# NOTES

## *Activation Energy for Creep to Failure*

### INTRODUCTION

An understanding of the lifetime of a polymer under load is of importance from both a fundamental and practical viewpoint. Practically, it can lead to the prediction of long-time behavior from short-time laboratory tests.

Zhurkov[1] and his co-workers have studied extensively the relationship between the lifetime of solids under load and the magnitude of the tensile stress and temperature. They have shown that Plexiglas, as well as several other polymers, exhibit a stress dependency term in the activation energy for creep to failure. The purpose of this communication is to show that this stress-dependent term for Plexiglas is an environmental factor.

### EXPERIMENTAL

Dogbone-type specimens of nominal cross section 0.286 in. × 0.067 in. in the gauge section were creep tested in air and under vacuum at several temperatures. Thermocouples in close proximity to the sample regulated furnaces and monitored sample temperatures.

Under vacuum, a load cell was incorporated in the load train. After attaining vacuum ($\sim 10^{-5}$ torr) and temperature stabilization, the samples were loaded and the time to failure measured.

### RESULTS AND DISCUSSION

Figure 1 shows the results for Plexiglas in both air and under vacuum. The broken lines are the results in air and the solid lines are those under vacuum. It can be seen that the results in air are very similar to the results of Zhurkov[1] and follow the equation

$$\tau = \tau_0 \exp\left(\frac{U_0 - \gamma\sigma}{kT}\right) \tag{1}$$

where $\tau$ is the time to failure, $\tau_0$ is a constant, $k$ is Boltzmann's constant, $T$ is the absolute temperature, $U_0$ is the activation energy in the absence of stress, $\sigma$ is the applied load, and $\gamma\sigma$ is the work put into the system which lowers $U_0$ to the observed value of the activation energy.

The vacuum results (solid lines with data points) show that the creep-to-failure process is considerably simplified. The slopes of the lines at various temperatures are parallel in contrast to the converging slopes for the air run tests. The stress dependency of the activation energy has been removed, i.e., $\gamma = 0$, and

$$\tau = \tau'_0 \exp(U/kT). \tag{2}$$

In Figure 1, the solid circles are tests where the sample was first exposed to vacuum for times of 24 to 96 hr before load was applied to the sample. It can be seen that once the environment is removed from the surface of the sample, further exposure to vacuum has no effect. This implies that the mechanism of creep in air is associated with reactions at new surfaces produced by "crazing" by application of load. With increasing loads,

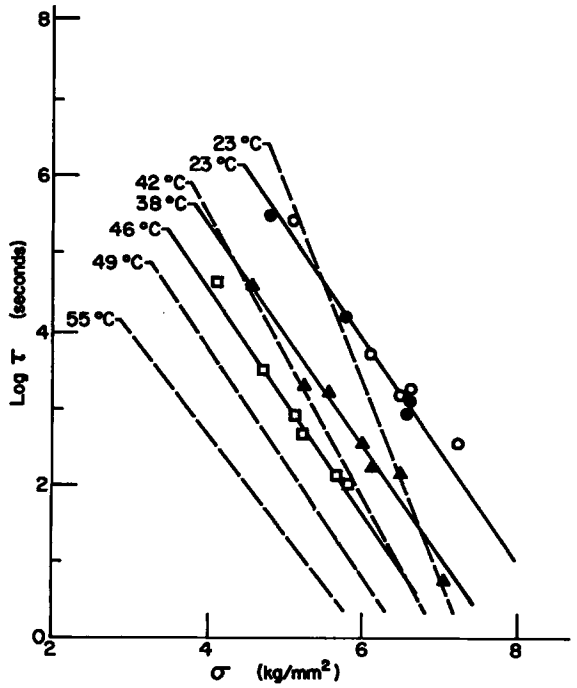


Fig. 1. Time and temperature dependence of the lifetime of Plexiglas under stress. Broken line: air results; solid lines with data points: vacuum results.

more "crazing" is obtained with subsequent increase in reaction which decreases the observed activation energy via $U = U_0 - \gamma\sigma$.

The activation energy for the results under vacuum depicted in Figure 1 is 45 kcal. The activation energy for thermal decomposition under vacuum (as measured by weight loss[2]) for this Plexiglas is also 45 kcal. The latter process is associated with the breakage of bonds in the absence of oxidative reactions. Creep to failure under vacuum also involves nonoxidative bond fracture so that the equality of activation energies may be more than fortuitous. Therefore, it is here suggested that the reaction occurring at the "crazing" sites in air is oxidation rather than possible effects of moisture.

Preliminary results in air for Lexan show that this material follows eq. (1).

## References

1. S. N. Zhurkov, Proceedings of the First International Conference on Fracture, Sendai, Japan, 1965.

2. H. A. Papazian, *J. Appl. Polym. Sci.*, **16**, 2503 (1972).

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