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Strain rate effects on the ratio of recoverable to non-recoverable strain in linear polyethylene

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The yield point of a crystalline polymer is ill-defined in terms of the structural processes and of the continuum mechanics involved. An investigation has been carried out on the effect of strain rate on the amount of unrecovered strain, as determined by long term and accelerated recovery tests. This has revealed that the extrapolated yield point cannot be associated with the onset of permanent flow. It has also revealed that the strain rate dependence of the yield point is controlled by recoverable rather than irrecoverable processes. Doubt is therefore cast on the way in which activated rate process theory has been applied to the yield phenomenon by previous authors.

1. Introduction

1.1. Definition of the yield point

The "yield point" of a material has been defined in different ways for different materials and even in different ways by different authors for the same material. For example, Argon [1], experimenting with polystyrene has used the term yield point to describe the limit of linearity on the stress strain curve and has noted that this point coincides with the appearance of deformation bands. These were found, however, to be recoverable on heating. Bowden and Jukes [2], working with the same material have used the term yield point to describe the maximum stress in the stress strain curve, obtained for a sample under compression. Commonly for polymers, the yield point is defined as the maximum in the tensile stress strain curve. Since this is merely the point at which necking commences and is defined primarily by the condition that the rate of work-hardening has fallen to a critical value it must be regarded, to some extent at least, as an arbitrary definition. In metals the yield point is associated with the onset of plastic deformation, where the word "plastic" implies "irrecoverable", and for materials which have no sharp discontinuity in their stress strain curve at the onset of plastic flow the yield point has been defined by specifying an arbitrary level of non-recoverable strain (i.e. an offset yield point).

In general the definition of the yield point in any material involves either the identification of a reproducible point on the stress strain curve for that material at which the compliance may be considered to increase markedly, or the detection of a point beyond which irrecoverable deformation takes place. It is by no means obvious or necessary that the two points should coincide or even be related.

For materials which show a progressive increase in compliance but which have two distinct linear regions of different slope in their stress strain curve, a yield point may be defined by extrapolating the two linear regions to the point of intersection, which effectively assumes that two different mechanisms are responsible for the deformation in the respective linear portions of the curve. This point is termed the "extrapolated yield point" and has been shown to be highly reproducible for low-density polyethylene by Cherry and McGinley [3], who used a plane strain compression test to facilitate true stress measurement. High-density polyethylene (HDPE) is also amenable to this definition of yield.

The use of recoverability as a test for a yield point has been complicated by the difficulty of obtaining data as to whether a given strain is entirely or only partially recoverable. Uhlmann and Park [4] report that for amorphous polycarbonate tested in tension to strains of 90% (well beyond the maximum in the stress strain curve which for their materials occurred at a strain of approximately 8%) the strain was entirely recoverable on heating to temperatures above the glass transition temperature. This was in contrast to the behaviour of low-density polyethylene and polypropylene which did not demonstrate complete recovery even when held for long periods at temperatures close to the melting point. Edward and Stachurski [5] similarly observed for low-density polyethylene that although recovery at room temperature approached 100%, recovery was not complete on the time scale of the experiment.

1.2. The different deformation mechanisms

The existence of two separate regions in the stress strain curve with markedly different values for the compliance implies that there might be two different mechanisms which dominate the deformation process at the different portions of the curve. Similarly, the existence of recoverable and irrecoverable strain in semi-crystalline polymers implies the existence of two different deformation mechanisms. These need not however coincide with the two mechanisms previously associated with different portions of the stress strain curve.

Two different shear mechanisms have been identified by Buckley and McCrum [6] which are potentially capable of allowing deformation by simple slip. These are *c*-axis slip within the crystalline lamellae on either an $(hk0)$ or an $(h00)$ plane, and interlamellar slip. Various authors, e.g. Stachurski and Ward [7], Davies *et al.* [8] and Buckley and McCrum [6] have suggested that interlamellar slip is responsible for the α relaxation in high-density polyethylene, and Stachurski and Ward [7] that *c*-axis slip is responsible for the β relaxation. Young *et al.* [9] have shown that the orientation changes which occur during the deformation of oriented HDPE indicate that a $\langle 001 \rangle$ slip process in the crystalline region accounts for the permanent deformation while interlamellar slip contributes largely to the recoverable deformation. Young [10] has used these observations to suggest a mechanism for yield in high-density polyethylene involving the initiation of screw dislocations at the edges of the crystalline lamellae. However it should be noted that his model depends upon the yield point defining the onset of macroscopic permanent flow, a definition which has yet to be proved.

An alternative model of the yield point, suggested by Cherry and Holmes [11], also involves the motion of dislocation loops through the crystalline lamellae. This model, however, assumed that slip in the crystalline region of the polymer caused the inter-fibrillar tie molecules to be stretched, so that the stretching of these tie molecules acted as an elastic process in parallel with the deformation of the crystalline regions. Yield in this model is associated with the rupture of the inter-fibrillar tie molecules after the achievement of a critical strain value, and the time dependence of the yield point is attributed to the kinetics of the pre-yield dislocation motion. Since the inter-fibrillar tie molecules were assumed to be responsible for recovery processes it can be seen that with such a model the onset of permanent deformation coincides with the yield point.

1.3. The role of recovery forces

The Cherry and Holmes model highlights the importance of taking account of recovery as well as deformation processes at yield, since if a recovery process is acting in parallel with the deformation process, the energy input to the system at yield must be divided between the two (or more) processes.

The Eyring treatment of an activated flow process [12] which has been invoked by a number of authors [13, 14] to account for the time dependence of the yield point, requires that the whole of the applied stress acts on the activated deformation process and is dependent upon the strain after yield being permanent. By way of contrast the model proposed by Haward and Thackray [15] to describe the stress strain curve of thermoplastics below the glass transition temperature includes a Langevin spring with an ultimate limiting network strain in parallel with the activated yield process and a Hookean spring in series with the parallel array. This model implies both a sharing of stress between the activated rate process and the Langevin spring and also that in the absence of permanent damage to the network which forms the Langevin spring, all deformations, even beyond the yield point (as defined by the peak in the stress strain curve) are recoverable.

1.4. The present work

The work to be reported in this and a subsequent paper has therefore three objectives. It is intended to clarify the relationship between the extrapolated yield point and the onset of irrecoverable strain, and to determine whether recoverable, time dependent (by our definition having a relaxation time in excess of 1 sec) strain increases beyond the extrapolated yield point.

It is also hoped to determine whether the time dependence of the extrapolated yield point arises from flow mechanisms which occur before this point or ones which are initiated at the yield point.

2. Experimental

2.1. Apparatus and materials

In order to examine the extent of strain recovery in the vicinity of the yield point it is essential to avoid the discontinuities due to necking which occur in tensile tests. Accordingly, a compression test was chosen for this work and the plane-strain configuration described by Williams and Ford [16] and as used by Cherry and McGinley [3] was employed, in order to allow the direct measurement of true stress and to minimize the effects of bulging. The specimen dimensions were modified from those used in the previous work [3] to allow for the higher modulus of the present material and were; die breadth 0.5 in., specimen width 2.0 in., specimen thickness (initial) 0.1 in. approximately. The strain was measured by summing the signals from two LVDT transducers at the opposite ends of the dies.

The material was a high-density polyethylene supplied by Hoechst Australia Pty. Ltd. and designated GA7260. It was prepared without antioxidant, and moulded at 180° C in induction heated platens which were then rapidly cooled to 80° C by circulating water, at which point the plaque was removed. Specimens were machined with a sharp cutter to an accuracy of ± 0.001 in. for each specimen. Examination of thin sections of the prepared polymer by polarized light microscopy as well as by scanning electron microscopy [17] showed a high proportion of well-formed spherulites.

2.2. Initial recovery measurements

All the compression tests were carried out using an Instron model TT-D with a GR load cell in an environmental cabinet maintained at 27 ± 0.5° C. Specimens were compressed to a range of nominal strain values up to 0.5 and at cross-head speeds between 0.002 and 2 in. min^{-1}. After testing the load was removed rapidly and the specimen allowed to recover for approximately nine months

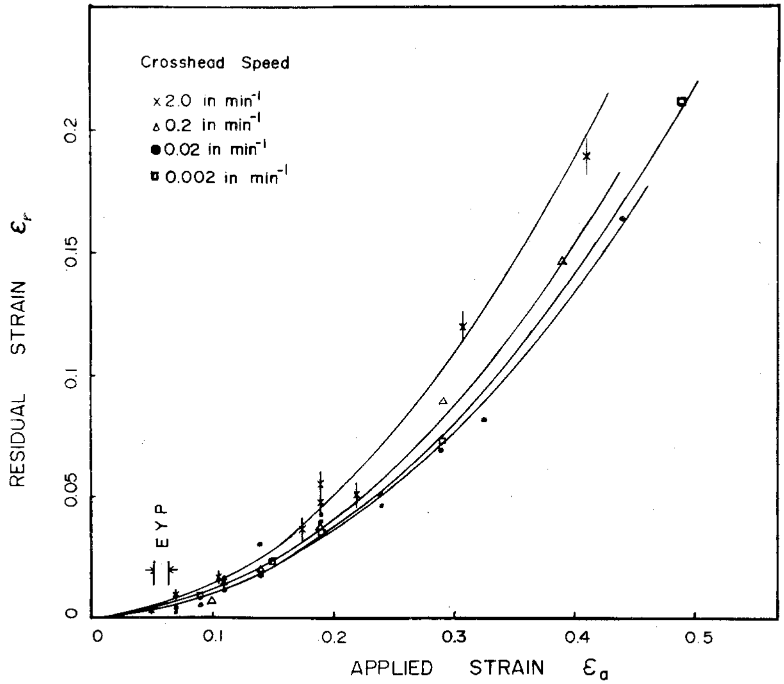

Figure 1 Residual strain after recovery for 9 months at 27° C plotted as a function of applied strain. Curves are of the form $\epsilon_r = C\epsilon_a^2$.

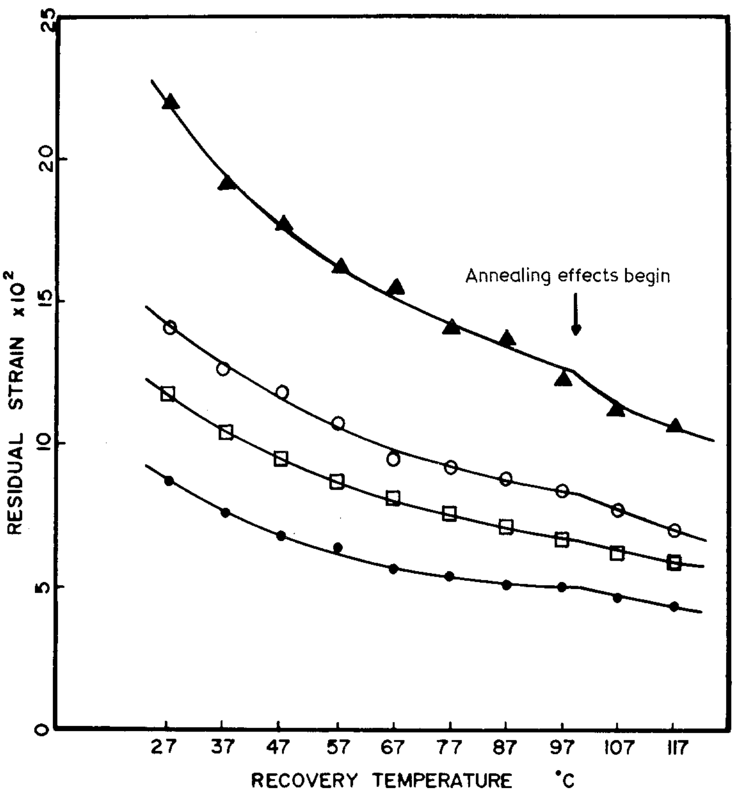

Figure 2 Residual strain after recovery at the temperature shown for one day plotted for four initial strain values. Cross-head speed was 0.01 in. min^{-1}.

at the test temperature. The unrecovered or residual strain was measured using a micrometer with a tip diameter of $\frac{1}{4}$in., i.e. half the width of the compression dies. By taking readings from the centre of the deformed zone it was possible to minimize the effect of the shoulders on the recovery process. In fact the portion of the deformed zone used for measurement was found to be flat to within the limits of experimental error, and curvature commenced only in the region close to the shoulders of this zone. The results are shown in Fig. 1 which demonstrates the relationship between residual strain after nine months at the test temperature and the initial applied strain. It can be seen that for any given applied strain the residual strain increases with an increasing strain rate during the initial deformation. It was obvious, however, that even after nine months, recovery was still occurring although at a diminishing rate, and so it was decided to investigate the possibility of accelerating the recovery by means of an increased temperature [8].

2.3. Accelerated recovery measurements

An accelerated recovery test is valid only if it can be shown that the conditions which bring about the acceleration of the recovery process do not bring about changes in dimensions of undeformed material, eg. re-crystallization, degradation etc. do not occur. In order to determine the temperature to which a specimen could be heated in order to accelerate the recovery process, a set of four specimens was compressed at a rate of 0.02 in. min^{-1} to different initial strains and then allowed to recover for one day at the test temperature and at successively higher temperatures up to 117° C. After each recovery period the thickness of the deformed and undeformed regions were measured and Fig. 2 shows the changes as a function of recovery temperature. Above 97° C, changes were observed in the dimensions of the undeformed material as well as a slight change in the recovery rate and in the crystallinity as measured by X-ray techniques [3]. It was concluded that recrystallization was becoming significant in this range so that the optimum temperature for recovery was chosen as 96° C.

The specimens of Fig. 1 were also subjected to successive accelerated recovery tests and the results after recovery at 96° C are shown in Fig. 3. A similar relationship between residual strain and the applied strain was observed for each cross-head speed, but the scatter was reduced con-

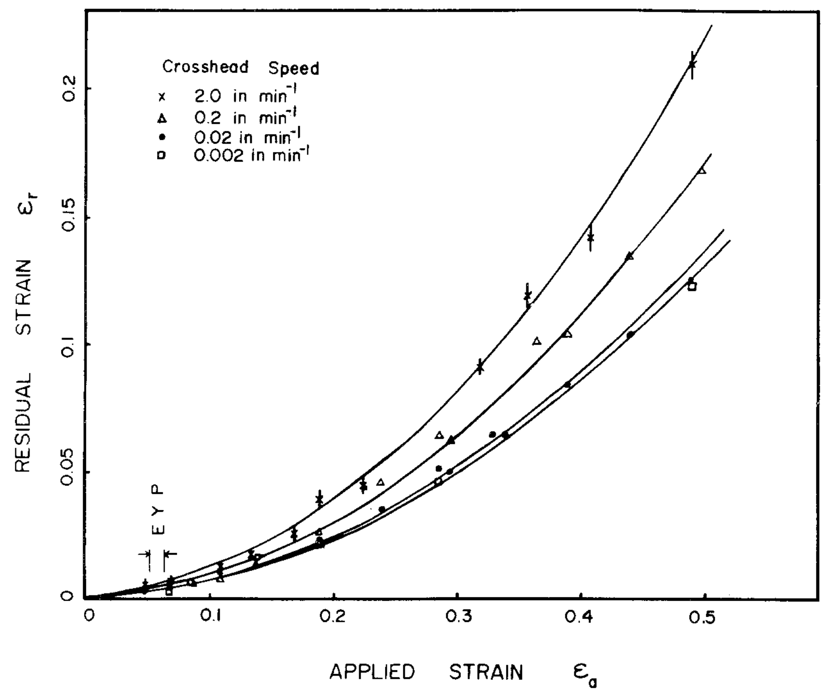

Figure 3 Residual strain as a function of applied strain after recovery at 96° C for one day. Curves are of the form $\epsilon_r = C\epsilon_a^2$.

siderably and the magnitude of the residual strains were decreased markedly, showing that considerable further recovery had occurred.

2.4. Results

The major fact to emerge from the results shown in Figs. 1 and 3 is that the amount of residual strain increases with the cross-head speed of the original deformation, over the whole range tested with accelerated recovery, and over the major part of the range with long term recovery.

It is also interesting to note that there is an apparent linear relationship between the residual strain and the square of the applied strain at any given cross-head speed. There are two reasons however why this result (which is the relationship which would be expected for a Maxwell body) is unlikely to have any great significance. During the initial deformation, the actual die displacement rates vary considerably as a result of testing machine deflections. In addition the relatively undeformed material in the shoulders of the specimen must exert a force which promotes recovery in the strained portion of the specimen; hence it seems likely that the measured residual strain is lower than it would be in the absence of such forces, and this effect would be more marked at large initial strains.

It may be seen, however, that neither of the two reasons given above for doubting the significance of the apparent parabolic relationship between residual and applied strain, could affect the overall result that the residual strain increases with cross-head speed of the original deformation.

3. Discussion

3.1. The yield point and the onset of plastic deformation

From Figs. 1 and 3 it may be seen that there is no obvious discontinuity in the values of residual strain close to the Extrapolated Yield Point, which from Fig. 4 can be seen to lie at a strain value between 0.052 and 0.064. In fact the points in both figures appear to approximate closely to a set of parabolae passing through the origin. There is certainly a measurable component of residual strain after deformations less than that which would bring the material to its Extrapolated Yield Point and although the accuracy of the strain measurement does not allow a definitive interpretation of the behaviour at low strain it should be noted that similar results have been found by other workers who have examined the recovery of semi-crystalline polymers [5, 19]. It should also be noted that there is no evidence to suggest that irrecoverable deformation commences at a parti-

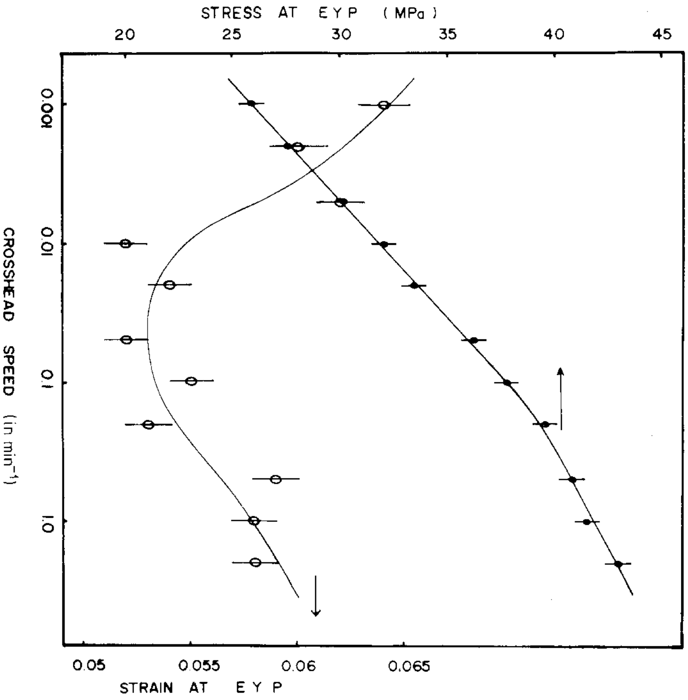

Figure 4 Effect of cross-head speed on the stress and strain at the extrapolated yield point. The strain values are measured directly from the die position and differ from those in an earlier paper which were calculated from the cross-head position.

cular point on the stress strain curve nor that the amount of residual strain can be related to the deviation from linearity of the stress strain curve.

3.2. The nature of the rate controlling process at yield

In what follows it will be assumed that there are at least three different types of mechanism which are responsible for the deformation of a semi-crystalline polymer. One of these types of mechanisms gives rise to a deformation which is instantaneously recovered on removal of the deforming stress, one gives rise to a deformation which is eventually recovered and one gives rise to an irrecoverable deformation. These will be termed the elastic, anelastic and plastic mechanisms respectively. Because of the significance in regard to the theories discussed in Section 1.2, it is of interest to determine whether it is the strain rate dependence of the anelastic or of the plastic processes which controls the strain rate dependence of the material response to an applied stress.

It is well known that in thermally activated deformation processes, the stress necessary to cause a given strain increases with the strain rate. The results shown in Figs. 1 and 3 indicate that the residual strain increases with strain rate for any given strain. It may therefore be deduced that the residual strain increases with the applied stress. Now, if it were the rate dependence of the plastic process which controlled the rate dependence of the material as a whole this would imply that at a higher strain rate a given stress will produce a lower residual strain, in contradiction to the experimental observation. This observation is true for any system in which the rate dependence of the plastic process controls the rate dependence of the material as a whole. Thus it must be the rate dependence of the recoverable component of strain which determines the rate dependence of the stress in this range and hence the rate dependence of the Extrapolated Yield Point.

Further evidence in support of the above conclusion can be found in the shape of the curves of applied stress against cross-head speed for a number of values of strain (Fig. 5). It will be seen that the basic shape, two linear regions with a change of slope around 0.1 in. min^{-1}, is the same for all strains above and below the Extrapolated Yield Point and at the Extrapolated Yield Point itself. It seems likely therefore that the mechanism controlling the rate dependence of the stress is the same over the range examined independent of whether recoverable or irrecoverable deformation is the major component.

These results suggest that the model proposed by Young [10] for the initiation of slip in linear polyethylene is not appropriate for this material.

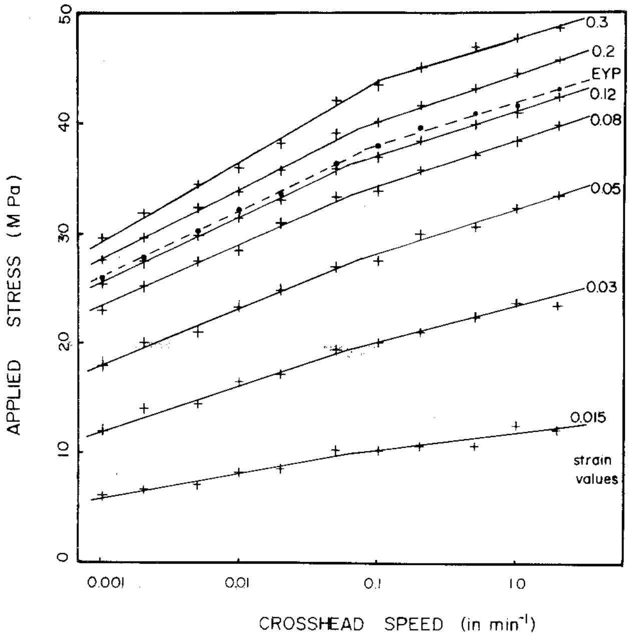

Figure 5 The variation of applied stress with cross-head speed for a number of values of strain.

It should however be noted that Young's model was not developed to account for the Extrapolated Yield Point but for the behaviour of the material in the post yield region, and also that processes other than slip, e.g. twinning [20] or martensitic transformations [21], may be responsible for plastic deformation at low strains.

The model suggested by Cherry and Holmes [11] is consistent with the results presented in this paper in that it assigns the time dependence of the yield point to the pre-yield process. The present results show however that the Cherry and Holmes model is not adequate to deal with this material since it assigns the control of the rate dependence of the yield point to dislocation motion which, as discussed in Section 1.2, appears to be associated with permanent flow. A model which is consistent with the observations reported in this paper consists of a markedly rate dependent anelastic process in association with a plastic process which is comparatively independent of deformation rate.

3.3. A molecular mechanism for yield and deformation

It is possible to propose a molecular model which is consistent with most of the observations cited in this paper although there is little direct evidence in support of the model.

Young *et al.* [9] have shown that deformation processes in the crystalline region account for the permanent deformation while interlamellar slip contributes largely to the recoverable deformation. It therefore seems likely that the anelastic component of strain observed in this work may be associated with interlamellar movement, part of which is instantaneous and part of which is time dependent; the nature of this time dependence will form the subject of a later paper. The more permanent component of strain is then attributed to deformation within the crystalline region. Since the effect of increasing the applied strain rate will be to decrease the amount of time dependent (anelastic) strain at any given stress, there will be a larger component of plastic strain to accommodate the total deformation applied to the system.

Such a model would predict the onset of plastic slip at the instant of application of an external stress and the observed relation between residual strain and strain rate.

3.4. Activated rate process theory of yield

Activated rate process theory in which the whole of the applied stress acts on the plastically deforming element has been applied by a number of authors [12, 13, 22]. However since it has been shown that it is the anelastic process whose rate dependence controls the rate dependence of the total material deformation, it is necessary to invoke a parallel model in which part of the applied stress acts on the recovery process and part only on the anelastic deformation in order to be able to predict the observed recovery behaviour. Therefore treatments of the activated flow process which assume that the whole of the applied stress acts on the process which is thermally activated, cannot be valid. An alternative is to use the concept of a "recovery stress" [21], as has been used in studies on metals. This approach to the rate dependence of the deformation will be pursued in a subsequent publication.

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