

## Time Dependence of Polymer Strain in Air and Under Vacuum

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### Synopsis

Creep tests were carried out in air and under vacuum for three polymers. The results, along with earlier Lucite work, show that not all polymers have stress-dependent activation energies for the creep process, and in some cases the stress dependent term is associated with the environment of the polymer. Surface effects related to oxygen were found for the materials discussed here.

### INTRODUCTION

From the study of time to failure of polymers under uniaxial tension at various stresses and temperatures, it is generally assumed that the activation energy for the process is a stress-dependent function.<sup>1-3</sup> It has also been stated that the influence of humidity is small, and therefore the time dependence of the strength of these materials under vacuum and in air is the same.<sup>2</sup> It is the purpose of this communication to show that these assumptions are not true generally.

A preliminary account<sup>4</sup> of this study showed the deviations of the methyl methacrylate Lucite from the assumptions. In air, it follows the assumed equation for the time dependence of the strength of polymers:

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

where  $\tau_0$  is a constant,  $\sigma$  is the applied stress,  $\gamma$  is a coefficient that depends on the material,  $U_0$  is the activation energy in the absence of stress, and  $\gamma\sigma$  is then the work put into the system that lowers the activation energy  $U_0$  to the observed  $U = U_0 - \gamma\sigma$ . In vacuum, however, Lucite follows the simplified equation

$$\tau = \tau_0' \exp\left(\frac{U'}{RT}\right). \quad (2)$$

This result requires modification of the underlying arguments used for the justification of eq. (1). Here, the work has been extended to other polymers, and the results bring into question all of the assumptions mentioned above.

## EXPERIMENTAL

Commercially available materials were cut to dogbone samples nominally  $1/16 \times 1/4 \times 1 1/2$  in. in the gauge section.

A load cell was incorporated into the load train. A small furnace enveloped the sample and thermocouples in close proximity to it, monitored the temperature, and controlled the furnace. The system pressure for the vacuum tests was nominally  $\sim 5 \times 10^{-5}$  torr. When temperature equilibrium was attained (about 20 min in air and 60 min under vacuum), the samples were loaded and the time measured. For Lucite, reported on earlier,<sup>4</sup> the time measured was time to failure. The materials reported on here did not fracture since extension was limited to about 14% in the gauge section by the travel available to the load train.

## RESULTS AND DISCUSSION

Figure 1 shows the results obtained for the acetal Delrin in air and under vacuum. As with Lucite, the stress dependence term in the activation energy is removed in the tests carried out under vacuum, i.e., the slopes of

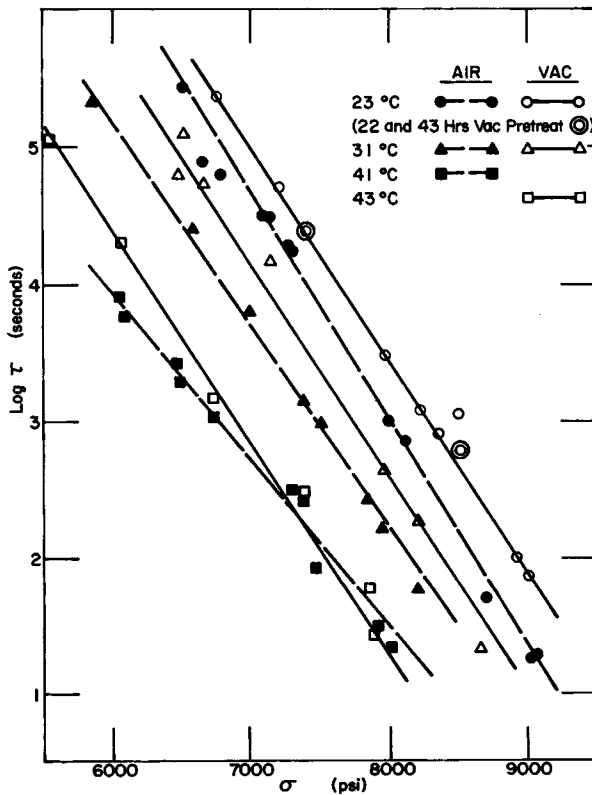


Fig. 1. Temperature dependence of creep time (see text) of Delrin under stress in air and under vacuum.

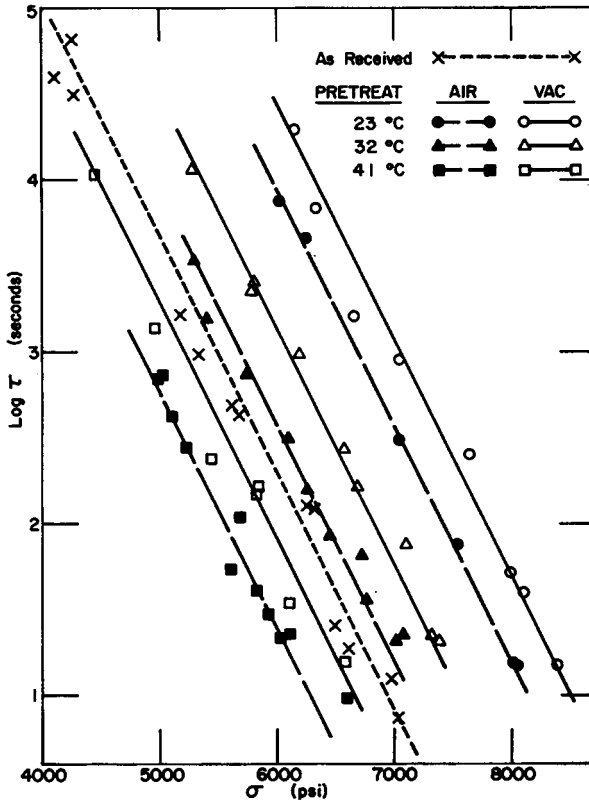


Fig. 2. Temperature dependence of creep time (see text) of cellulose acetate under stress in air and under vacuum.

the lines at the several temperatures are parallel, in contrast to the converging slopes for the air run tests. Also similar to Lucite, vacuum pretreatment prior to loading has no effect. This is shown by the double open circle points at 23°C. These points are the results for maintaining the sample under vacuum for 23 and 43 hr prior to loading. This implies that the behavior is controlled by eq. (2) immediately upon removal of air from the surface of the sample.

In Figure 2 are shown the results for cellulose acetate. The crosses with the broken line are the results in air with "as received" material. During tests under vacuum, it immediately became apparent that out-gassing of the material was important. Therefore, all samples were vacuum treated at ambient temperatures for several days. This resulted in an improvement in the ambient air test over the "as received" material [compare (X) with (●)]. If samples are then exposed to room environment overnight, the data revert to the "as received." Apparently, moisture is important in the creep behavior of this material. All data in the figure, except for the "as received," are for vacuum-pretreated samples. It can be seen that all

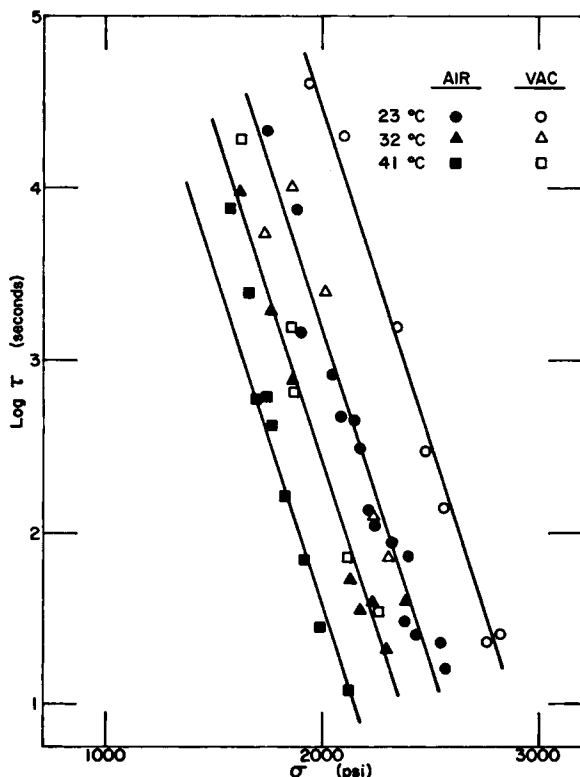


Fig. 3. Temperature dependence of creep time (see text) of polystyrene in air and under vacuum.

slopes are parallel, and thus, cellulose acetate is governed by eq. (2) in air as well as under vacuum.

It should be noted that there is also a surface effect. There is an improvement in behavior (as given by  $\tau$ ) under vacuum as compared to the air tests [compare (○) with (●)].

Figure 3 shows the results for polystyrene. It can be seen that in both air and under vacuum the results are governed by eq. (2), i.e., there is no stress-dependent term in the activation energy. Comparison at ambient temperature of the results in air with those under vacuum shows an improvement in behavior under vacuum [compare (○) with (●)]. Thus, for this material, also, there is a surface effect.

In Table I, the activation energies for the above physical tests are compared with those for thermal decomposition, both processes measured under vacuum. (The results for Lucite are from the earlier study.) The activation energies for the creep process are calculated by the usual methods<sup>2</sup> and those for thermal decomposition, from thermogravimetric analysis (TGA) described earlier.<sup>5</sup> If more than one activation energy is obtained from TGA, the one over the lowest temperature range is used in

TABLE I  
Comparison of Activation Energies Determined under Vacuum

Material	Activation energy, kcal	
	From creep	From thermal decomposition
Polystyrene	48	51
Delrin	45	50
Cellulose acetate	61	57
Lucite	43	43

Table I in order to most nearly coincide with the temperature range for the creep tests. The correlation between activation energies is very good.

Zhurkov<sup>1</sup> has compared  $U_0$  of eq. (1) with "the bond rupture energy  $E$  in thermal destruction of polymers for a number of polymers tested for their lifetimes as plates or fibers." It is not clear what the phrase in quotes describes, but if it is thermal decomposition as measured by weight loss, his results are contrary to those reported here. His studies were done in air, and he finds similar values for  $U_0$  and  $E$ . No such correlation was found for air tests between creep and thermal decompositions reported on here.

The correlation found between the values for vacuum studies may be intuitively understood by considering both processes to involve nonoxidative bond rupture. It is considerably more difficult to consider oxidative thermal decompositions as similar to creep in air.

Equations (1) and (2) are of a more general usefulness than usually assumed. They can be used for determining time to a fixed strain as well as time to failure. The assumptions (outlined in ref. 2) concerning environmental effects on polymer behavior and the arguments used to justify eq. (1) clearly must be questioned.

### References

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