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Aging Analyses of Aircraft Wire Insulation

Dr. Kenneth T. Gillen, Dr. Roger L. Clough, Dr. Mat Celina, Dr. James H. Aubert and Mr. G. Michael Malone, Sandia National Laboratories, Albuquerque, N.M.

INTRODUCTION

Over the past two decades, Sandia has developed a variety of specialized analytical techniques for evaluating the long-term aging and stability of cable insulation and other related materials [1-4]. These techniques have been applied to cable reliability studies involving numerous insulation types and environmental factors [5-7]. This work has allowed the monitoring of the occurrence and progression of cable material deterioration in application environments, and has provided insights into material degradation mechanisms. It has also allowed development of more reliable lifetime prediction methodologies [3,6]. As a part of the FAA program for intrusive inspection of aircraft wiring, we are beginning to apply a battery of techniques to assessing the condition of cable specimens removed from retired aircraft. It is anticipated that in a future part of this program, we may employ these techniques in conjunction with accelerated aging methodologies and models that we have developed and employed in the past to predict cable lifetimes. The types of materials to be assessed include 5 different wire types: polyimide, PVC/Glass/Nylon, extruded XL-polyalkene/PVDF, Poly-X, and XL-ETFE.

This presentation provides a brief overview of the main techniques that will be employed in assessing the state of health of aircraft wire insulation. The discussion will be illustrated with data from our prior cable aging studies, highlighting the methods used and our important conclusions. A few of the techniques that we employ are widely used in aging studies on polymers, but others are unique to Sandia. All of our techniques are non-proprietary, and may be of interest for use by others in terms of application to aircraft wiring analysis. At the end of this report is a list showing some leading references to papers that have been published in the open literature which provide more detailed information on our analytical techniques for elastomer aging studies.

The first step in our investigation of aircraft wiring is to evaluate the applicability of our various techniques to aircraft cables, after which we expect to identify a limited subset of techniques which are appropriate for each of the major aircraft wiring types. The techniques of initial interest in our studies of aging aircraft wire are as follows:

- optical microscopy
- mandrel bend test
- tensile test / elongation at break
- density measurements
- modulus profiling / (spatially-resolved micro-hardness)
- oxygen induction time/ oxygen induction temperature (by differential scanning calorimetry)

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- solvent-swelling/ gel fraction
- infrared spectroscopy (with chemical derivatization as warranted)
- chemiluminescence
- thermo-oxidative wear-out assessment

The first two techniques are the simplest and quickest to apply; those further down the list tend to be more information rich and in some cases more sensitive, but also generally more specialized and more time consuming to run. Accordingly, our procedure will be to apply the simplest tests for purposes of preliminary screening of large numbers of samples. For any given material type, it can be expected that only a limited number of the other techniques will prove to be useful, and therefore, the more specialized techniques will be used on a limited number of selected samples. Samples of aircraft wiring have begun to be released to us in late April; we include in this report some limited and preliminary data on these materials.

DISCUSSION AND RESULTS

For the past 20 years, we have been involved in studying the degradation of cable insulation and other related materials in DOE and commercial applications. During this time, we have used numerous techniques for following and understanding the degradation of polymeric materials. Some of the techniques entail standard methods (or modifications of standard methods) for analysis of polymeric materials. Others involve specialized techniques that have been developed and refined at Sandia. For FAA wire aging studies, we plan to initially focus on the techniques that we have found to be especially sensitive to detection and analysis of degradation of cable insulation. However, other techniques in our laboratories may also be applied as warranted, based on preliminary results of our examination of the insulation samples provided to us. Various techniques used in studying aging are useful for certain insulation types and formulations, and for particular types of degradation, but are not applicable to other insulation types or degradation conditions. The value which Sandia provides in this type of aging-evaluation program consists of extensive technical expertise in understanding cable insulation degradation, together with the very wide range of instrumental techniques and equipment available at the national labs for use in analytical evaluation of polymers and metals. A brief summary of the techniques to be initially evaluated follows.

Microscopic examination

Visual inspection with and without optical magnification will be used to provide a rapid screening capability for the occurrence of surface microcracks or other defects. It can be applied in conjunction with the mandrel bend test (below) to identify regions of materials that may be susceptible to cracking. If warranted, we can apply scanning electron microscopy to selected areas of the insulation materials, to provide higher resolution information on surface topology.

Mandrel bend test

In this evaluation, a cable will be wrapped around cylinders of progressively smaller diameter until crack initiation is noted. This simple test will allow rapid screening of a large number of samples to identify areas of materials which are worthy of more detailed examination. Since

crack initiation typically comes from the elongation of the outside surface of the cable material as it is bent around the mandrel, the results are closely related to the more difficult and time-consuming tensile elongation measurements (below).

Tensile test/elongation at break

For this test, the cable materials are first separated from their copper conductors (various procedures may be necessary dependent upon the particular cable). The materials are then clamped in opposing jaws and pulled linearly until breakage (we use pneumatically activated jaws to minimize experimental problems such as jaw slippage). The amount of strain to failure determines the tensile elongation and the force at breakage determines the tensile strength. Since the development of cracks is often associated with subsequent cable failure and since loss of tensile elongation correlates with crack susceptibility, elongation measurements offer one of the best methods for following cable degradation. As examples of typical results, Figs. 1 and 2 show some tensile property data versus oven aging time at 100°C for a chlorosulfonated polyethylene (CSPE) cable jacketing material and an ethylene propylene rubber (EPR) cable insulation material, respectively. Figure 1 plots the normalized tensile elongation e/e_0 (elongation divided by initial elongation) for the CSPE material [8]. After an initial small drop in elongation, the elongation then falls almost linearly with aging time, an ideal situation for monitoring the condition of the material. The top and bottom parts of Fig. 2 show normalized tensile strength data T/T_0 (tensile strength divided by initial tensile strength) and normalized tensile elongation data for the EPR [1], respectively. For this material, the properties change much more abruptly at later times after moderate (for e/e_0) and little (for T/T_0) change in the earlier stages. When changes in degradation parameters abruptly accelerate just prior to failure, the term "induction-time" behavior is often used as a description, where the induction-time refers to the period where little to no indication of aging is observed. In situations of induction-time behavior, predictions of material condition can be much more difficult since properties may abruptly fail without much warning. We have been working on the development of a method that we refer to as the Wear-out approach (below). This approach [9] allows us to circumvent such difficulties by estimating the remaining lifetime even for materials showing induction-time behavior.

Density measurements

There are several methods for measuring density. For macroscopic samples (>5 mg or so), we utilize the Archimedes approach [10] of weighing the sample in air followed by weighing in liquid. Microscopic measurements can be made using a density gradient column. We pioneered this latter approach as a means of mapping density variations across degraded materials [1]. Figure 3 shows density data from the Archimedes approach for the oven aging of a PVC cable jacketing material at 110°C [8]. The density changes are quite large (easily measurable) and reasonably linear with aging time. Also shown for comparison are the normalized elongation results. It is clear that the density changes offer a very sensitive means of following the mechanical degradation. Figure 4 shows density profile results [1] for the same EPR cable insulation material whose elongation and tensile strength results are shown in Fig. 2. The x-axis variable P represents the percentage of the distance from the outside of the cable insulation (0) to the inside (100) that contacts the copper conductor. The unaged insulation had a flat density profile that followed the dashed line in Fig. 4. After 86 days at 100°C, an easily measurable

increase in density is noted on the inside surface of the insulation and this increase becomes more substantial with aging (Fig. 4). It turns out that this increase was due to copper-catalyzed oxidation caused by the diffusion of copper ions into the insulation during processing of the cable and storage before the onset of oven aging (the conductor was removed prior to beginning the oven aging exposures). Comparing the results of Figs. 2 and 4 shows that an easily measurable density increase occurs after 86 days, which is before any significant changes have occurred in mechanical properties.

Modulus profiling

As shown above for the EPR material (Fig. 4), insulation frequently degrades in a non-uniform way, and an identification of the nature and cause of the degradation is dependent on identifying this occurrence. Besides the copper-catalyzed oxidation effect responsible for the results shown in Fig. 4, many other mechanisms can lead to heterogeneous aging effects. For instance, materials such as cable insulations may degrade primarily at air-exposed surfaces due to interaction with various degradation-inducing agents contained in the air (oxygen, ozone, chemical contaminants, moisture, etc.). One of the most useful techniques for following such heterogeneous effects is modulus profiling, a unique approach developed at Sandia [2]. This technique allows us to quantitatively map the modulus of a material with a resolution of ~50 micrometers. After aging, we prepare samples by exposing and then polishing a cross-section through the aged material. Modulus measurements are then made across the aged cross-section. Figure 5 shows some typical results [3] for 2-mm thick nitrile rubber material after oven-aging at four temperatures (125°C, 110°C, 95°C and 80°C). Again, P gives the percentage of the distance from one air-exposed surface to the opposite air-exposed surface. For the unaged sample, the modulus values are approximately constant across the 2-mm cross-section. With aging at the highest temperature of 125°C, the modulus values rapidly increase near the sample surfaces with much smaller changes occurring in the interior region. This phenomenon is caused by diffusion-limited oxidation (DLO). Whenever the dissolved oxygen in the material is used up by reaction faster than it can be replenished by diffusion effects from the surrounding air atmosphere, the oxygen concentration in the interior will decrease relative to the (equilibrium) value at the sample surfaces. This can lead to a reduction in oxidation with depth into the sample. The importance of DLO will depend on sample thickness and upon the ratio of oxidation rate to oxygen permeation rate. For constant sample thickness, DLO effects will become less important as the temperature is reduced (see Fig. 5) because the activation energy for oxidation is larger than the activation energy for oxygen permeation.

It turns out that similar results (DLO effects causing oxidative hardening at the surfaces to occur faster than hardening in the interiors) are found for the oven aging of many other elastomeric materials. Since such effects will be temperature and thickness dependent, one might expect strange and unintelligible mechanical property results. Surprisingly, elongation results are well-behaved and can usually be successfully analyzed in terms of simple Arrhenius models. This is due to the fact that equilibrium oxidation occurs at the sample surface and modulus increases are maximum at this location. During tensile testing, one might expect cracks to initiate at the surface where hardening (modulus) is maximized. If these cracks immediately propagate through the material, the equilibrium oxidation at the sample surface will then determine the elongation.

Another example of the power of modulus profiling results is highlighted in Fig. 6 which shows some results for high-energy radiation aging of a 2-mm thick styrene-butadiene rubber (SBR) material [11]. The unaged material had uniform modulus values of ~5 MPa across its cross-section. Radiation aging in an inert environment led to a uniform increase in modulus (to ~27 MPa) caused by chemical crosslinking processes. Radiation aging in air to the same radiation dose led to a very complex W-shaped modulus profile. It turns out that high-energy radiation of air leads to small concentrations of ozone. By surrounding the sample with a glass wool cocoon impregnated with an ozone trap (KI) during the radiation aging, the sharp upturns near the surface were eliminated. This showed that ozone degradation effects were responsible for the sharp upturns near the sample surfaces. The remaining heterogeneity was due to DLO effects.

Oxygen induction time/ oxygen induction temperature

When a small polymer sample has its temperature raised at a constant rate in the presence of oxygen, utilizing a differential scanning calorimeter (DSC) or similar equipment, there is often a temperature, referred to as the oxygen induction temperature (OITP), above which a rapid oxidative degradation of the sample is observed. This rapid oxidation results in heat given off by the sample (an exotherm) which leads to a measurable DSC peak. Similarly, the exposure can be done isothermally until the exotherm appears, where the time period to the exotherm is referred to as the oxygen induction time (OIT). For many materials, the onset of the exotherm corresponds to the point at which the remaining antioxidant in the sample has been used up during the DSC exposure. Degradation of the polymer (by laboratory accelerated aging experiments, or by aging in ambient application environments) before DSC exposure will lead to a reduction in OIT and OITP values. This method thus provides an indicator of aging for some, but not all, organic materials. Figures 7 and 8 show comparisons of elongation results with OIT and OITP data for the 125°C oven aging of a chemically crosslinked polyolefin cable insulation material [12]. Both OIT and OITP values drop in a reasonably linear fashion before any noticeable change occurs in the elongation results, indicating that they may be useful as a warning before the elongation suddenly begins to drop.

Solvent-swelling / gel fraction

Swelling and gel fraction measurements on crosslinked polymers are carried out by extracting a small sample under a refluxing solvent chosen to match the solubility parameter of the specific polymer. By measuring the initial weight of the material, its swollen weight and the subsequent weight of the swollen material after drying, one obtains both the gel fraction (final weight divided by initial weight) and the swell ratio (swollen weight over final weight). Degradation in the mechanical properties of polymers usually involves changes in molecular structure due to aging-induced chain crosslinking and/or aging-induced chain scission, both of which effect the gel fraction and swelling ratio. Figures 9 and 10 show swell ratio and gel fraction results versus elongation values for the same chemically crosslinked polyolefin material under the identical aging condition (125°C) discussed in Figs 7 and 8. Both swell ratio and gel fraction are clearly useful parameters for following mechanical degradation.

IR spectroscopy (with chemical treatment as appropriate)

Measurements of the infra red spectrum of organic materials is a widely used technique which provides information on chemical structure. In many cases, this technique allows a means of assessing whether degradation has taken place, and if so, can provide information on the nature and cause of the degradation. For example, degradation may lead to the formation of additional bands, i.e. carbonyl species, or to the consumption of others, i.e. loss in unsaturation. Other chemical changes, such as crosslinking or scission, may also be reflected in the spectroscopic data. In some cases, the IR spectrum is complex, and degradation peaks can be difficult to identify. Such things as fillers and pigments in the insulation, high absorbance of the polymers, and small sample size can complicate spectroscopic analysis. We have used IR micro-spectroscopy successfully in the past to evaluate chemical degradation of insulation and rubber materials [13,14]. This requires the microtoming of sample specimens for direct IR transmission analysis. To enhance band sensitivity and selectivity we have also utilized derivatization techniques with chemical gas exposure treatments, to either identify specific degradation species by shifting bands to new positions, or by increasing their overall absorbance intensity [15,16]. For example, key hydroperoxide intermediates, alcohols or other intermediates related to the degradation can be analyzed this way. Alternatively, very weak changes or changes next to large native IR bands can be analyzed with sophisticated chemometric approaches in order to more precisely identify and quantify the degradation. In the past we have applied multi-variate curve resolution (MCR) techniques, coupled with classical least square treatments that do not require pure components or standards for analysis, to polyolefin-based rubbers that are also used as cable insulation materials [17]. This procedure eliminates background noise and allows us to confidently deconvolute degradation bands to extract pure components and identify specific chemical degradation species. Another capability that is currently being investigated is the application of IR imaging transmission microscopy (Biorad Stingray) that would allow us to easily study heterogeneous degradation on small samples.

Chemiluminescence

Materials which are undergoing degradation in oxidative environments often form meta-stable (i.e., relatively unstable) chemical species which are intermediates in the chemical degradation process. The most important intermediates that are being formed during the early stages of the degradation are hydroperoxides. These hydroperoxides will decompose relatively easily and initiate further oxidation but also accumulate in relatively low concentrations. While their presence can signify the beginning of polymer degradation, they are difficult to quantify with traditional analytical techniques. Chemiluminescene, on the other hand, is capable of measuring the minute amounts of light given off by the sample caused by the thermal decomposition at elevated temperatures of the hydroperoxide intermediates. Detection is accomplished by a temperature-ramp exposure of the sample under nitrogen in the presence of a very sensitive photon counting device. This technique, though often less quantitative than some of the others described above, nevertheless provides one of the most sensitive indicators of incipient aging available for organic materials [18]. The degradation of polyolefin-based materials and polyamide polymers (nylon) has been studied extensively with this technique since they involve high concentrations of intermediate hydroperoxides [19]. However this approach is easily applied to any polymer with similar oxidation chemistry.

Thermo-oxidative Wear-Out Assessment

The initial objective of our program is to use the techniques described above and any other promising analytical methods in order to characterize the condition of cables removed from aircraft. The next stage would be to carry out and model accelerated aging experiments to make predictions of the expected lifetime of such cables. It is clear from some of the examples shown above (and other cases of "induction-time" behavior) that predictions of lifetime (or remaining lifetime) can be important even for materials that show little evidence of mechanical degradation after extended times in the field. We have spent a considerable amount of time over the past 20 years developing improved methods for collecting, analyzing and extrapolating accelerated aging results. For the interested reader, details and further references can be found in several publications [3,6,20]. We have recently been working on the development of a new predictive technique that we call the Wear-out approach [9]. This technique assesses the remaining life of samples of materials that have been returned from service applications by completing the aging under accelerated (e.g., elevated temperature) environments. This technique should be especially useful for the potentially difficult materials that show "induction-time" behavior. As such, we may apply this approach to selected samples in our initial screening study.

Preliminary results for aircraft wires

Although we have yet to receive the vast majority of the cable bundles removed from the first two aircraft in this program (Airbus-300 and Boeing-747), we have obtained a few short bundles from the Airbus and very recently from the 747. This has allowed us to at least do some initial screening tests to exercise our approaches. We have been able to successfully remove many of the insulations from their conductors, allowing elongation/tensile strength measurements to be made. It also appears that density measurements can be made on many of the materials, even on individual layers after careful separation. Infrared spectroscopy of the individual layers can often be done, although no evidence of aging (e.g., oxidation peaks) is apparent for the few materials looked at to date. Modulus profiling also looks applicable to at least some of these materials. We applied this technique for instance to a three-layer insulation from the Airbus (teflon-polyimide-teflon). After removing the insulation from its conductor, two 1-cm long sections of insulation were squeezed side-by-side between aluminum plates in our vise-holder. The holder was then metallographically polished, exposing the cross-section of the two insulation pieces. A photo looking down on the exposed cross-section is shown in Fig. 11, where the two dark loops are the polyimide (kapton) sections of the insulation (the lighter material inside and outside the polyimide is teflon). Our modulus profiling apparatus was then used to make modulus measurements at the 5 points marked on the photo; the results are shown in Fig. 12. Since aging can often have a large effect on modulus values, this technique may offer one of the better methods to follow potential degradation.

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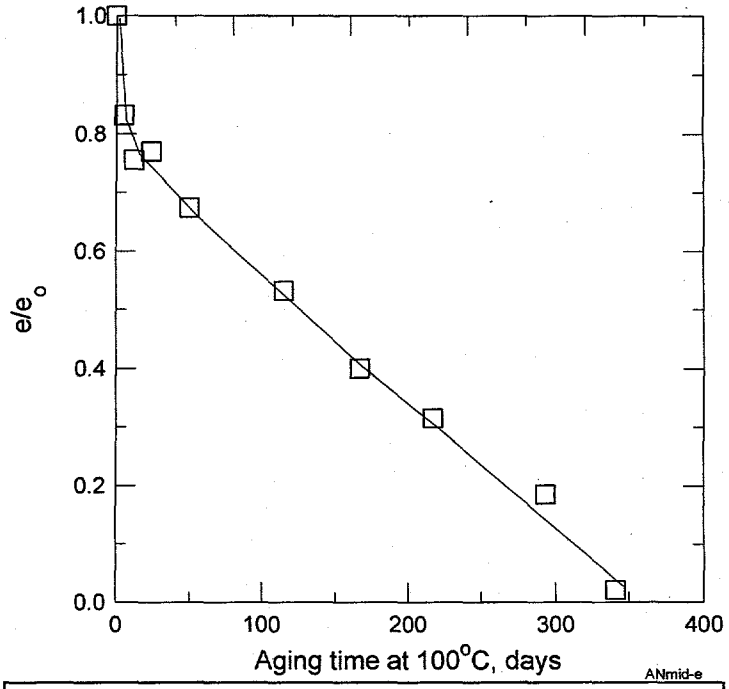

Figure 1. Normalized elongation versus aging time at 100°C for a CSPE cable jacket.

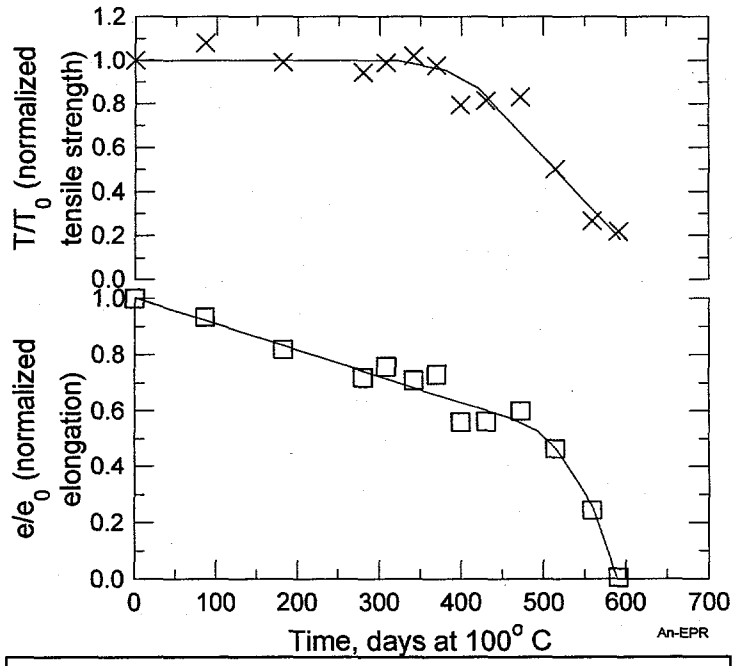

Figure 2. Normalized elongation and tensile strength versus aging time at 100°C for an EPR cable insulation material.

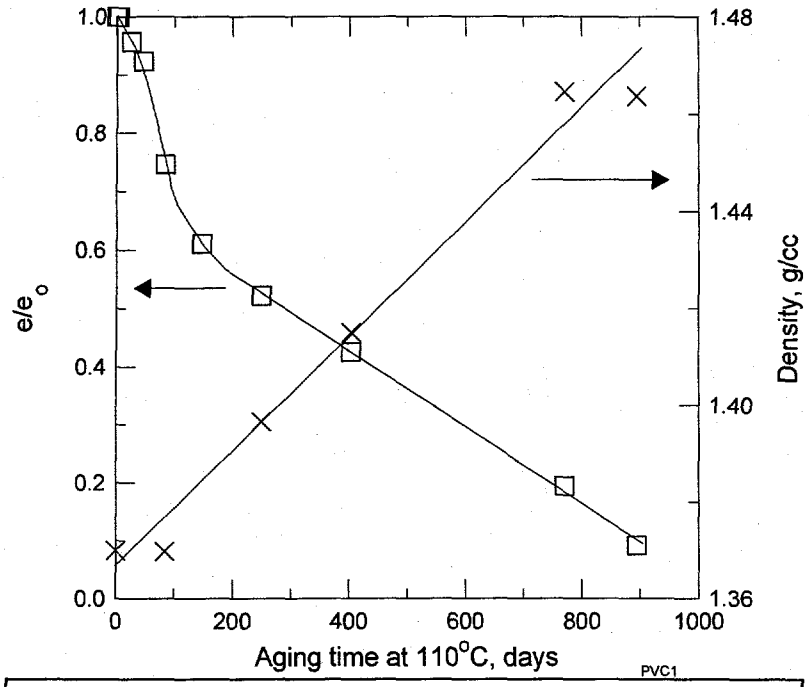

Figure 3. Normalized elongation and density versus aging time at 110°C for a PVC cable jacket.

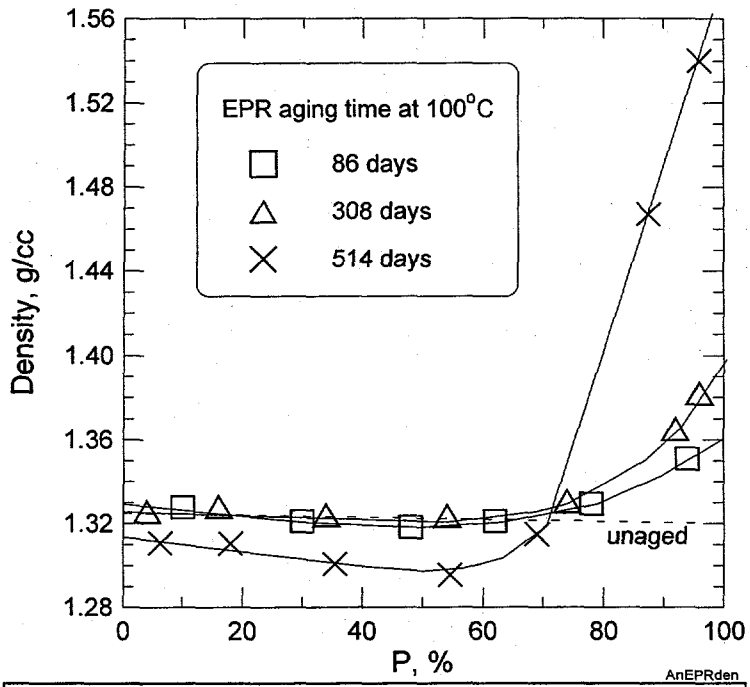

Figure 4. Density profiles for the EPR cable insulation at the three indicated aging times.

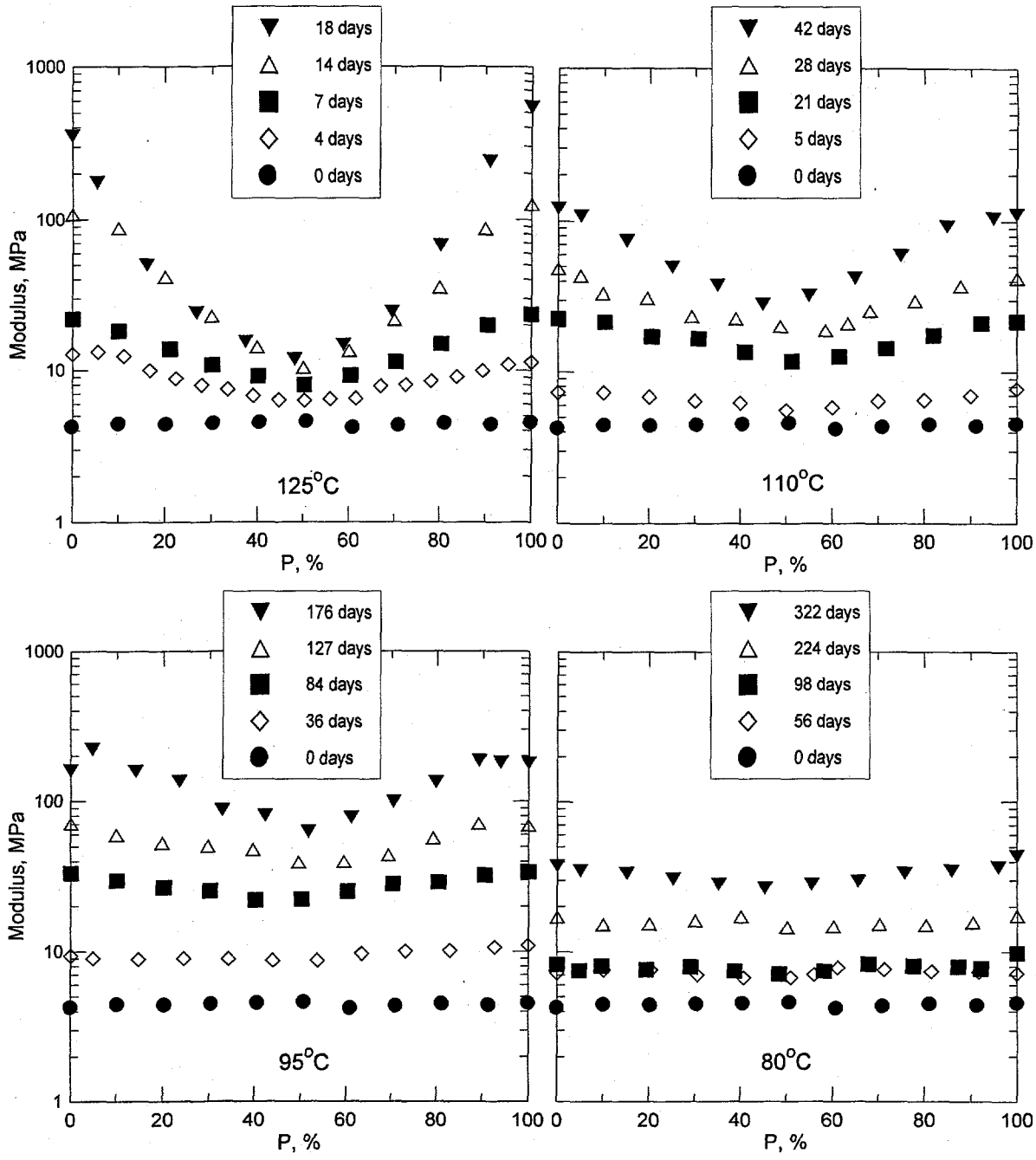

Figure 5. Modulus profiles versus aging time and temperature for a nitrile rubber material.

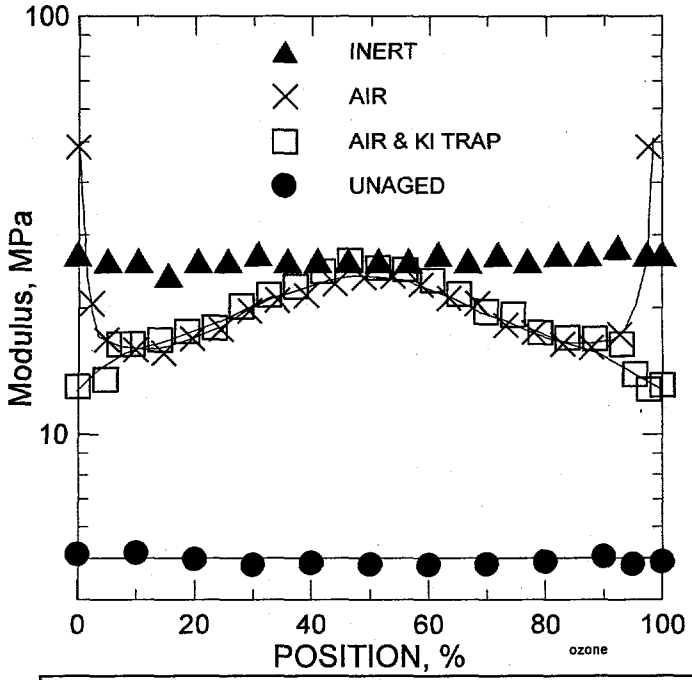

Figure 6. Modulus profiles for an SBR material after radiation aging under the indicated conditions.

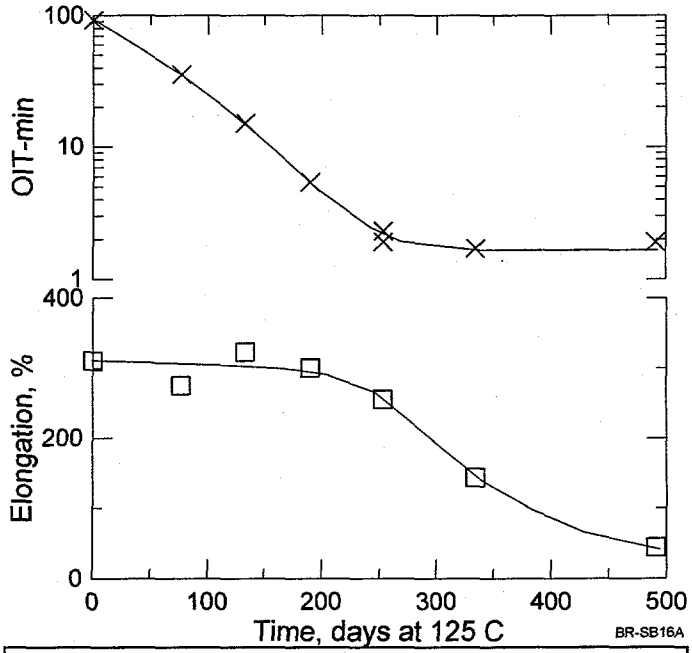

Figure 7. OIT and elongation versus aging time at 125°C for a CLPO cable insulation.

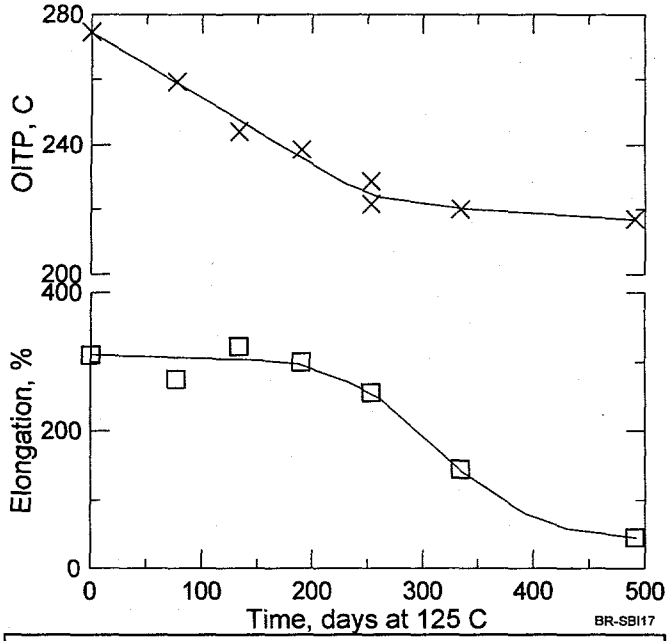

Figure 8. OITP and elongation versus aging time at 125°C for a CLPO cable insulation.

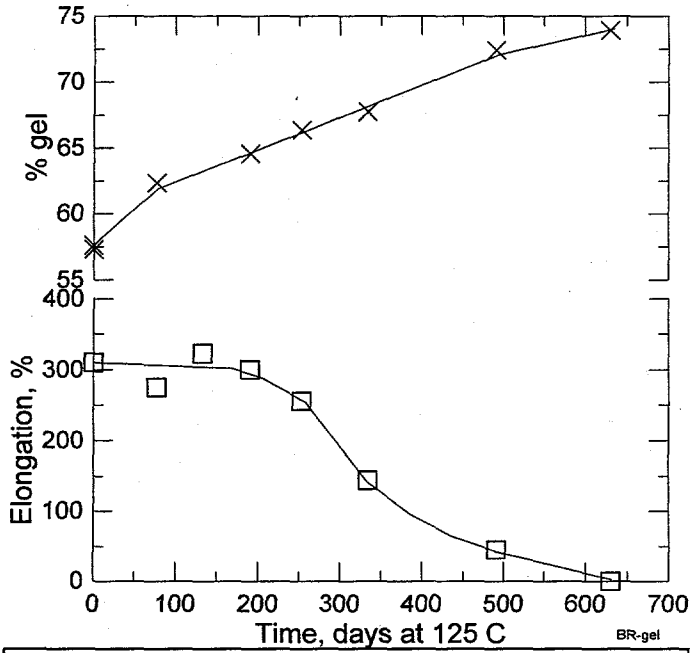

Figure 9. Percentage gel and elongation versus aging time at 125°C for a CLPO cable insulation.

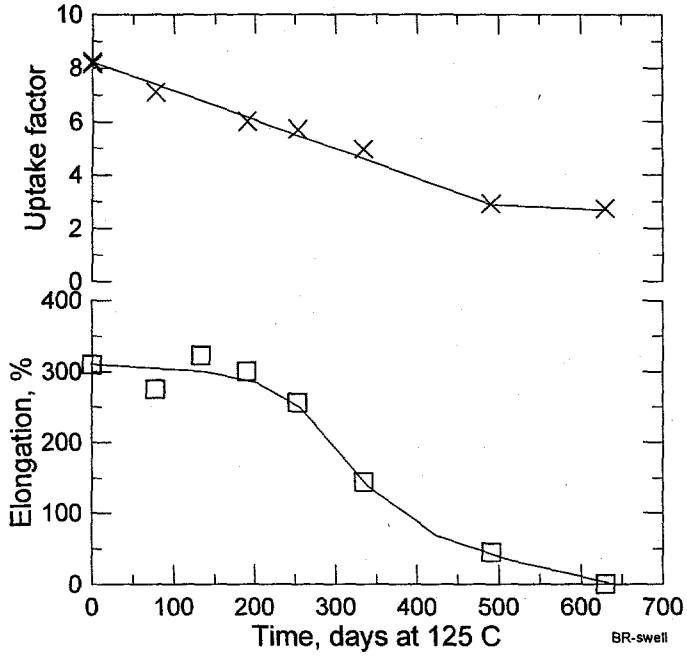

Figure 10. Swell ratio and elongation versus aging time at 125°C for a CLPO cable insulation.

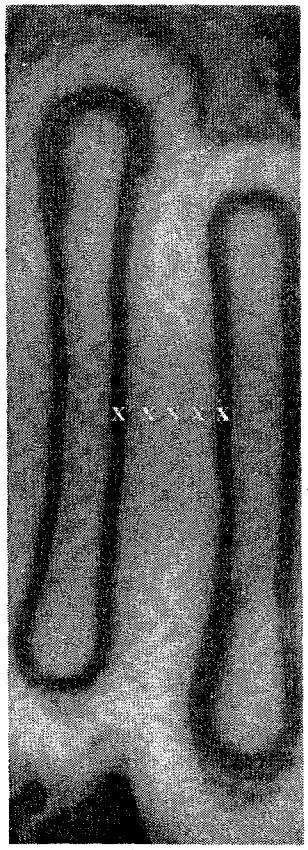

Figure 11. Photo looking down on polished cross-section of two side-by-side, three-piece insulations. The dark colored loops are polyimide layers and the surrounding lighter material is teflon. The five points marked with an x are the locations used for modulus measurements (shown in Fig. 12).

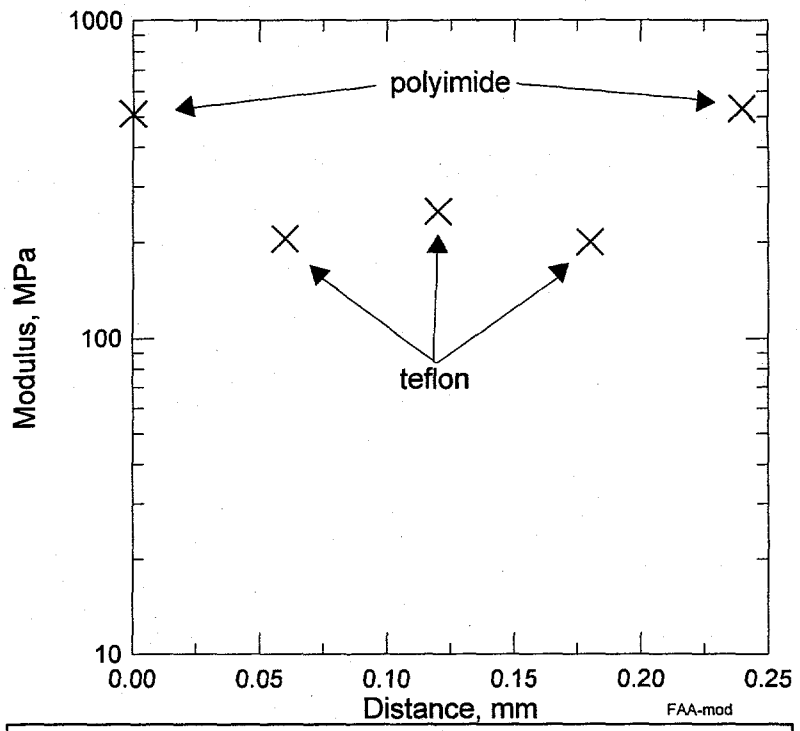

Figure 12. Modulus profile results for the material shown in Fig. 11.