Authors' reply to 'Comment on "J and G_c analysis of the tearing of a highly ductile polymer"'

The comment on our paper [1] by Andrews [2] highlights the difficulties in this area of fracture analysis and a short reply may be useful. There are two quite distinct aspects covered in the paper and it is helpful to separate them clearly.

The energy analysis based on the experimental method of Begley and Landes [3] gives a *total* energy absorption rate for fracture propagation. The analysis here is not applied conventionally as it was previously in metals, but instead is used to describe a propagating crack. However, there is no ambiguity in this definition and no grounds for uncertainty as to what the number means. That such a parameter may be computed from the stress, strain or energy distribution, if they are known, is a matter of fairly straightforward analysis.

Uncertainty arises in the interpretation of J and whether it is a material property and whether in any sense it defines the fracture behaviour in a unique way. It is only in this sense that J is empirical and GFM, as used by Andrews [4], offers an interpretation in terms of the true surface work, T_0, and a function which computes all other energy dissipation throughout the body. For points remote from the crack tip, the computation is sensible but it is less clear when one is concerned with the very local crack tip region. As Andrews observes, there may well be local processes like crazing which cannot be separated by any simple continuum analysis, in which case one may in general have to separate the energy absorption into that which is specific to processes around the crack tip and those which are not. Clearly, if one has a stress analysis, one can, in principle, compute the second of these and by difference find the local part.

A key factor is the difficulty of such computations. Complete numerical descriptions are often attempted, particularly for elastic–plastic bodies and Andrews uses a grid-measuring experimental method. The latter is difficult to perform and the choice of a β value, the hysteresis ratio, for a propagating fracture in a viscoelastic material is not a simple matter. The suggestion made in this paper is that it might be sensible to divide the total energy absorption rate, J, into that which is currently absorbed at the instant of fracture and that which is absorbed prior to the event. It seems reasonable to suppose that the former is supplied by the current energy release rate and this may be deduced from the short-time loading characteristics of the specimens. Such calculations are easy to perform and give G_c values which are not strongly geometry dependent and, it is suggested, could be regarded as fracture characterizing parameters.

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Filamentary and dendritic growth of lead chloride crystals in silica gel

In recent years crystal growth from silica gel has gained a new momentum by virtue of its unusual combination of low temperature growth and exceedingly simple and inexpensive equipment. Extensive work has been carried out on growth mechanisms, characteristics and nucleation of crystals in gels [1–4]. However, dendritic crystals have been grown only in a very few cases [5–8]. The results of experiments on the growth of lead chloride dendrites in gel are reported here.

Growth was accomplished by the counter diffusion of the respective ions through a gel medium of 75 cm^3 of sodium metasilicate solu-

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tion (specific gravity 1.05) mixed with the required quantity of 2N HCl. This solution was transferred to a 250 cm^3 beaker in which a glass tube of about 1.5 cm diameter and 20 cm length, open at both ends, was placed. When the gel was set, a 0.1 N solution of $Pb(NO_3)_2$ was poured into the beaker above the gel and 0.1N HCl into the glass tube. All the chemicals used for the growth purpose were of Analar grade. The following chemical reaction in the gel resulted in single crystals of $PbCl_2$.

$$Pb(NO_3)_2 + 2\ HCl \longrightarrow PbCl_2\downarrow + 2\ HNO_3. \tag{1}$$

Needle-shaped crystals of $PbCl_2$ appeared at the gel–feed solution interface after about half an hour and were found to grow downwards penetrating into the gel. Long needles of about 3 to 4 cm were obtained within four days. Fig. 1 shows typical needle crystals grown in the gel. These crystals were removed from the gel and repeatedly washed with distilled water before any further analysis was carried out.

The crystals were analysed using X-ray techniques. X-ray diffraction photographs revealed that they were single crystals with their needle axes parallel to [1 0 0]. Optical studies of the crystals revealed that the needles were usually pointed and their habit faces were devoid of any significant growth features.

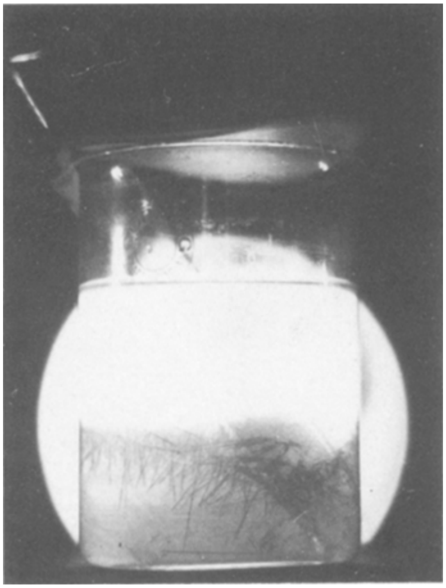

Figure 1 Needle-shaped $PbCl_2$ single crystals in gel (× 5).

The kinetics of growth of these crystals was determined from their rate of growth. Plots of the length of the needle against time of growth were invariably parabolic for all gel compositions. When the square of the length was plotted against the time of growth, straight lines were obtained. Thus the relation between the length and the time of growth may be expressed as $l^2 = kt$ where l is the length of the needle, t is the time of growth and k is a constant called the growth rate constant. The parabolic and straight-line curves obtained in the case of $PbCl_2$ grown in a gel prepared by mixing 74 cm^3 of sodium metasilicate solution of 1.05 specific gravity with 25 cm^3 of 2N HCl are shown in Fig. 2. The results agree with the results obtained in the kinetic study of ionic crystals grown in gel by Henisch *et al.* [9] and those of lead dendrites grown by Liaw and Faust [7].

For gels kept in air it was found that the older the gel the slower the growth of the crystals. This is to be expected because the longer a gel takes to set the greater the amount of water that evaporates. The effect of water evaporation should be considered in two parts, namely before and after the formation of a gel framework. Before the gel is set the evaporation of water will cause an increase in the gel density which in turn will decrease the diffusivity of ions in the gel and hence decrease the growth rate. After the gel is set, evaporation of water causes not only a lack of ionic carriers in the channels of the gel framework, but also discontinuities in the channels due to the shrinkage of the gel. Both of these would adversely affect the diffusion of ions.

In order to study the effect of concentration on the growth of these crystals, they were grown at different concentrations of the feed solution. At higher concentrations of $Pb(NO_3)_2$ (>0.2N) the crystals grew as dendrites. As the concentration was increased a greater number of nucleation centres developed. In order to control the nucleation and study the dendritic growth systematically a very dilute solution of $Pb(NO_3)_2$ (about 0.025N) was poured initially above the pre-set gel to restrict nucleation to a few sites. After about 10 min a concentrated solution of $Pb(NO_3)_2$ of about 1 N was added. Under these conditions extremely regular dendrites were found to grow.

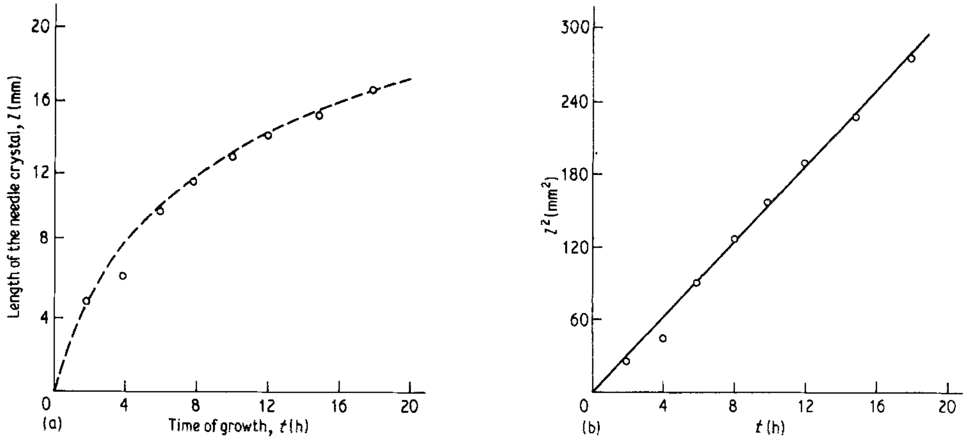

Figure 2 (a) Graph showing time–size relation of crystal growth (b) plot of l^2 against t.

Growth of lead chloride dendrites seems to occur in two stages. In the first stage when the feed solution was poured into the gel, hundreds of tiny nuclei were found at the interface of the gel and the feed solution. These started growing horizontally in the form of thin filaments. However, as mentioned earlier, the number of nucleation centres can be reduced by initially adding a very dilute solution of $Pb(NO_3)_2$ followed by a concentrated one. At this stage the main stem of the dendrites started developing primary branches which in turn developed secondary branches leading to a two-dimensional structure. A typical two-dimensional dendrite grown in our experiment is shown in Fig. 3. It may be mentioned that such primary and secondary branching may occur in all three directions so as to form three-dimensional dendritic patterns as shown in Fig. 4.

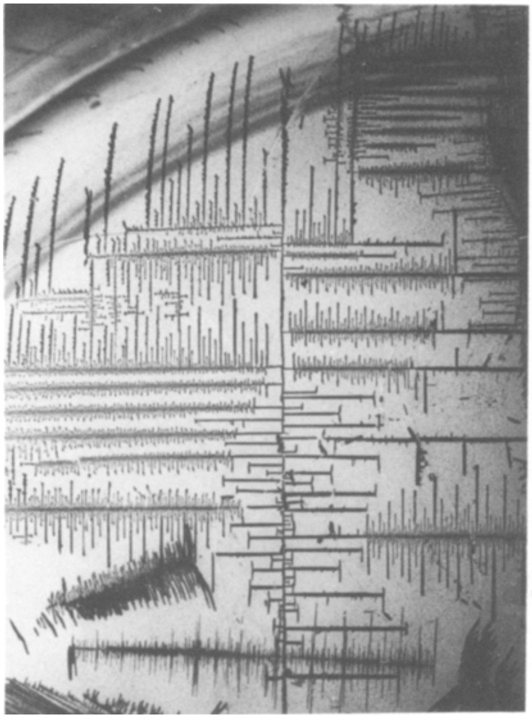

Figure 3 A typical two-dimensional dendrite (× 4).

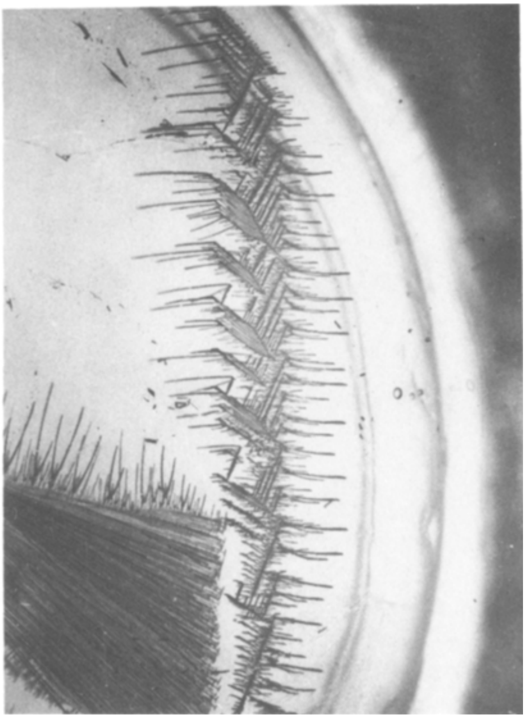

Figure 4 A typical three-dimensional dendrite (× 4).

The two- and three-dimensional dendrites grown in the first stage, had their main stems extending horizontally along [1 0 0] directions from which the primary and the secondary branches grew at 90°, both horizontally and vertically to the original direction. In the second stage of growth, the secondary branches became indistinct because of the filling up of the space between these branchings by growth sheets giving rise to lath-like or plate-like crystals.

The growth kinetics of $PbCl_2$ needle crystals in gels follow a parabolic law which is characteristic of one-dimensional diffusion-controlled processes.

Needle-shaped crystals grow at low concentrations of the feed solution whilst at high concentrations dendritic growth occurs.

The growth at higher concentrations seems to occur in two stages: first the formation of two- or three-dimensional dendrites and second the filling up of the space between secondary branchings by growth sheets.

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Microhardness for evaluation of the environmental stress cracking resistance (ESCR) of low-density polyethylene (LDPE)

The object of the work reported in this letter was the determination of the most important physicochemical parameters which occur in the environment stress cracking (ESC) phenomenon for telephonic cable sheath materials.

It was found necessary to characterize physically the texture of the polymers and a technique was used between the two crystalline-amorphous phases approximation and an accurate size distribution of spherulites. Methods of test for environmental stress rupture under constant tensile load [1] or under constant bending [2] often arbitrarily determine the environmental stress cracking resistance (ESCR), where Antarox Co 630 is the environmental agent. Its behaviour with regard to the polymer is not completely understood. Some workers [3] believe that it plastisizes the polymer and changes the stress concentration at the craze tip; others [4] suggest the ability of the liquid to penetrate into the craze to decrease the strain energy release rate.

However, in this work, we are particularly interested in the structural parameters which modify the ESCR of low-density polyethylene (LDPE). Attention has been given to the influence of the average molecular weight, the molecular weight distribution and density on the resistance, also investigated previously by many authors [5], but consideration of only these indirect parameters (for example, molecular weight and long-chain branching) was insufficient for an understanding of the behaviour of LDPE since account must also be taken of the thermal and the shearing history of the sample. For this reason two LDPE samples having the same crystalline ratio may

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