weathering experiments, both in the laboratory and outdoors, specimens were subjected to broadband UV radiation or solar radiation. The different energies could cause a variety of chemical reactions, depending on the bond dissociation energy of the various chemical moieties in the material. It was impossible to separate these reactions. If chemical change is to be quantified from laboratory and outdoor tests, filters need to be used to expose specimens to specific wavelength ranges and the energy normalized in some way to compare the degradation. We now have the filters, sensors, and sophisticated analytical instrumentation to measure the

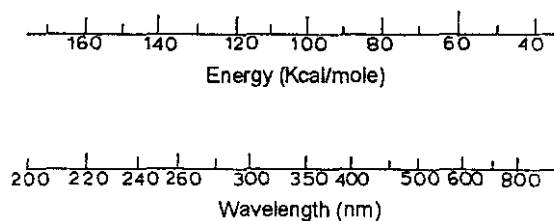


Figure 6. Relationship between bond dissociation energy and wavelength of solar radiation.

chemical changes that occur at narrow wavelength ranges. By understanding the chemical reactions that occur at specific wavelengths, during laboratory and outdoor tests, it is possible to accelerate degradation in the laboratory. If the law of reciprocity applies to the specific photochemical reaction, increasing the photon flux in a laboratory experiment can increase the rate of degradation, thus giving an accelerated test. This is the approach being used by Jonathan Martin, Tinh Nguyen, Joannie Chin, and others at National Institute of Standards and Technology (NIST).

Cyclic Fatigue

As part of the ongoing work at the Forest Products Laboratory (FPL) in Madison, Wisconsin, on the performance of materials used in residential construction, several apparatus have been built to induce cyclic movement (fatigue) of sealants during exposure. The FPL field site, which is 5 km west of Madison, has been fully instrumented to collect weather data during outdoor exposure of materials (Figure 7). This includes temperature, relative humidity, precipitation, and UV radiation. UV radiation is measured at 18 wavelengths, and the intensity at each wavelength can be integrated to get dose. The dose for other weather factors can also be calculated from the data (total rainfall, degree days, time at dew point). This work involves detailed laboratory and field studies designed to develop SLP methods for sealants. The data from our studies shows a clear link between the materials response during weathering and the weather conditions causing this response.

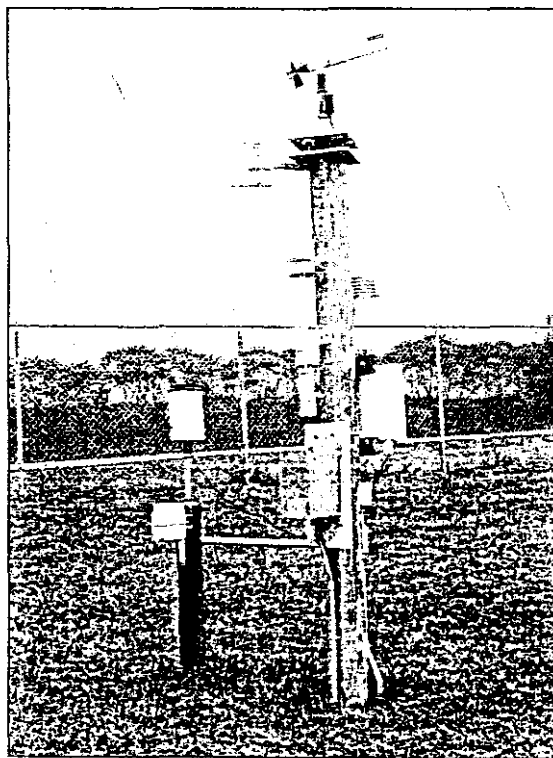


Figure 7. Weather station at Forest Products Laboratory test facility near Madison, Wisconsin.

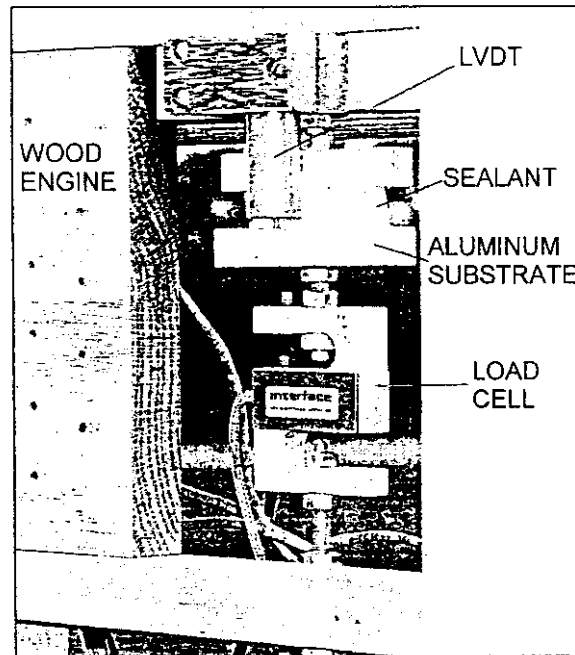


Figure 8. Sealant test specimen.

Using the dimensional change caused by moisture-induced movement of wood or thermally induced movement of aluminum, apparatus were built to subject materials to cyclic fatigue. Each specimen is configured with a load cell and a linear variable differential transformer (LVDT) (Figure 8). The cyclic fatigue is caused by the changes in weather, and the load and deflection of each specimen is recorded along with all weather data. Data is collected every 2.5 to 25 minutes depending on the rate of motion. The computer is programmed to collect more data during periods of rapid motion.

Figure 9 shows the strain of two specimens during outdoor exposure during the winter. The wood driving the cyclic movement gave almost the same strain on the two types of sealant. The daily cyclic changes indicate the movement caused by changes in relative humidity and temperature. Note that the rate of increasing and decreasing strain is not the same. This is most obvious from days 11 to 22. The sealant went from 3% to 23% strain on day 11, then cycled back to 8% at day 22. This type of nonsymmetric behavior is typical of what would be expected with sealants used in conjunction with wood construction. Wood absorbs moisture much quicker than it releases it during drying. Drastic changes in strain, such as on days 4 and 11, were a result of rain and therefore placed the sealants in greater tension. The rain/snow on days 69 to 71 was very heavy and resulted in additional increases in strains. Heavy rain during the winter was not expected. The test apparatus had been operating within its design parameters throughout the winter and had been keeping the specimens under tension with strains of 5%–25%, until the 3 days of heavy precipitation. This unusual weather event caused some specimens to fail in adhesion to the aluminum substrate. The data collection system was functioning during this time and failure of the specimens was readily apparent.

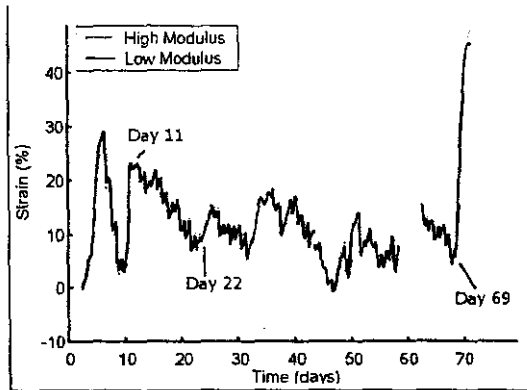


Figure 9. Strain on two sealant specimens as a function of time.

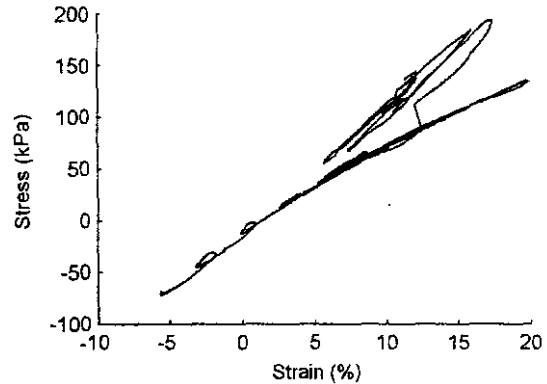


Figure 10. Stress/strain plot of specimen showing failure of sealant

A partial adhesion failure was detected in another experiment. Figure 10 shows several cycles with an abrupt change in the slope of the stress/strain plot. This abrupt change occurred at 2:27 p.m. on May 12, 2004, following a day of rain. The figure shows the “apparent stress” because it is not corrected for the decrease in the bond area.

By instrumenting exposure sites, it is possible to track specimens at all times through all types of weather. From our experience over the last 2 years, degradation has occurred during periods of extreme weather, usually at 2:00 a.m. (at times when I really don’t want to be watching the specimens). The computer doesn’t sleep nor does it care about the weather—except for lightning. But that’s another story!

Other Planned Experiments

As part of our test protocols for paints and coatings at FPL, we are investigating ways to place sensors and instrument test panels. For example, dimensional change of the wood often causes coating failure. Probes can be inserted into the wood to monitor the wood moisture content. The change in specimen dimensions can also be measured. If visual evaluations are important, these can automatically be collected digitally and stored along with moisture and weather data to get a complete history of the weather causing the response and the material response. We are also incorporating test panels into wall assemblies to get more robust tests. The wall assemblies are designed to subject the panels to a variety of moisture regimes. We are using nondestructive tests to monitor decay in the wall assemblies.

Conclusions

From what I have learned through my association with other researchers and experience at FPL, I believe we can get far more value from our outdoor field tests by

- instrumenting specimens to measure moisture content, temperature, and dimensional change,
- using computers to collect, store, and automatically process data,
- developing quality check methods to assure specimen quality prior to testing,

- setting up weather stations and recording exposure conditions,
- evaluating the response of panels in terms of dose, and
- measuring the chemical change on the surface every few hours, even minutes,

By making these techniques part of our outdoor test protocols, we can vastly improve the quality and quantity of data from outdoor tests. The dose response information from outdoor tests can be correlated with dose response data from accelerated tests. It is only through comparison of dose and response that we can develop confidence in our accelerated tests.

Many new sensors, data collection systems, and analytical instruments have become available. The computer power to analyze vast amounts of data in a short time makes it possible to do analyses never before possible. The cost of adding sensors and data collection systems to an outdoor field study seems small in comparison to the cost of maintaining the outdoor field site. I believe the scientific community has the creativity to develop new data collection systems to further advance reliability-based service life prediction methods.

References

- ASTM. 2001. Annual Book of ASTM Standards, Vol. 06.01. American Society for Testing and Materials, Philadelphia, PA
- D 3274–95, Evaluation of degree of surface disfigurement of paint films by microbial (fungal or algal) growth or soil and dirt accumulation
 - D 662–93, Evaluation of degree of erosion of exterior paints
 - D 661–93, Evaluation of degree of cracking of exterior paints
 - D 772–93, Evaluation of degree of flaking (scaling) of exterior paints
 - D 822–96, Standard practice of conducting tests on paint and related coatings and materials using filtered open-flame carbon-arc light and water exposure apparatus
 - D 5031–96, Standard practice of conducting tests on paint and related coatings and materials using enclosed carbon-arc light and water exposure apparatus'
 - G 26–96, Standard practice for operating light-exposure apparatus (xenon-arc) with and without water for exposure of nonmetallic materials
 - G 53–96, Standard practice for operating light- and water-exposure apparatus (fluorescent UV-condensing type) for exposure of nonmetallic materials
 - D 4587–91, Standard practice of conducting tests on paint and related coatings and materials using a fluorescent UV-condensation light- and water-exposure apparatus
- Martin, J.W. and D.R. Bauer [eds.]. 2001. Service life prediction methodology and metrologies. American Chemical Society Series 805. Oxford Press, New York.
- McKellar, J.F. and N.S. Allen. 1979. Photochemistry of man-made polymers. Applied Science Publishers LTD, London.
- Rånby, B. and J.F. Rabek 1975. Photodegradation, photo-oxidation and photostabilization of polymers, Principles and applications. John Wiley and Sons, London.

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