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A CRITICAL ASSESSMENT OF THE ARRHENIUS OVEN-AGING METHODOLOGY*

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The Arrhenius approach assumes a linear relationship between the log of the time to a certain amount of material property change and the inverse absolute temperature (the Arrhenius activation energy, E_a, is defined from the slope of the line). This model has been used for many years to extrapolate accelerated oven-aging data to lower temperature conditions. Although, at first glance, Arrhenius behavior seems to be valid in many instances, closer examination leads to some troubling concerns for most data sets. For instance, in studies of elastomers, ultimate tensile elongation results are often used to "confirm" Arrhenius behavior, even though the ultimate tensile strength data available from the same mechanical property testing (typically not given) are definitely non-Arrhenius. In addition, many researchers will overprocess their data by using a single "failure" criterion for their Arrhenius plot (e.g., a 50% drop in the elongation), thereby eliminating most of their data and significantly depreciating the value of any conclusions.

In recent years, we have been critically examining the Arrhenius approach in order to better understand its capabilities and limitations.[1,2] This paper describes some recent advances in our understanding which help resolve the type of concerns described above. Figure 1 shows normalized elongation results versus air-oven aging temperature for a 1.9-mm thick nitrile rubber (NR) material. We attempt an empirical Arrhenius shift of all the raw data to 50°C, using various trial activation energies, and find that a shift factor based on a constant E_a of 22 kcal/mol (e.g., independent of degradation level) leads to excellent time-temperature superposition, as seen by the results shown in Fig. 2. However, use of the same shift factor for normalized tensile strength (TS) data does not result in superposition (Fig. 3). In fact, the TS data could never be superposed since the TS tends to drop in the later stages at high temperature, whereas it tends to increase at lower temperatures. Such behavior definitely indicates that changes occur with temperature in the dominant chemical reactions underlying the degradation, contrary to the assumptions of the Arrhenius methodology.

We are therefore left with a dilemma as to why the Arrhenius approach appears to work so well for the elongation, but not for the TS. This dilemma can be resolved through the use of modulus profiling data. Our modulus profiling apparatus[3] allows us to quantitatively map modulus values across the cross-section of degraded samples with a spatial resolution of approximately 50 μm. Representative modulus profiles for the NR material at selected aging times are shown in Fig. 4 for the three indicated aging temperatures. At the highest temperature of 125°C, heterogeneity in the modulus is evident at the earliest aging times and becomes quite pronounced later on. This effect is caused by diffusion-limited oxidation (DLO) in which the rate of oxygen consumption within the material is greater than the rate at which it can be replenished by diffusion from the surrounding air atmosphere.[1,2] For aging experiments at lower temperatures (Fig. 4), the importance of DLO effects at early aging times becomes less significant. This occurs because there is a comparatively larger decrease with temperature (higher E_a) in the oxygen consumption rate compared to the oxygen diffusion rate. Later in the degradation, however, hardening (modulus increases) in the material leads to a significant reduction in the oxygen diffusion rate,[2] resulting in the delayed appearance of heterogeneity, caused again by DLO effects. Given this complexity, it is now easy to rationalize the TS results shown in Fig. 3: TS is a property which depends upon the force at break <u>integrated</u> over the cross-section of the material, and NR samples aged at different temperatures clearly experience very different degrees of degradation in their interior regions.

The modulus values at the sample <u>surfaces</u> are, however, not affected by DLO anomalies. Figure 5 shows results for the edge modulus values of the NR material versus time and temperature. Similar to the procedure used for the elongation results in Fig. 2, we can shift the edge modulus values to a 50°C reference temperature using an Arrhenius shift factor with its value of E_a adjusted until the best superposition results. It turns out, as shown in Fig. 6, that the best superposition occurs for an E_a of 22 kcal/mol. Since this must represent the E_a appropriate to the underlying degradation reactions and since this value is exactly the same as that found earlier for the elongation, it is now clear why Arrhenius behavior occurred for elongation. When a material is tensile tested, cracks can be expected to initiate

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first at the hardened, oxidized surface; if such cracks quickly propagate through the remainder of the material's cross-section, the elongation value will be dominated by the surface degradation. Further evidence that changes in edge modulus determine the elongation results can be seen in Fig. 7, which shows the experimental correlation for these properties. These results indicate that severe mechanical degradation ($e/e_0 \sim 0.1$) will occur when the edge modulus value increases by approximately an order of magnitude.

[1] K. T. Gillen and R. L. Clough, Polym. Degrad. & Stabil. **24**, 137 (1989).
[2] R. L. Clough and K. T. Gillen, Polym. Degrad. & Stabil. **38**, 47 (1992).
[3] K. T. Gillen, R. L. Clough and C. A. Quintana, Polym. Degrad. & Stabil. **17**, 31 (1987).

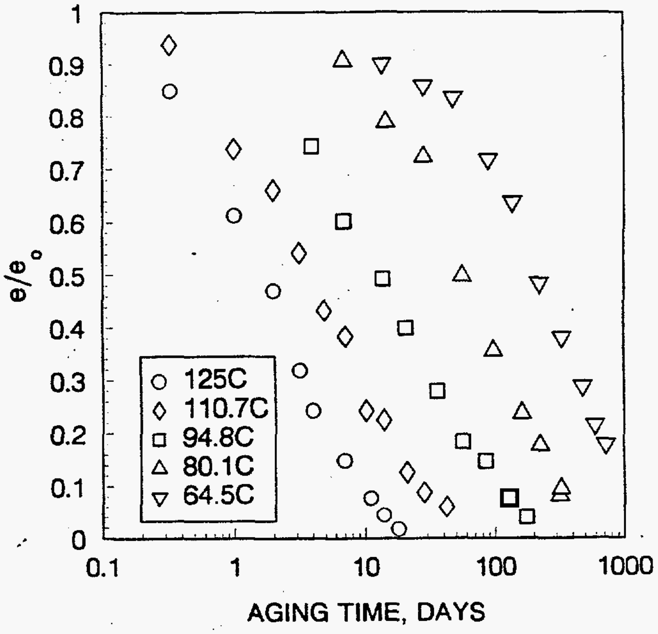

Fig. 1. Ultimate tensile elongation divided by its unaged value (e/e_0) versus aging time in air at the indicated temperatures for the NR material.

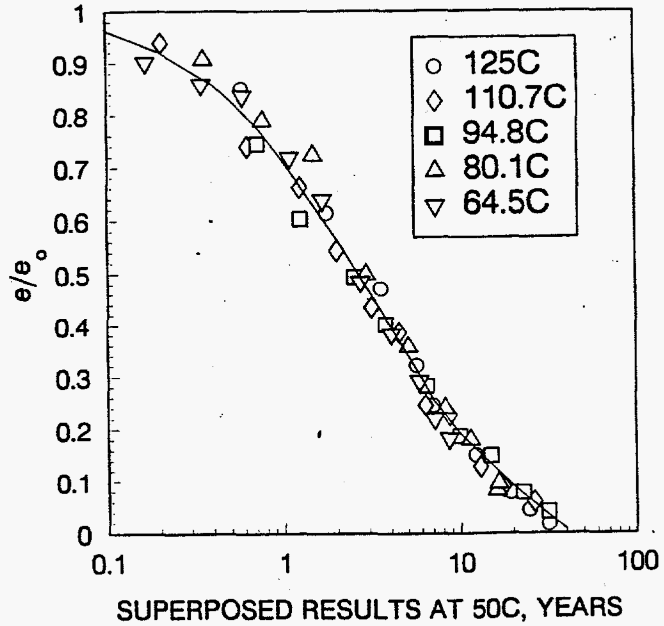

Fig. 2. Time-temperature superposition of the NR e/e_0 data from Fig. 1 using an Arrhenius activation energy of 22 kcal/mol (see Ref. 1 for details).

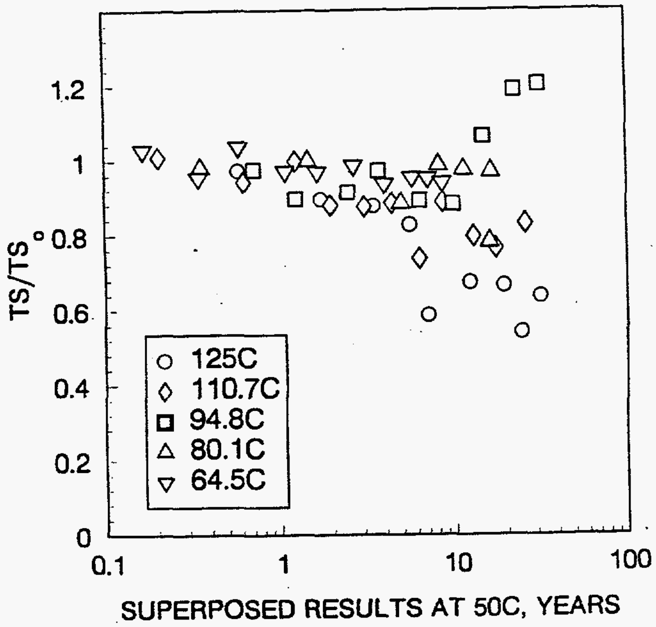

Fig. 3. Time-temperature superposition of the NR normalized TS data using an Arrhenius activation energy of 22 kcal/mol (see Ref. 1 for details).

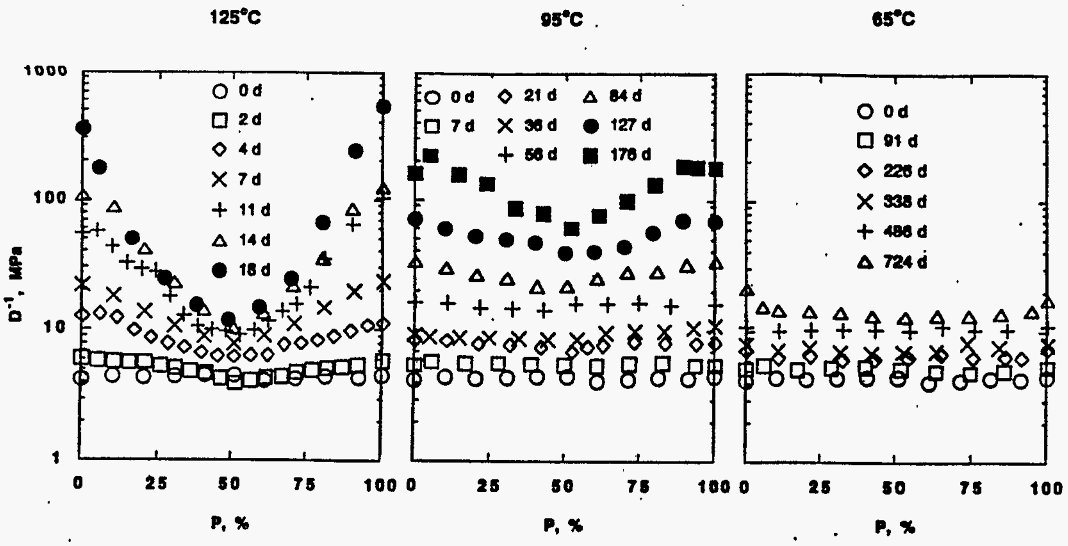

Fig. 4. Modulus profiles for the 1.9-mm thick samples of the NR material after air-oven aging for various times at the indicated temperatures. The abscissa, P, refers to the percentage of the total distance from one air-exposed sample surface to the opposite air-exposed surface.

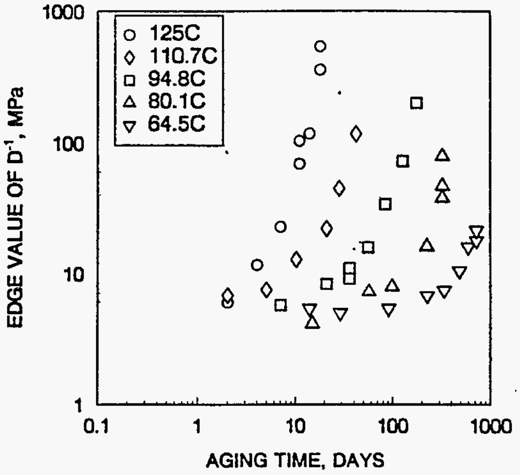

Fig. 5. Edge modulus values for the NR material versus aging time and temperature.

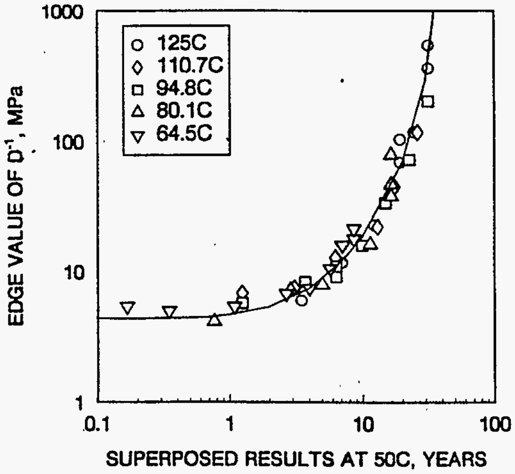

Fig. 6. Time-temperature superposition of the edge modulus values from Fig. 5 using an Arrhenius E_a of 22 kcal/mol.

Fig. 7. Normalized elongation (e/e_0) plotted versus the normalized edge modulus value for the NR material at the indicated temperatures.