

THE EFFECT OF OZONE ON THE CREEP-RUPTURE OF BUTYL-ADHERED EPDM SEAM SPECIMENS

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EPDm roofing seam specimens, prepared using a commercially available butyl-based adhesive, were subjected to a creep-rupture experiment in peel in the presence of ozone. The times-to-failure of 12 replicate specimens were recorded at five ozone concentrations: ambient (about 0.01-0.03), 0.14, 0.26, 0.50, and 1.0 parts per million. The results of the study indicated that an increase in the ozone concentration significantly reduces the times-to-failure over those observed at ambient levels. The shorter times-to-failure at elevated ozone levels were attributed to ozonolysis of the adhesive. The results emphasize the need to minimize incorporating peel stresses into seams of EPDM roofing membranes.

KEYWORDS

Adhesive performance, building technology, creep-rupture, EPDM, low-sloped roofing, ozone, seams, single-ply roofing, time-to-failure.

INTRODUCTION

Background

The National Institute of Standards and Technology (NIST) is conducting research to predict the life of roofing membranes under service conditions. This includes creep-rupture experiments to characterize the behavior of seams of ethylene-propylene-diene terpolymer (EPDM) vulcanized rubber membranes under load over time.¹⁻⁵ The objective is to determine the sensitivity of seam time-to-failure under creep-rupture loads to various factors associated with seam formation and environmental exposures. In a creep-rupture experiment, a seam specimen of a fixed length is stressed under a constant load and the time over which it sustains the load before total delamination is recorded. This time is called the time-to-failure. Evaluating the creep-rupture performance of seams is important, as field experience has shown that seams, which are watertight when the roof is installed, sometimes develop defects after a short time in service (e.g., within three years⁶). The development of seam defects soon after installation implies that the cause may be reasonably assigned to the rheological behavior of the

adhesive as opposed to chemically-induced deterioration.^{2,3}

Creep-rupture experiments in peel have been found to be a more sensitive method for characterizing factors affecting seam performance under load than short-term peel and lap-shear strength measurements or long-term lap-shear experiments.^{2,3} For example, it was found that the creep resistance of butyl-based joints varies exponentially with adhesive thickness; whereas the short-term peel strengths varies linearly. Additionally, it has been observed that: (1) under normalized loads, EPDM butyl-based seam specimens in shear have times-to-failure that are 100 times or more longer than those of peel specimens, and (2) in a peel configuration, specimens fabricated with well-cleaned EPDM and thick layers of butyl-based adhesive have significantly longer creep lives than those prepared with particulate-contaminated EPDM and thin layers of adhesive.*

Experience with the field performance of seams is consistent with previous laboratory findings regarding factors that affect performance such as surface cleanliness, adhesive thickness, and mode of applied stress. One of the authors, Ream, has been installing EPDM sheet rubber roofing since the 1970s using seaming methods and adhesives developed mainly by the major manufacturers of these products. The experience has been that seams have generally performed well, and the industry has encountered fewer problems in the late 1980s and 1990s than in the 1970s. Many of the problems observed have been associated with workmanship factors such as inadequate cleaning of the rubber, application of inadequate amounts of adhesive, and the incorporation of "fishmouths" in the seams. In the latter case, the roofing mechanics, in making the seams, force wrinkles or buckles in the sheets down into the adhesive, instead of cutting them out and patching as required by the manufacturers. The "fishmouths" are initially sealed watertight, but are a source of peel stress in the seam. Consequently, over time, these sealed areas of the seam may disbond and the contractor may be called back to fix a leak.

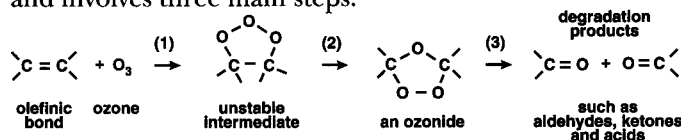
This paper reports the results of a creep-rupture study in which butyl-based EPDM seam specimens were loaded in peel in an ozone-containing atmosphere. Ozone was selected because it is a wide-spread air pollutant that has long been known to have an adverse effect on the performance

*NIST unpublished data.

of many polymeric materials, particularly rubbers.⁷⁻¹³ As described in this paper, the creep resistance of the peel specimens studied in the presence of ozone concentrations within the range typically found in U.S. urban areas is significantly less than that of specimens tested under ambient laboratory ozone levels.

The Effect of Ozone on Rubber—Ozone reacts with many organic compounds but, in the case of saturated compounds (e.g., hydrocarbons), the rate of reaction is relatively slow.¹¹ As a consequence, ozone plays only a minor role in the degradation of these compounds. In contrast, ozone reacts readily with olefinic double (unsaturated) bonds (i.e., $>C=C<$). The reaction may be fast, even at ozone levels found outdoors under normal environmental conditions.^{9,10}

The reaction, called ozonolysis, has been well studied and involves three main steps:¹⁴



Ozonolysis generally causes scission of the olefinic bond and the formation of oxidized degradation products including aldehyde, ketones, acids, peroxides, and hydroperoxides. The rate of ozonolysis is accelerated when an olefinic bond is stressed.¹¹

Rubbers with carbon-carbon double (i.e., olefinic) bonds in the polymer and under tensile stress are vulnerable to ozone-induced degradation.⁷⁻¹³ When the location of the double bonds is in the backbone chain, the reaction with ozone can result in polymer chain scission. The effect of ozonolysis on the rubber manifests itself as surface cracks oriented perpendicular to the direction of the applied stress.^{9,12} Thus, if a fresh surface of the rubber is exposed (e.g., due to the mechanical stress or cyclic movement), the surface cracks can grow in time and lead to failure.

In the case of rubber roofing systems, the effect of ozone on the performance of the EPDM membrane material has not been an issue. EPDM rubber has good resistance to ozone, as it has few sites of unsaturation, and those present are located in side chains and not in the backbone of the polymer.^{8,15} As an illustration, Gaddy et al.¹⁶ reported that typical commercial EPDM membrane products underwent little change in properties such as load-elongation and glass transition upon exposure to ozone under stress.

In contrast, the neoprene-based** and butyl-based adhesives commonly used in fabricating EPDM seams may be susceptible to ozonolysis. The generic chemical formulas for these polymers are given in Figure 1; note the carbon-carbon double bonds in the backbones of the polymer chains. These two elastomers are less reactive to ozone than some other elastomers and are, thus, regarded as possessing a degree of ozone resistance.⁸ Nevertheless, for outdoor exposure, stabilization with an antiozonant may be necessary, particularly if the product is subjected to mechanical stress.⁸ In the case of neoprene, the lower reactivity is attributed to the chlorine atom (Figure 1), which lessens the affinity of the carbon-carbon double bond to

ozone. In the case of butyl, the amount of unsaturation in the polymer backbone (about 2 percent)¹⁷ available for reaction with ozone is relatively low. In the present study, only a butyl-based adhesive was investigated.

Ozone in the Environment—Ozone is a natural constituent of the atmosphere continuously formed from oxygen under the effect of ultraviolet radiation. In a "standard clean" environment, the concentration at the earth's surface fluctuates generally between 0 and 0.07 parts per million (ppm).¹⁸ In areas where pollutants are high due to sources such as industrial processes and automobiles, the concentrations are generally much higher. Figure 2 shows a map of the United States displaying average peak ozone levels for urban areas for 1990.¹⁹ For most urban sites, these levels range from 0.1 to 0.15 ppm with the greatest average value, 0.3 ppm, recorded in the Los Angeles basin. Los Angeles has also recorded the largest urban ozone concentration of about 1.1 ppm.¹⁸

EXPERIMENTAL

Experimental details are given in the Appendix. In brief, T-peel seam specimens, having dimensions 25 x 125 mm (1 x 5 in.) with a 75 mm (3 in.) bond, were prepared using well-cleaned EPDM membrane material and a commercially available butyl-based adhesive. Before conducting the creep-rupture tests, the thickness of the adhesive layer in each specimen was determined. Additionally, the short-term T-peel strengths of two sets of three specimens were determined; one at 21°C (70°F) and the other at 31°C (88°F).

The specimens were cured at ambient laboratory conditions (about 21°C/70°F and 45-50 percent relative humidity (RH)) for a minimum of two weeks prior to conducting peel or creep tests. This cure time was considered sufficient, as past experience has shown that the strength of EPDM joints, prepared using this butyl-based adhesive, showed no significant change after about a one-week cure under ambient laboratory conditions.²⁰

For a single creep-rupture experiment, a set of 12 specimens was placed under load in a chamber having a pre-selected concentration of ozone, and the times-to-failure of the specimens were determined. The load applied to each specimen was 3.9 N (0.88 lbf), and the chamber temperature was 31°C (88°F). Five experiments were conducted at varying ozone levels: ambient (about 0.01-0.03), 0.14, 0.26, 0.50, and 1.0 ppm.

RESULTS AND DISCUSSION

Characterization of the Seam Specimens

Characteristics of the seam specimens are given in Table 1. All specimens had adhesive thicknesses in the range of 0.18-0.20 mm (7-8 mils). Adhesive thicknesses in this range provide specimens having relatively long times-to-failure versus specimens with thinner adhesive layers.² They are also representative of acceptable adhesive thicknesses for butyl-based seams fabricated in the field.

The average T-peel strength at 21°C (70°F) was 1.8 kN/m (10.3 lbf/in.) (see Table 1). This was comparable to previously-determined peel strengths of EPDM seams prepared in the laboratory using clean rubber and butyl-based adhesives.^{2,21,22} The peel strength at 31°C (88°F), which

**Neoprene is generally used as a generic name in the U.S. roofing industry (and others) to describe polychloroprene rubbers, and is the name used in this paper.

was the temperature of the creep tests, was 1.4 kN/m (8.1 lbf/in.). Thus, the 10°C increase in temperature produced a 21 percent decrease in strength. The reduction in strength with increasing temperature is due to the viscoelastic nature of the adhesive. Chmiel has previously reported data for butyl-based adhesives that show a decrease in peel strength with an increase in temperature.²³

The load applied during creep testing, 3.9 N (0.88 lbf), was 8.6 percent of the average short-term strength measured at 31°C (88°F). It was found in previous experiments that loads up to 25 percent of the short-term peel strength result in times-to-failure that are practical for laboratory testing.¹⁻⁵

Creep-Rupture Results

Table 2 gives a summary of the results of the creep-rupture tests (times-to-failure and failure modes) conducted at the five different ozone concentrations. The ambient, 0.14, and 0.26 ppm concentrations are typical of those found in many urban areas of the United States (see Figure 2). Even the highest concentration of 1 ppm represented a value that has been recorded, as mentioned above, for the Los Angeles area.

Figure 3 provides plots of the cumulative percent of specimens failed versus the times-to-failure. The analysis of the data was conducted according to the procedure given by Nelson.²⁴ Each set of data was found to fit a lognormal distribution. This is evidenced in Figure 3 where, for each ozone concentration, the ordered times-to-failure fall on or close to each probability-plot line. The mean times-to-failure and standard deviations given in Table 2 were obtained from the fits of the data to the lognormal distribution. The fact that the data fit the lognormal distribution signifies that the failures of the specimens are governed by a random process. The plotted data do not provide support for a change in failure mechanism from the first to last failure. Note in Figure 3 that the slopes of the lines for ozone concentrations above ambient are approximately the same and are much greater than the slope of the line for ambient ozone concentration. In this analysis, the higher slopes indicate that the standard deviations of the average times-to-failure for specimens exposed to elevated ozone concentrations are much smaller (i.e., less spread in the data) than that for specimens subjected to ambient ozone concentrations. The smaller standard deviation implies that, at the elevated ozone concentrations, a more efficient degradation process is occurring, and also hints that a different mechanism may take place in the degradation.

The creep-test results (Table 2 and Figure 3) showed that an increase in the ozone concentration caused a decrease in the mean time-to-failure. The effect of each incremental increase in the ozone concentration was statistically significant, as there were no overlaps in the individual data points for set numbers 1-4 (Figure 3). There was one overlap between data points in set numbers 4 and 5, as two specimens exposed at ambient ozone concentrations exhibited times-to-failure less than those exposed at 0.14 ppm. The reasons for this were not explored.

Regardless of ozone concentration, all of the seam specimens failed. Although there was no visual difference in the failure mode of the specimens exposed to elevated levels of ozone from that of the specimens subjected to ambient lev-

els, the failure mechanisms may be different. At elevated ozone concentrations, the failure process (i.e., crack growth through the adhesive) may be driven by ozonolysis of the adhesive in addition to rheological effects of the adhesive under load; whereas at ambient ozone concentrations, the process may be predominantly controlled by the rheological properties of the adhesive with some contribution from ozonolysis. The supposition that chemical degradation at elevated ozone concentrations makes a major contribution to the creep-induced seam failures is consistent with the known adverse effects of ozone on the mechanical properties of stretched olefinic rubbers due to polymer chain scission.⁷⁻¹³ Moreover, Wood²⁵ has shown that both physical and oxidative-chemical creep occurs in a rubber vulcanizate, and that, for the case he studied, the chemical component of the creep was sensitive to the amount of ozone in ambient air.

Our creep data are consistent with such a supposition because, as previously mentioned, the plots in Figure 3 imply a change in degradation mechanism at elevated ozone concentrations versus ambient concentration. To obtain evidence that chemical degradation might be contributing to the times-to-failure in the presence of ozone, a small number of Fourier transform infrared (FTIR) multiple internal reflection spectroscopic analyses of delaminated surfaces of adhesive layers were performed at the conclusion of the creep-rupture experiments. One specimen per set was analyzed. In addition, infrared (IR) analysis was conducted on a control specimen that was not subjected to creep-rupture testing. In this case, the adhesive surface was obtained by manually delaminating a seam specimen that was prepared according to the procedure used for the creep-rupture specimens. Figure 4 shows IR spectra taken of the delaminated adhesive layers; the specimen was: (a) not exposed (i.e., the control), (b) exposed to ambient ozone, and (c) exposed to 0.25 ppm ozone. The latter spectrum is illustrative of those obtained from the specimens exposed to ozone concentrations above ambient.

For purposes of this limited analysis, the absorption band of interest is that near 1700 cm⁻¹. This band is indicative of the presence of carbonyl groups present in oxidized compounds that may be formed in the ozonolysis of the adhesive, as previously illustrated in the chemical equation. The results of the IR analysis are consistent with the suggestion that ozonolysis of the adhesive contributed to the seam-specimen failure under creep loading. Note in Figure 4 that the 1700 cm⁻¹ band, indicative of oxidized products, is present in the spectra of the adhesive layers exposed to both ambient and elevated ozone levels; in contrast, the 1700 cm⁻¹ band is not apparent in the IR spectrum of the control. Note also in Figure 4 that the 1700 cm⁻¹ band height is less in the case of ambient ozone exposure than for elevated exposure, which implies that less oxidized product is present in the specimen exposed to ambient ozone. This suggests that the contribution of ozonolysis to specimen failure is greater at the elevated ozone levels.

The IR analysis is a technique for determining the presence or absence of oxidized compounds in the adhesive layers and does not address the mechanism by which they are produced. Consequently, this limited study cannot rule out definitively that an oxidative reaction, other than ozonolysis, also contributed to the production of the oxida-

tion products observed. However, it is believed that the creep-rupture experiment conditions were conducted at temperatures too low to cause any substantial thermal oxidation. Further experimentation would be needed to investigate this possibility.

Figure 5 is a plot of the time-to-failure versus the ozone concentration. The data were found to fit a power law function of the form:

$$t_f = a \times [O_3]^b$$

where t_f is the time-to-failure, $[O_3]$ is the ozone concentration, and a and b are empirical constants with values of 2.95×10^4 and -0.48 , respectively. The r^2 -value was 0.75, and the residual standard deviation was 0.36. The r^2 -value would have been higher except for the large scatter in the data for ambient ozone concentration. Relatively little scatter was observed for the elevated concentrations.

Figure 5 can be used to illustrate the effect of increasing ozone concentration on the creep-rupture lives of the seam specimens stressed in peel. As one example, at ambient ozone concentration, the average time-to-failure was about 600 h; whereas at 1 ppm, it was about 1/4th as much or approximately 100 h. As another example, at 0.3 ppm (the average peak level for the Los Angeles basin²²), the average time-to-failure was about 150 h, or one quarter of that at ambient concentrations.

At this time, the effect of ozone on the performance of seams in the field has not been established. This would require the analysis of field data from comparable weather regions, but having areas of different ozone concentrations. As a minimum, the type and thickness of the adhesives would need to be known. Additionally, the magnitude of stresses experienced by seams in the field should be determined, as data quantifying seam stresses are currently not available.

The results of the study emphasize, however, a recommendation made from our previous studies:^{2,3} to reduce the risk of delaminations in service over time, seams should, to the extent possible, be kept out of peel configurations and peel stresses should be minimized. Coupled with having seams fabricated with relatively thick adhesive layers and well-cleaned rubber, this recommendation constitutes "good practice" and is advisable whether or not the seams experience ozone exposure in service above normal "clean" concentrations. Manufacturers' requirements on fabricating seams provide direction for cleaning rubber surfaces, applying quantities of adhesive, and avoiding some peel configurations. Voluntary consensus standard guidelines are not available. The requirements of manufacturers could serve as a starting point for their development.

SUMMARY AND CONCLUSIONS

Seam specimens of EPDM roofing membrane materials were subjected to creep-rupture testing in a peel configuration in the presence of ozone. The specimens were prepared using a well-cleaned EPDM rubber sheet and a butyl-based adhesive. The times-to-failures of five sets of specimens were measured under different ozone concentrations: ambient (about 0.01-0.03), 0.14, 0.26, 0.50, and 1.0 ppm. The concentrations less than 0.50 ppm are typical of those present in urban areas of the United States.

The study showed that increases in ozone concentration

resulted in decreased times-to-failure of the specimens. In particular, the times-to-failure of specimens exposed to ozone concentrations typical of urban areas were reduced by a factor of 2 to 4 times from those observed at ambient concentrations. The decreased times-to-failure at elevated ozone levels were attributed to ozonolysis of the adhesive. Infrared analysis of the surfaces of the peeled adhesives indicated a greater presence of oxidized products on the specimens exposed to the ozone concentrations above ambient than for the specimens tested at ambient ozone.

The results emphasize the need to follow "good practice" in fabricating EPDM seams to ensure that peel loads are minimized. Previous studies have shown that seams stressed in peel are quite susceptible to creep delamination, particularly if the adhesive layer is thin and the rubber surface is not well-cleaned. The present study provides further evidence that peel stresses in seams should be avoided, to the extent possible, as ozone has a significant effect in reducing the creep-lives of seams stressed in peel.

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EPDM rubber thickness:	nominal 1.5 mm (60 mils)
Rubber surface condition:	well-cleaned
Adhesive thickness:	0.18-0.20 mm (7-8 mils)
Peel strength, 21°C (70°F):	1.8 kN/m (10.3 lbf/in.) ^a
Peel strength, 31°C (88°F):	1.4 kN/m (8.1 lbf/in.) ^b

^a Average of three specimens; coefficient of variation = 0.8%.
^b Average of three specimens; coefficient of variation = 2.5%.

Table 1 Characteristics of the seam specimens.

Set No.	Ozone Conc ^a ppm	Time-to-Failure					Failure Mode
		min	max	mean	sd	COV	
				hours		%	
1	1.0 ± 0.05	63.3	105.5	84.7	16.4	19	Cohesive
2	0.50 ± 0.03	90.3	173.3	133.7	32.8	25	Cohesive
3	0.26 ± 0.02	24.7	236.6	176.4	36.3	21	Cohesive
4	0.14 ± 0.03	228.0	324.0	272.2	36.0	13	Cohesive
5	ambient ^b	183.8	1422.2	706.4	382.3	54	Cohesive

^a For set 1, the concentration and range are based on visual observation of the output of the ozone monitor; for sets 2, 3, and 4, the concentrations are based on averages of the hourly-recorded values and the ranges are approximately twice the standard deviations (see section A.2.3).

^b Approximately 0.01-0.03 ppm.

Table 2 Times-to-failure and failure mode of the specimens for the different ozone concentrations.

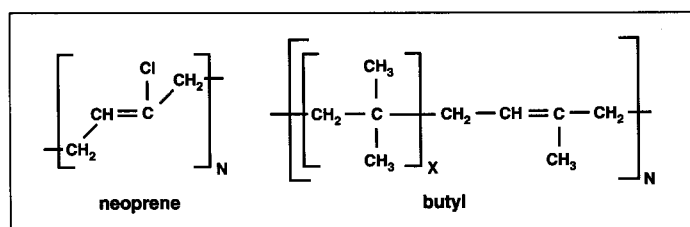


Figure 1 Chemical formulas of (a) neoprene (chloroprene) and (b) butyl polymers.

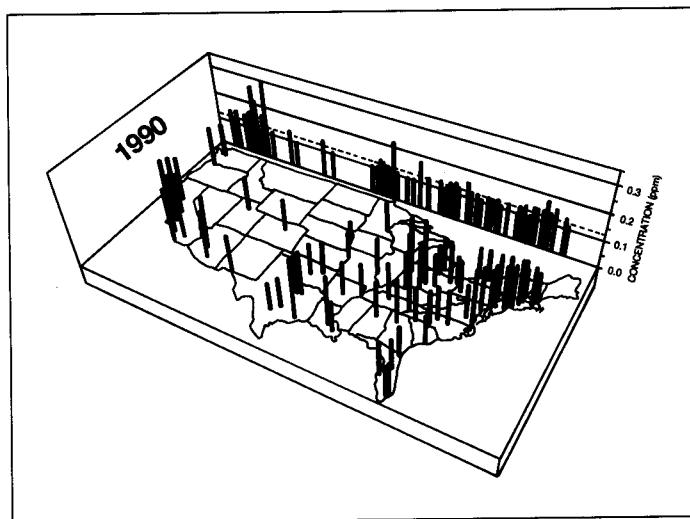


Figure 2 Average peak ozone levels for U.S. urban areas for the year 1990.¹⁸

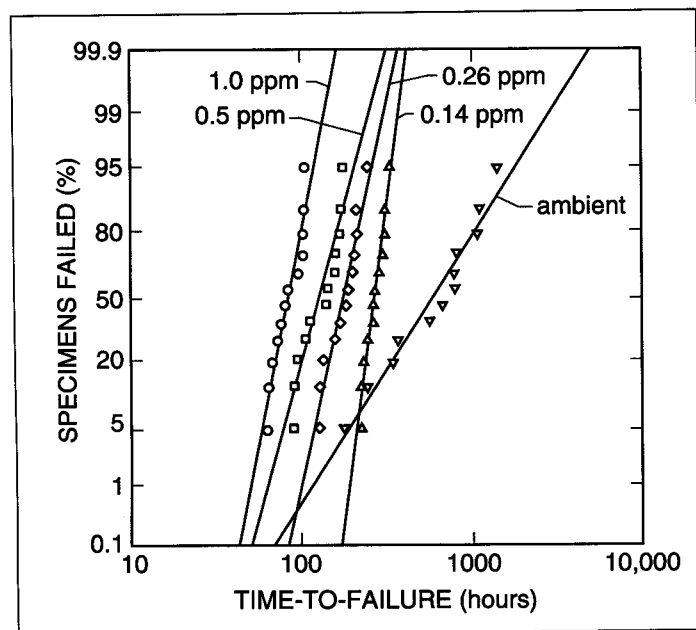


Figure 3 Cumulative percent of specimens failed versus time-to-failure; the data are for the set numbers and ozone concentrations given in Table 2.

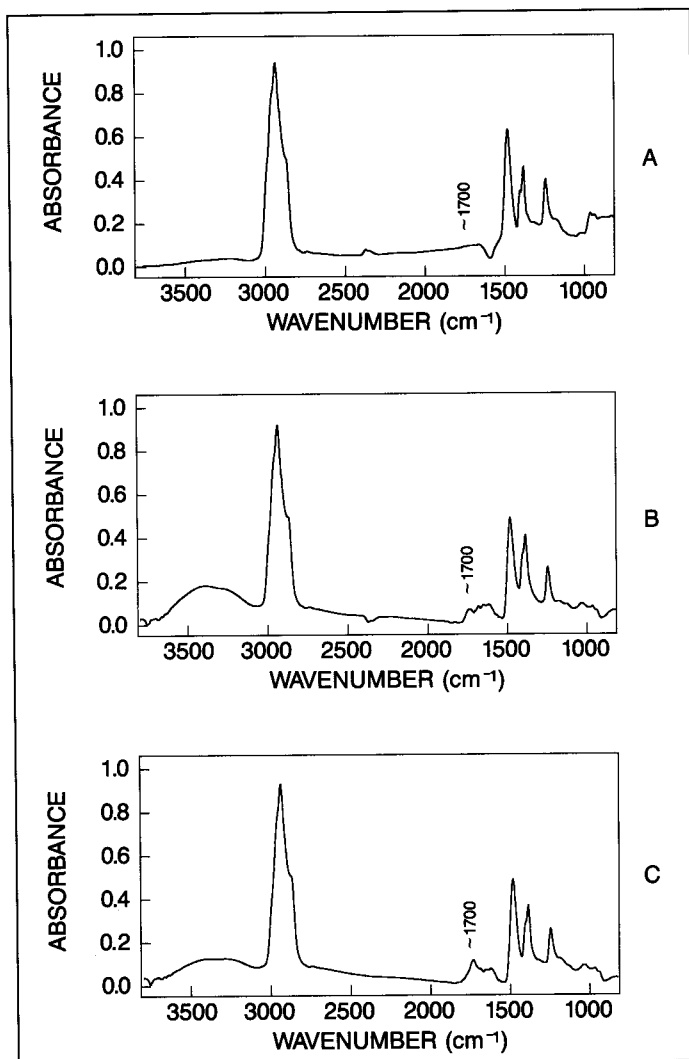


Figure 4 Infrared spectra of surfaces of delaminated adhesive layers; the specimen was: (a) not exposed, (b) exposed to ambient ozone, and (c) exposed to 0.25 ppm ozone. The absorption band at 1700 cm^{-1} is indicative of carbonyl groups in oxidized compounds that may be formed in the ozonolysis of the adhesive.

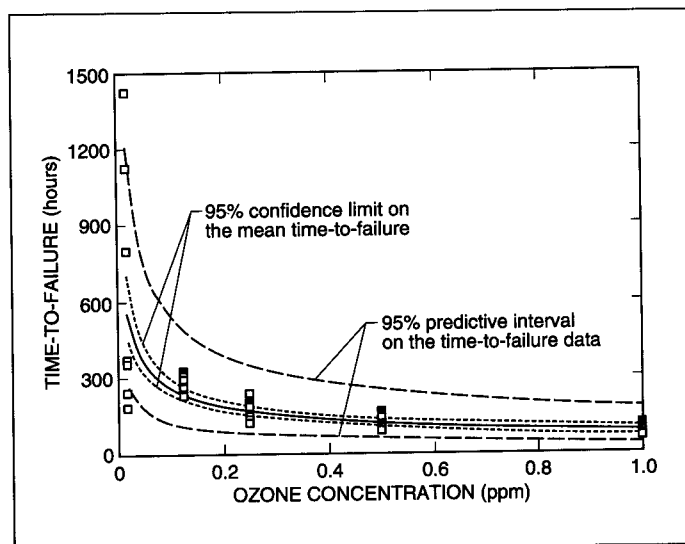


Figure 5 Time-to-failure versus the ozone concentration; the specimens were under a 3.9 N (0.88 lbf) load at $31 \pm 1^\circ\text{C}$ ($88 \pm 2^\circ\text{F}$).

APPENDIX

Experimental Details

A.1 Seam Specimen Preparation

The EPDM roofing material was a commercial rubber sheet having a nominal thickness of 1.5 mm (0.060 in.). The sheet was non-reinforced and had a talc-like release agent on its surfaces. The EPDM surface was cleaned by scrubbing with detergent and water, rinsing with water, and drying at ambient conditions. Strips having dimensions of 25 x 125 mm (1 x 5 in.) were cut from the cleaned sheet. The mass and thickness (average of four measurements at different locations) of each dry strip were determined using an analytical balance and dial-faced thickness gauge, respectively. Immediately before adhesive application, the water-washed surface of each strip was further cleaned by rubbing with a cloth soaked with reagent grade heptane. A commercial EPDM seam adhesive was applied to the cleaned surface over a 25 x 75 mm (1 x 3 in.) area at one end of the strip using a drawdown blade technique. After a 30 minute open time, two adhesive-coated strips were mated together and placed in a laboratory press at 0.7 MPa (100 lbf/in.²) for approximately 10 s. Each specimen was kept at ambient laboratory conditions (about 21°C/70°F and 45-50 percent RH) for a minimum of two weeks prior to conducting peel or creep tests.

A.1.1 Adhesive Thickness—Adhesive thickness of the seam specimens was determined just before conducting the peel and creep tests. Using a dial-faced thickness gauge, the average thickness (four measurements at different locations) of the bond area was determined. The adhesive thickness was calculated as the average thickness of the bond area minus the average thicknesses of the two rubber strips.

A.2 Tests and Measurements

A.2.1 Peel Tests—Peel tests (T-peel) were conducted at either 21° or 31°C (70° or 88°F) at a rate of 50 mm/min. (2 in./min.). The universal testing machine was equipped with hardware and software that calculated the average peel strength. After testing, the mass of each separated strip (with adhesive) was determined.

A.2.2 Creep-Rupture Tests—Creep-rupture tests were conducted in an ozone chamber (Ozone Research & Equipment Corp., Model No. 0300-M***) according to the general procedure described by Martin et al.² A built-in fan maintained uniform ozone concentrations during testing. In the laboratory, the chamber was equipped with accessory items such as rods, clamps, hooks, and wires required to load a set of 12 specimens and record their times-to-failure. The temperature of the chamber was 31 ± 1°C (88 ± 2°F), as visually monitored during testing. This was about the lowest temperature at which the chamber could be stabilized using its built-in, water-jacket cooling system.

For each exposure experiment, 12 specimens were simultaneously subjected to creep loading. First, the specimens were placed in the chamber in clamps with weights attached (but not suspended under load) where they were conditioned at the test temperature for 24 h without

ozone. Then ozone was generated and the concentration in the chamber was increased, over a three h period, to about 1 ppm where it was maintained for 15 minutes. This step was conducted to ozonize any reactive materials in the chamber and, thereby, reduce the possibility of unwanted ozone consumption during the initial periods of creep testing. After initial ozone conditioning, the chamber door was opened and the specimens were loaded at 3.9 N (0.88 lbf). After closing the door, the concentration of ozone was stabilized within five minutes at the pre-selected value. For the study, experiments were conducted at five different ozone concentrations: ambient (0.01-0.03), 0.14, 0.26, 0.50, and 1.0 ppm. During each test, the times under load, until the two rubber strips comprising the specimens completely separated, were monitored electronically for each specimen. The separation caused deactivation of an electronic clock assigned to the specimen, and the recording of the time-to-failure.² Upon completion of the test, the mass of each of the separated rubber strips (including adhesive) was measured.

A.2.3 Determination of Ozone Concentration—An ozone monitor (Dasibi Environmental Corp., Model No. 1008) was used to determine the ozone concentration in the chamber. This device gave a continuous digital display of the ozone concentration. In the laboratory, the chamber was equipped with a strip-chart recorder, which provided a continuous record of the ozone concentrations at the 0.14, 0.26, and 0.50 ppm levels. These values were the averages of hourly readings over the time of testing. The recorder could not log levels above 1 ppm and was not sensitive enough either to record a value or follow fluctuations at ambient concentrations. Consequently, visual observation of the digital display of the ozone monitor was used to estimate the values and ranges at these extremes.

A.2.4 Determination of the Mode of Seam Specimen Failure—Upon completion of the peel and creep-rupture tests, the mode of failure (i.e., adhesive or cohesive) of the bond was characterized according to the procedure described by Martin et al.² The procedure involves visual examination of the delaminated specimens and calculation of the mass percent of adhesive on each of the two rubber strips comprising the original seam specimen. The assumption is that, when the failure appears to be cohesive, about 50 percent of the adhesive applied should remain on each of the separated strips. For each specimen, the calculation was performed using the previously determined masses of the two original cleaned rubber strips comprising the seam (differentiated as strips A and B) and the two separated rubber strips (A and B) obtained at the completion of the tests. First, the mass of the adhesive on each strip was calculated:

$$\text{Mass (adh}_a\text{)} = \text{Mass (separated}_a\text{)} - \text{Mass (original}_a\text{)}$$

$$\text{Mass (adh}_b\text{)} = \text{Mass (separated}_b\text{)} - \text{Mass (original}_b\text{)}$$

These values were used to calculate the percent mass on each strip:

$$\% \text{ Mass (adh on strip}_a\text{)} = \text{Mass (adh}_a\text{)} / [\text{Mass (adh}_a\text{)} + \text{Mass (adh}_b\text{)}] \times 100$$

$$\% \text{ Mass (adh on strip}_b\text{)} = \text{Mass (adh}_b\text{)} / [\text{Mass (adh}_a\text{)} + \text{Mass (adh}_b\text{)}] \times 100$$

***Certain company products are mentioned in the text to specify adequately the experimental procedure and equipment used. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the equipment is necessarily the best available for the purpose.

A.2.5 Infrared Analysis of the Adhesive Surfaces—The IR analysis was made directly of the surface of the adhesive (intact on the EPDM rubber strip) obtained from delamination of a seam specimen. The equipment used for the analysis was a Perkin-Elmer 1760X Fourier Transform Infrared (FTIR) spectrometer with a mercury-cadmium-tellurium (MCT-A) detector and a Spectra-Tech horizontal attenuated total reflectance (HATR) attachment. A germanium IR crystal was used in the HATR attachment, which was also equipped with a clamping device that enabled the samples to be placed reproducibly onto the IR crystal. A spectrum consisted of the average of 1000 scans at a resolution of 4 cm^{-1} . Using software available with the spectrometer, each spectrum was smoothed to reduce noise and normalized to the peak at 1463 cm^{-1} to ease comparisons between spectra.