

NOTES

Comments on "Investigation of Creep Phenomena in Polyethylene and Polypropylene"

I wish to draw attention to several misprints, errors, and omissions in the paper recently published under the above title.¹ On page 1000, no distinction is drawn between ΔH in eq. (1), the "activation energy," and $\Delta H'$ in eq. (4), the "energy of activation." It is stated that $\Delta F = \Delta H' - T\Delta S$, but ΔS is not defined. Can it be a change of entropy, even though S is later used for at least one other variable? On page 1001, S and S' are defined as "the stress levels involved," but by page 1007, S has become a "structure factor."

On page 1002, both polyethylene and polypropylene are reported as undergoing, as a result of deformation, "a change from an amorphous or random material to that of a material showing orientation which can almost be called crystalline." Would the authors please give details of how they obtained amorphous polyethylene, and amorphous polypropylene which was not an atactic gum? These materials are normally crystalline even if quenched immediately after moulding or extrusion. Deformation does cause orientation of existing crystallite structure, but the amount of orientation would probably be small in strains of the order of 0.1, where most of the deformation is recoverable. Were any measurements made of the development of birefringence with strain? (Some typical results have been given in Figure 3 of a recent paper by Hadley, Pinnock, and Ward.²)

No mention is made of the way in which the test specimens were annealed or mechanically conditioned prior to measurements being taken. My own work^{3,4} has not provided the only statement of the necessity for the specimen to be in an equilibrium state prior to testing. A conditioning treatment is particularly important in the case of polypropylene, where the initial cycle of deformation may be completely unreliable unless a prolonged and careful annealing process is performed.

In some as yet unpublished work on the temperature dependence of creep in polypropylene, I find that above about 30°C the specimens may never reach a complete equilibrium, even at strains of the order of 0.01, where the permanent set is negligible after the first few deformation cycles, despite annealing and continuous cycling for periods up to several months. In such circumstances the interpretation of creep curves is fraught with dangers and difficulties, which may be somewhat reduced at small strains by carrying out all measurements on a single sample, conditioned as fully as possible at the maximum experimental temperature.

Equation (11), page 1006, is in error; it should read:

$$\dot{\epsilon} = S e^{-(\Delta H' - B\sigma)/RT}$$

and the ordinates in Figures 6 and 7 should read "true strain" rather than "true stress."

In extrapolating the experiments to zero stress, use is made of the expression

$$K = S e^{B\sigma/RT}$$

which is valid only at high stresses. Is such a procedure justifiable, or would a more meaningful analysis result from using $K = S'\sigma^n$? In Figure 10, the activation energy is obtained by linear extrapolation of measurements at high stresses. I see no reason why the extrapolation should be linear down to zero stress.

Finally, even if all the assumptions made are valid, the activation energy is obtained by a considerable extrapolation of only a few experimental points. Could some limits of error be given in the cited values of 21.5 and 12.1 kcal/mole?

I can find no citation in the text to references 8 and 9, and the authors' initials in reference 2 are incorrect.

References

1. J. E. Sinclair and J. W. Edgmond, *J. Appl. Polym. Sci.*, **13**, 999 (1969).
2. D. W. Hadley, P. R. Pinock, and I. M. Ward, *J. Mater. Sci.*, **4**, 152 (1969).
3. D. W. Hadley and I. M. Ward, *J. Mech. Phys. Solids*, **13**, 397 (1965).
4. D. W. Hadley, *J. Text. Inst.*, **60**, 312 (1969).

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