

The advantages of this transducer are: (1) as a result of the geometry and relative positions of reed and mirror, a large light change occurs for a small reed translation; (2) the reed being studied can be placed practically coincident with the plane of the most intense light concentration, with no ill effects on the sample, such as undesirable heating; (3) there is a minimum number of optical parts, no moving part, and only one electronic part, the photovoltaic cell; (4) the optical parts including the photocell are always in permanent, precise alignment; (5) the device can be very speedily applied and adjusted to the reed being studied; this includes the ability to "reach" into an environmentally controlled test chamber.

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Received November 15, 1961

An Intercomparison of Methods for Calculating Normal Stresses

The purpose of this note is to describe the results of an intercomparison between certain methods of calculating normal stresses. For example, Bagley¹ has outlined a method, originally proposed by Philippoff and Gaskins,² for separating elastic and viscous effects from a Poiseuille flow experiment. This method relates the total end correction ϵ , derived experimentally by plotting pressure drop versus different length-to-radius ratios at constant nominal shear rate, to the recoverable shear strain S_R , under the assumption of the validity of Hooke's law in shear.³ Although Bagley does not proceed further under this assumption one can, in principle, also compute a component of the elastic (normal) stress from the relation:³

$$p_{11} = \tau^2/\mu = \tau S_R \quad (1)$$

where τ is the wall shearing stress corrected for end effects, and p_{11} is the normal stress in the direction of the 1-coordinate.

In contrast, a different method, yet one which also embodies the principle of the Poiseuille flow experiment, has been proposed by Metzner and associates.⁴ It involves a force balance in terms of the momentum flux and the tensile elastic stress, and a measurement of the Barus effect;⁵ here the diameter d_j of an extrudate jet emerging from a capillary of internal diameter D is expressed in terms of a swelling index $\beta = d_j/D$. The total normal stress component p_{11} is then computed from the relation:

$$p_{11} = \frac{\rho D^2}{64 n'} \left(\frac{8V}{D} \right)^2 \times \left[\frac{(n' + 1)(3n' + 1)}{(2n' + 1)} - \frac{1}{\beta^2} \left\{ n' + 1 + \frac{d \ln \beta}{d \ln \left(\frac{8V}{D} \right)} \right\} \right] \quad (2)$$

Here ρ and $(8V/D)$ denote the fluid density and nominal shear rate, respectively, while n' is the flow index in the power law flow model.

Now McIntosh⁶ recently investigated the swelling of jets in a 2% solution of carboxymethylcellulose (CMC) over a wide range of shear rates. Fortunately he also obtained data relative to the Bagley end corrections for the same conditions as the jet experiments. As a matter of interest we have computed p_{11} values for both the end correction and jet expansion procedures by applying eqs. (1) and (2), respectively, to McIntosh's original data. The end correction method was applied only over the range of shearing stress where ϵ exhibited a linear dependence on τ ; the same restriction was used in applying the jet expansion method, even though the power law flow model was valid over a much wider range of shearing stress.

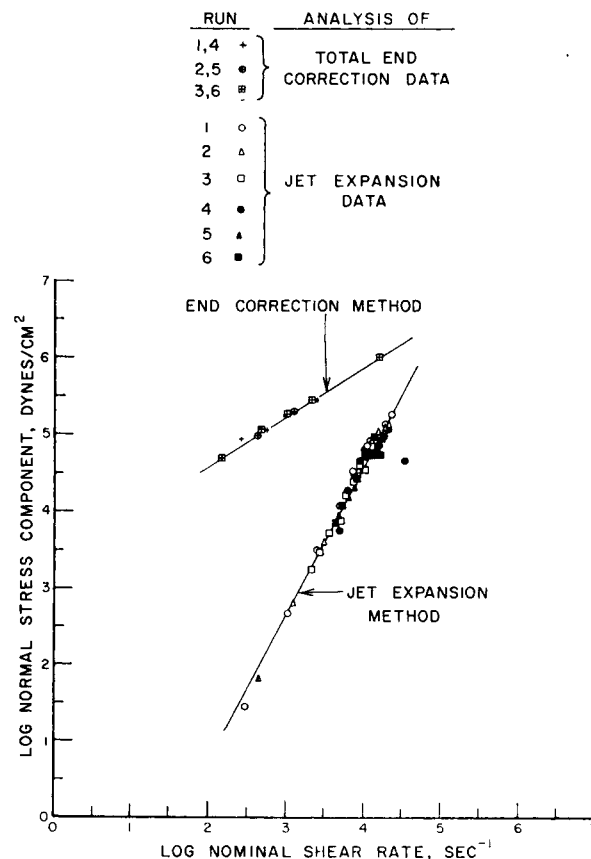


Fig. 1. Comparison of normal stress predictions for a 2% CMC solution (original data from reference 6).

The principal results are summarized in Figure 1. If one adopts eq. (1), the range in p_{11} appears to be about 5.16×10^4 dynes/cm.² to 10^6 dynes/cm.², whereas eq. (2) predicts a range of about 29.3 dynes/cm.² to 1.84×10^6 dynes/cm.². Qualitatively, at least, both methods should yield the same description of elastic effects in shear. Obviously, further experimental intercomparisons of this kind are needed to establish that method which yields the more realistic measure of normal stresses. It is hoped that these observations will stimulate others to obtain more detailed intercomparisons of these methods with the use of a variety of viscoelastic materials.

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Received January 9, 1962

Radiation-Induced Crosslinking of Polymers and Polymerization of Paraffinic Hydrocarbons

Damage in polymers and other organic solids caused by ionizing radiation is currently receiving much attention, not least because the problem of "radiation protection" requires solution in many practical applications. Ideally, a study of "protection" should be preceded by an understanding of the mechanisms by which these radiation-induced chemical changes take place. This applies particularly also to the topic of radiation-induced crosslinking in such polymers as polyethylene and related solid paraffinic hydrocarbons.

Lawton et al.¹ have interpreted the results of electron spin resonance studies of irradiated polyethylene as lending support to a mechanism of hydrogen atom abstraction. On this hypothesis, free radicals are supposed to be formed in pairs on neighbouring molecules and to combine to form a crosslink. Migration of the free radicals plays no part in this theory. However, similar experiments on polyethylene by Charlesby et al.² have been interpreted in terms of migrating free radicals which form crosslinks when they meet. It is therefore necessary first of all to examine briefly the experimental data from which these deductions were made.

The major part of these two papers consists of a study of the decay of electron spin resonance amplitude at room temperature subsequent to irradiation at liquid nitrogen temperature. Concerning the shape of the decay curve,

the two papers are in apparent disagreement. Lawton et al.¹ find it to be exponential, while Charlesby et al.² state that it is hyperbolic, corresponding to second-order kinetics. A closer perusal of the published curves reveals that the time scales over which the decay has been measured are rather different in the two cases, and that the actual decay shows approximately hyperbolic and exponential forms successively. It seems, therefore, that analysis of the results in terms of either monomolecular or bimolecular recombination is not satisfactory.

Interpretation of the E.S.R. experiments involves two assumptions. The first is that the six-line spectrum is that of the ($-\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2-$) free radical. The second, of a more doubtful nature, is that the disappearance of these free radicals is directly related to the formation of crosslinks. However, no proof exists to show that these two events are connected with one another.

There are certain experimental results on crosslinking which any competent theory must be able to explain unless future work should prove these results to be incorrect, viz., (1) the extremely small temperature dependence³ of the crosslinking efficiency between -196 and 100°C ., and (2) the protection against crosslinking⁴ afforded by small concentrations of suitable "impurities."

Neither of the theories is capable of explaining both these facts. The Lawton hypothesis cannot account for the protection effect, as the effective concentrations of impurities are so low that a given impurity center would be on the average too far away from a (hypothetical) radical pair to be effective, and the diffusion coefficients of impurities must be very small.

The Charlesby mechanism cannot account for the experimental facts given under (1), as free-radical migration (which at best is effectively hydrogen atom migration) would have a significant activation energy of not less than 0.3 e.v. The curve given by Charlesby and Davison³ shows two activation energies, the larger of which works out at approximately 0.004 e.v. They found in the yields an increase by a factor of 4, from -100°C . to $+100^\circ\text{C}$., whereas assuming an activation energy of 0.3 e.v. one would get an increase by a factor of 5×10^4 .

Unfortunately, we do not, in fact, possess any information about the temperature dependence of the actual yield of crosslinking at low temperatures because the data referred to above correspond to measurements of crosslinking at ambient temperature and nothing is known about how much and at which temperature the actual crosslinking takes place during the "warming-up period," e.g., in going from liquid nitrogen towards room temperature. It would clearly be essential to use a method by which the crosslinking can be assessed at the temperature at which the irradiations are carried out.

One must conclude, therefore, that the above suggestions do not provide an adequate basis for a crosslinking mechanism unless the experimental findings are shown to be considerably in error. It may well be that the processes described by these authors occur in irradiated polyethylene but their relevance to the phenomenon of crosslinking has not been established.

Dependence of the crosslinking on dose rate could give some very valuable information on the mechanism of this process. There are, however, no published figures available except a short reference³ to certain yields of crosslinking