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Prediction of Elastomer Lifetimes from Accelerated Thermal-Aging Experiments

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For elastomers that will be used in applications involving long lifetimes, it is often necessary to first carry out and model accelerated aging experiments at higher than ambient temperatures, and then extrapolate the results in order to make lifetime predictions at the use temperature. Continuing goals in such endeavors are to better understand potential problems with such modeling approaches and to find ways of improving confidence in the predictions when the data are extrapolated. In this paper we will address several important issues involved in these procedures for elastomers exposed to air (oxygen), and discuss some potentially useful techniques and approaches which can increase confidence in lifetime predictions.

Issue 1- Expectation of time-temperature superposition

The approach normally used to accelerate the oxidative aging of elastomers is to raise the air-oven aging temperature, thereby increasing the rates of the oxidative reactions which typically dominate the degradation. The reactions underlying oxidative degradation of elastomers can be extremely complex and usually have not been worked out in detail. Fortunately, variants[1] of the basic autoxidation scheme (BAS), derived many decades ago by Bolland[2], Bateman[3] and co-workers for the homogeneous oxidation of liquid hydrocarbons, have proved to offer reasonable approximations to elastomer degradation[4,5]. For illustrative purposes, we will use the simplified scheme shown below; it represents a first approximation for the oxidation of stabilized elastomers containing antioxidants (AH).

$$\begin{aligned}
\text{Elastomer} &\xrightarrow{k_1} \text{R}\bullet \\
\text{R}\bullet + \text{O}_2 &\xrightarrow{k_2} \text{RO}_2\bullet \\
\text{RO}_2\bullet + \text{RH} &\xrightarrow{k_3'} \text{RO}_2\text{H} + \text{R}\bullet \\
\text{RO}_2\text{H} &\xrightarrow{k_4} 2\text{R}\bullet + \text{ROH} + \text{HOH} \\
\text{RO}_2\bullet &\xrightarrow{k_5=k_5'[\text{AH}]} \text{Products} \\
\text{R}\bullet &\xrightarrow{k_6=k_6'[\text{AH}]} \text{Products}
\end{aligned}$$

DISCLAIMER

Analysis of this kinetic scheme under steady-state conditions for R• and RO_2• and ROOH leads to

$$\frac{d[O_2]}{dt} = \frac{C_1[O_2]}{1+C_2[O_2]} \tag{1}$$

where C_1 and C_2 are constants involving various of the kinetic rate constants[4,5]. The first important conclusion from the result shown in eq. (1) is that such kinetic analyses predict a constant rate of reaction under constant temperature conditions. This turns out to be a reasonable approximation for many stabilized elastomers. Figure 1 shows isothermal experimental oxygen consumption rate results versus aging time for three important elastomers[6,7]. For this plot, the time co-ordinate for the aging of each material is normalized to the time necessary for the ultimate tensile elongation to reach 10% of its initial value, which we arbitrarily define as the material's mechanical lifetime. The results show that the oxygen consumption rate is relatively constant over the entire mechanical degradation lifetime for all three materials.

When the oxidation is approximately constant throughout a material's mechanical property lifetime, an important consequence is the expectation that mechanical property degradation curves at any two temperatures will be related by a constant multiplicative factor representing the ratio of the two constant oxidation rates appropriate to the two temperatures. This means that degradation curves at different constant temperatures should have approximately the same shape when plotted versus the log of the aging time. Results consistent with such expectations can be seen in Fig. 2, which shows normalized elongation results (elongation divided by the elongation for the unaged material) for the nitrile rubber material aged at five temperatures.

The most common method of analyzing aging data, such as that shown in Fig. 2, involves first choosing some arbitrary failure criterion, for instance the time for the elongation to reach 25% of its initial value. A simple model for the results, such as the Arrhenius approach, is then tested by seeing if a plot of the log of the failure time versus inverse absolute aging temperature is reasonably linear. Unfortunately, this procedure uses only one processed data point from each curve, eliminating most of the experimental points from analysis. A consequence of the expectation that a constant multiplicative factor will relate each temperature pair is that the same functional relationship between time and temperature will hold regardless of where on the degradation curve one chooses to analyze (that is, if the results are Arrhenius at 25% of initial elongation, they should be Arrhenius at 50%, 75%, etc. with the same linear slope).

To test for the presence of constant multiplicative factors and for the relationship between time and temperature, the best approach involves the time-temperature superposition concept[6,8]. For this approach, we first select the lowest experimental temperature (64.5°C for the data shown in Fig. 2) as the reference temperature. Then, for each set of data at a higher temperature T, we multiply the experimental times at this temperature by a constant shift factor, a_T, chosen empirically to give the best overall superposition with the reference temperature data ($a_T = 1$ at the reference temperature). Figure 3 shows the results of using this procedure on the elongation results of Fig. 2, where the bottom x-axis gives the superposed results at the reference temperature of 64.5°C. The excellent superposition that occurs is not surprising, given the earlier observation that the raw experimental results at the various temperatures had similar degradation shapes when plotted versus log of the aging times. The next step is to determine whether a simple model can be used to explain the relationship between the empirically determined shift factors and the temperature. The most commonly used model involves the Arrhenius relationship, which would predict that

$$a_T = \exp \frac{E_a}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right) \tag{2}$$

where E_a is the Arrhenius activation energy. If Arrhenius is valid, a plot of the log of a_T versus the inverse absolute temperature should give linear behavior. Figure 4 shows that the elongation results for a_T (the crosses on the solid line labeled nitrile) are consistent with the Arrhenius assumption, with $E_a \sim 90$ kJ/mol, determined from the slope of the line through the results. To make predictions below the lowest experimental temperature of 64.5°C ($a_T = 1$), the normal procedure would then be to extrapolate the result (the dashed line extension). For instance, at around 25°C, the extrapolated a_T would be ~0.02, which would imply that this material would last ~50 times longer at this temperature compared to its lifetime at 64.5°C.

It is important to note that, unlike the normal Arrhenius testing procedure that may use only one processed data point from each curve, the time-temperature superposition procedure illustrated in Fig. 3 uses all of the raw data generated in the study. In addition, if time-temperature superposition is not found for a given set of data, the functional relationship between time and temperature must depend on the amount of degradation. This implies an oxidation rate (or other critical degradation-controlling process) that depends strongly on time as well as temperature, which makes modeling much more difficult and extrapolation of results extremely tenuous.

Issue 2- Diffusion-limited oxidation

At equilibrium in air environments, oxygen is dissolved in polymeric materials; its concentration is given by the product of the oxygen partial pressure surrounding the material and the solubility coefficient for oxygen in the material. During oxidative aging, this oxygen will react. If the rate of reaction uses up the dissolved oxygen faster than it can be replenished by diffusion effects from the surrounding air atmosphere, the oxygen concentration in the interior of the material will drop, potentially leading to reduced or non-existent oxidation in these regions. The importance of such effects will depend primarily on three factors, the oxygen permeability coefficient (equal to the product of solubility and diffusivity), the rate of oxygen consumption and the material geometry (e.g., sample thickness)[4,9,10]. It turns out that such diffusion-limited oxidation (DLO) effects are quite often observed for elastomers under typical accelerated aging conditions[4,6,11]. There are many experimental methods that can be used to screen for such effects[12]. One of the most useful for elastomers is modulus profiling[13], which involves an instrument that allows the modulus to be quantitatively mapped (typical experimental scatter of ±5%) across the cross-section of a material with a resolution of approximately 50 µm. Figure 5 shows modulus profiles across the 2-mm thick nitrile rubber material after aging for various times at the three highest accelerated aging temperatures[6]. The x-axis variable, *P*, gives the percentage of the distance from one air-exposed surface to the opposite air-exposed surface. At the highest aging temperature of 125°C, important DLO effects cause highly heterogeneous degradation to occur. Oxidative hardening is important at the sample surface, but becomes much less important in the interior regions. As the temperature is lowered, the rate of oxygen consumption goes down faster than the oxygen permeation rate, leading to reductions in the importance of DLO. At the lowest temperature of 64.5°C, where DLO effects are no longer important, the degradation gives steady, homogeneous increases in modulus[6]. Besides various experimental methods capable of monitoring DLO effects, it is now possible to theoretically model DLO and therefore estimate its importance before any accelerated aging experiments are initiated; the curves through the results in Fig. 5 in fact come from theoretical modeling studies of this material[6].

Given the importance of DLO for the aging of the nitrile material and its complex dependence on temperature, it is perhaps surprising that the elongation results for this material are so well-behaved, displaying both excellent time-temperature superposition and Arrhenius behavior. This turns out to be due to a fortunate circumstance, which occurs for the elevated temperature oxidation of many elastomeric materials[6]. As shown in Fig. 5, the oxidative hardening is maximum at the sample surfaces, where the oxidation is uninfluenced by the DLO effects. During tensile testing, cracks would be expected to initiate at the hardened surface. If such cracks immediately propagate through the rest of the material, the ultimate tensile elongation will be directly dependent on the true, equilibrium (non-DLO influenced) oxidation. This turns out to be the case for most materials where oxidative hardening dominates the degradation. Time-temperature superposition of the surface modulus results for the nitrile material leads to shift values (the diamonds on Fig. 4) virtually identical to those found for the elongation results, consistent with this picture.

For properties that depend upon the entire cross-section of a material, DLO effects will lead to anomalous results. For instance, time-temperature superposition turns out to be impossible to achieve for the tensile strength of the nitrile material, because it goes up at some temperatures and down at others[6]. This is expected since the tensile strength at break will represent the integrated force across the entire sample cross-section, implying complex behavior due to the changing importance of DLO as the temperature drops. In a similar fashion, since the decaying stress for compression stress relaxation experiments is integrated across the entire sample, it would be necessary to quantitatively understand the effects of DLO before such experiments could be interpreted or extrapolated.

Issue 3- Extrapolation of accelerated aging models

When accelerated aging experiments have been carried out such that DLO anomalies have been eliminated or understood, and the resulting data have been successfully fit to some model (e.g., Arrhenius) over the accelerated temperature range, the next step is to extrapolate that model (e.g., the Arrhenius line) beyond the experimental temperature range to the application temperature of interest. This is perhaps the weakest link in accelerated aging methodology, since it is quite possible that the slope of the Arrhenius line will change in the extrapolation region. There are many possible reasons for this change in slope, including such things as (1) a change in the dominant reactions at the lower temperatures (if present, this will usually cause a switch to a lower activation energy), (2) mechanistic changes caused by extrapolation through polymer transitions (e.g., across the crystalline melting point region of a semi-crystalline material), and (3) complications caused by the crystalization, evaporation, or surface blooming of antioxidants[14,15]. One way to minimize potential extrapolation errors is to minimize the extrapolation distance, by carrying out accelerated aging experiments down to the lowest practical temperature, usually dictated by the time allowed for the study. But even if the lowest accelerated aging temperature corresponds to mechanical property lifetimes of a year or so, an extrapolation factor of up to two orders of magnitude may still be required for long-term applications.

For all of the above reasons, it is desirable to have methods available that allow more confidence in extrapolated predictions. These methods must clearly involve ultrasensitive approaches that measure a property connected closely to the chemistry dominating degradation. One approach that we have developed for thermally oxidized elastomers involves oxygen consumption measurements based on gas chromatography techniques[5,6]. With experimental care, this approach results in sensitivity capabilities of better than 10^{-13} mol/g/s. For most elastomers, this sensitivity allows measurements to be made at temperatures corresponding to expected mechanical property lifetimes of greater than 100 years. For the nitrile rubber material, conventional mechanical property measurements were made at temperatures down to 64.5°C; under these conditions, mechanical deterioration required more than 2 years of aging (Fig. 2). The sensitivity of our oxygen consumption method allowed rates to be measured from 96°C all the way down to ambient (23°C). The results were integrated and time-temperature superposed at 64.5°C in order to get shift values versus temperature. These are plotted as triangles for the nitrile data on Fig. 4. By superposing at 64.5°C, we could immediately see that the higher temperature oxygen consumption results were consistent with the mechanical property shift values, which offers compelling evidence that the two properties are dependent on the same underlying chemistry. Since the oxygen-consumption shift factors at the three lowest temperatures (52°C, 40°C and 23°C) are reasonably consistent with an unchanged Arrhenius slope (dashed line) in the extrapolation region, these results offer increased confidence in the viability of a linear extrapolation for the nitrile material. Therefore, we can utilize the oxygen consumption shift factor at 23°C to shift the 64.5°C time scale shown at the bottom of Fig. 3 to allow extrapolated mechanical property predictions at 23°C. From the resulting 23°C time scale (top x-axis in Fig. 3), we predict greater than 100 year mechanical property lifetime at ambient temperatures.

Conventional aging experiments were also run on an EPDM material down to 111°C, which corresponds to a mechanical property lifetime of ~2 years. Time-temperature superposition at that temperature was performed for several degradation parameters, including tensile elongation, modulus, density and the decay in compressive force for mechanically strained samples. The resulting shift factors from all of these measurements were in excellent agreement and indicated Arrhenius behavior with an activation energy of 118 kJ/mol for temperatures of 111°C and above (Fig. 4). Oxygen consumption measurements at 111°C and above gave shift factors consistent with the conventional results, but a change in mechanism led to an activation energy reduction to ~82 kJ/mol below 111°C[5]. Thus, the application of the oxygen consumption technique to temperatures lower than those used in the mechanical-property-change experiments leads to the conclusion that a straight-line extrapolation of the mechanical property data is not warranted. This result indicates the potential dangers inherent in extrapolating beyond the range of the data without some sort of confirmatory evidence.

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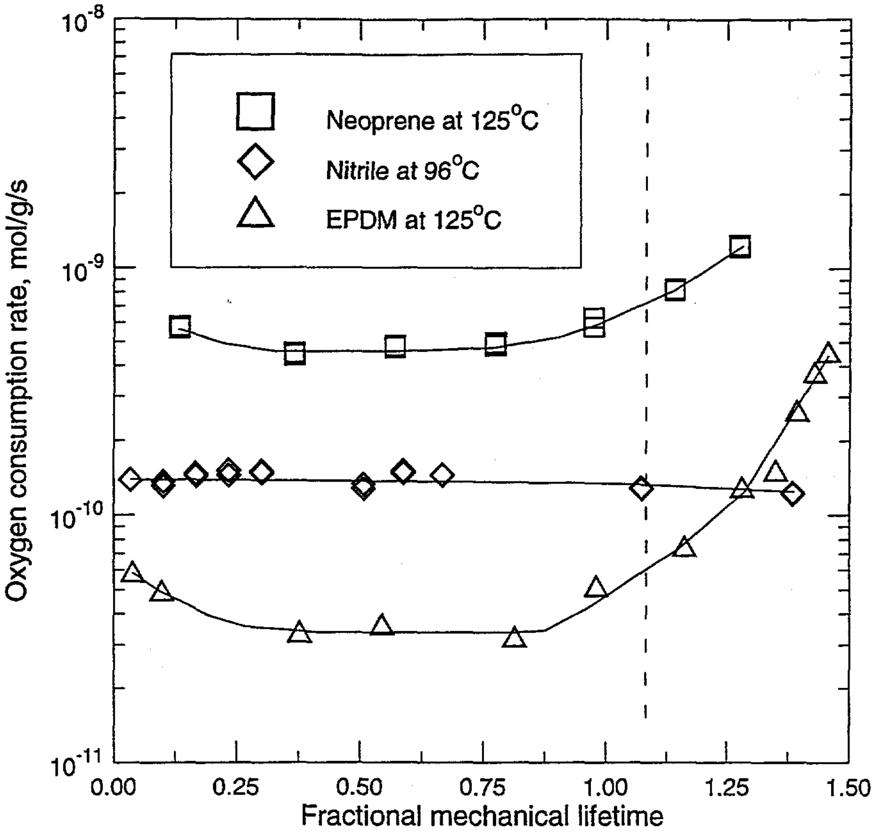
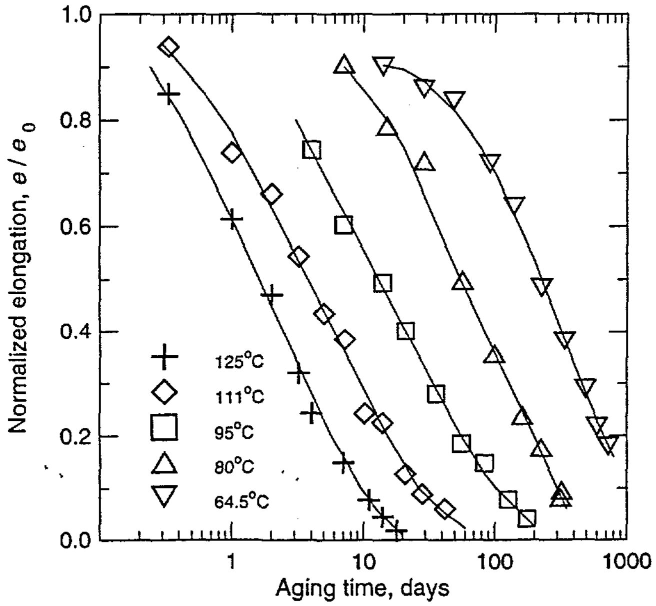


Fig. 1. Oxygen consumption rates for the three indicated materials and aging conditions. For each material, the results are plotted versus the fractional mechanical property lifetime (the aging time divided by the time required for the ultimate tensile elongation to reach 10% of its initial unaged value).



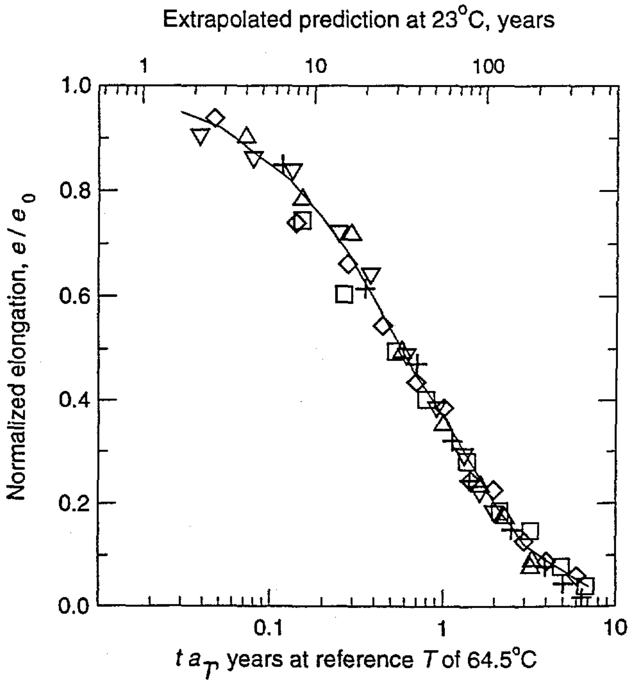


Fig. 2. Normalized elongation results for the nitrile rubber material versus time at the five indicated temperatures.

Fig. 3. Empirical time-temperature superposition of the Fig. 2 results at 64.5 C (lower x-axis). The upper x-axis gives extrapolated predictions at 23 C.

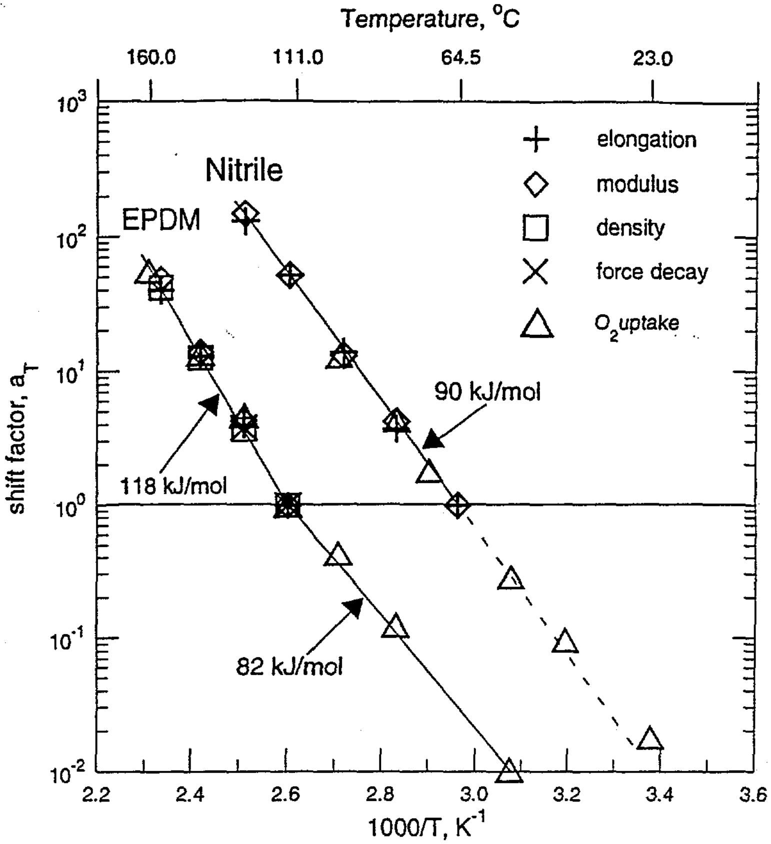


Fig. 4. Arrhenius plots of shift factors obtained from empirical time-temperature superpositions of various degradation parameters for a nitrile and an EPDM material.

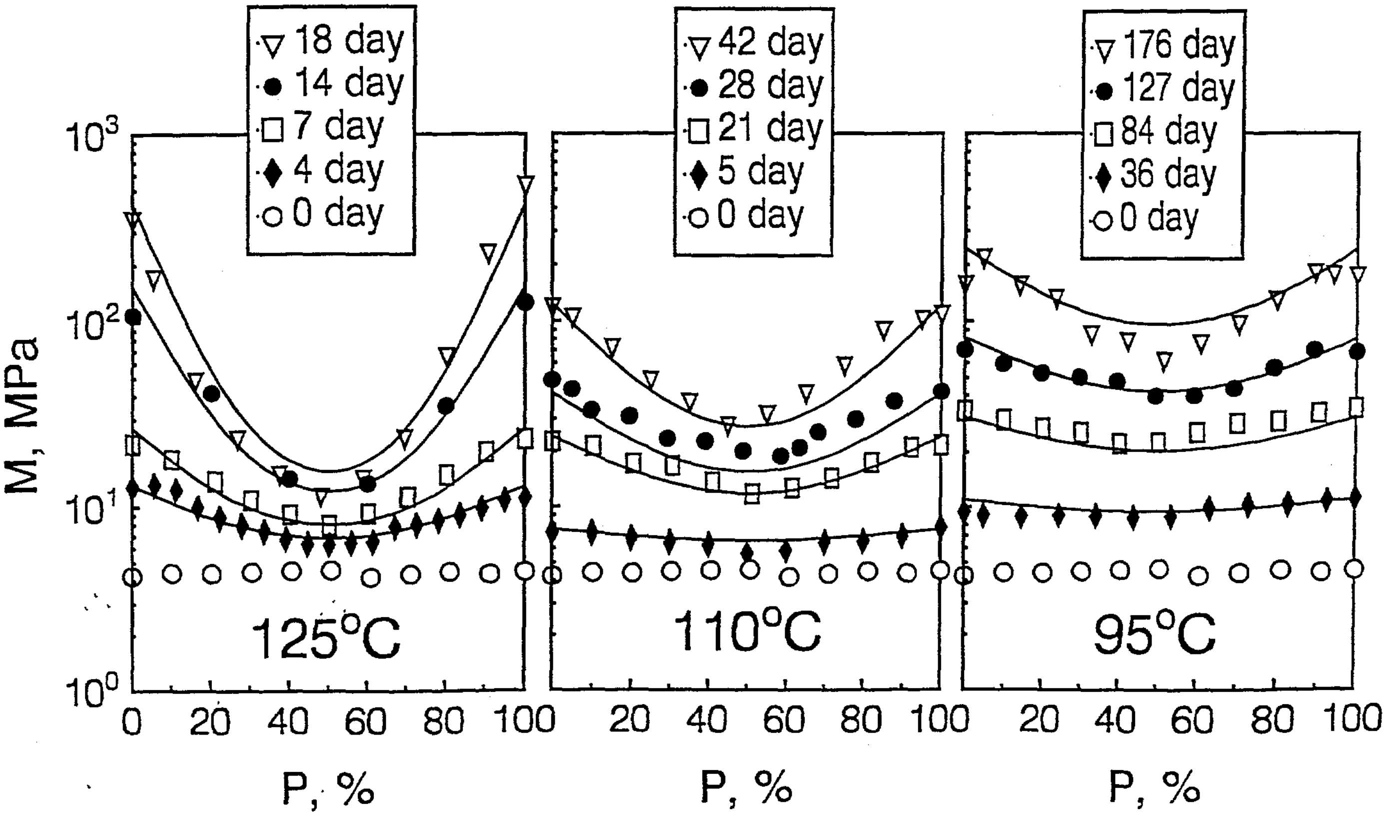


Fig. 5. Modulus profiles for a 2-mm thick nitrile rubber material versus aging time at the three indicated temperatures.