Spectral broadening of light scattered from polysaccharide gels – oscillations and long range, long term fluctuations

In a recent publication[1], it was reported that long range density fluctuations were observed by scanning through an alginate gel with a focussed laser beam and measuring the changes in scattered intensity. Whereas long range fluctuations in scattered intensity do, in fact, occur over distances of the order of a few tenths of a mm, they do not represent fluctuations in alginate density. The fluctuations arise from the almost stationary 'speckle' pattern, which is characteristic of scattering when the degree of spectral broadening is small. The statistics of such a speckle pattern should be such that:

$$\frac{\text{R.m.s fluctuation in intensity}}{\text{mean intensity}} = \frac{\gamma}{(2)^{1/2}} \quad (1)$$

where γ is the coherence factor of the detecting system[1], and this has now been quantitatively verified for the results previously reported*. However, it was also reported that long term fluctuations in scattered intensity, over periods of the order of tens of min, were observed with the gel stationary. An analysis of the results shows that equation (1) also applies for these fluctuations. This is indicative of complete but very narrow spectral broadening – a possible explanation being that there are continouos long term rearrangements at a molecular level, as was previously suggested[1]. These rearrangements are however not now thought to involve long *range* fluctuations in alginate density. The long term fluctuations would not be observed by normal autocorrelation techniques, as they occur over periods long compared with the integration times usually employed.

Oscillations sometimes observed in the autocorrelation function of intensity fluctuations of light scattered from gels were shown, in the previous publication[1], to be associated with very small bulk oscillations of the specimen. A theory was presented which explained the marked angular variation in the magnitude of these oscillations, in terms of optical interference resulting from oscillatory relative movements within a single coherence volume, resulting from the oscillating strain. The theory as previously presented, which predicted oscillations in the autocorrelation function at twice the frequency of the strain oscillation, applies only when the scattered light detector system is centred on a maxima or minima in the speckle pattern. At other positions, oscillations will be observed at the frequency of the strain oscillation. Oscillations in the autocorrelation function can also occur without relative movement within the coherence volume. A spatially uniform oscillatory movement will produce autocorrelation function oscillations, due to unpredictable oscillatory changes in the otherwise stationary speckle pattern, resulting from changes in the statistics of the scattering centres within the coherence volume. It must be emphasized, however, that in either case oscillations will be observed in the autocorrelation function only if either the degree of spectral broadening is small, or the relaxation times involved are comparable with, or longer than, the period of mechanical oscillation. In the latter case the phase and amplitude of the oscillations in scattered intensity will vary at random with time, and the form of the autocorrelation function and its variation with time will, in general, depend upon the integration time employed. In some cases a damped oscillation may be observed, even though the mechanical oscillations are undamped over a similar period. In the case of a high degree of spectral broadening with relatively short relaxation times, the phase of the oscillations in scattered intensity will change at random over periods short compared with their period, so that no oscillations will in effect be observed.

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REFERENCE

1 Mackie, W., Sellen, D. B. and Sutcliffe, J. *Polymer* 1978, **19**, 9

* Similar fluctuations may be observed with angle of scatter over angular distances of the order of a fraction of a degree. The autocorrelation width of these fluctuations is approximately equal to the width of the cone of light, which would just enable the illuminated volume from which light is actually received to be resolved (in an image forming sense). The magnitude of the fluctuations is given by equation (1).

Impact yielding of high density polyethylene

In a paper recently published in this journal (*Polymer* 1976, **17**, 1099–1102, 'Impact yielding of high density polyethylene'), we reported an anomalously high value of flow stress for high density polyethylene at a temperature of 20°C and at a strain rate in compression of $\sim 3 \times 10^3$ sec^{-1}.

The experimental method, involving geometrical measurements on cylindrical specimens before and after free impact against an anvil, had not been previously applied to polymers; in the absence of a theoretical analysis more suitable for such materials, the method used by Taylor (1948) for metal specimens was adopted. Recent theoretical work and experimental studies of polycarbonate[1] suggest, however, that application of Taylor's analytical method to polymers may lead to overestimation of the yield stress. We believe that if allowance were made for the large elastic strains which polyethylene suffers before yielding, by employing a theoretical analysis specifically developed for polymers[1], the anomalously high flow stress reported would be significantly reduced. The magnitude of the error can unfortunately not be calculated without further experimental data. An additional error is introduced by long term recovery which has been observed in polyethylene projectiles; with polycarbonate this effect is negligible and the theory proposed in ref 1 suggests behaviour which is in good agreement with the experimental data.

We hope to be able to correct our data for polyethylene in the near future.

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1 Hutchings, I. M. 'Estimation of yield stress in polymers at high strain-rates using G. I. Taylor's impact technique', *J. Mech. Phys. Solids* in press