

Fracture Theories in Industrial Use of Thermoplastics and Glassfiber Reinforced Plastics

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INTRODUCTION

The "International Conference on Fracture" has been organized not only to represent all aspects of the science of material disintegration but also to provide a forum for cross fertilization between the different branches of this science, between theory and experiment, laboratory research and industrial application. This morning it is our aim to introduce - in two ways - fracture problems connected with polymeric materials. For one thing we would like to say, when and why fracture causes a problem in industrial use of polymers and what we have learned from fracture theory to solve or at least handle these problems. Secondly we would like to describe the fracture behavior of polymeric materials and what experimental and analytical tools we have developed or adapted for their investigation.

CHARACTERISTIC PROPERTIES OF POLYMERIC MATERIALS

It is two properties by which high polymers are distinguished from all other materials: the large anisotropy of cohesive forces and the strong dependency of (mechanical) properties on time and temperature. Although this statement is quite generally valid we will restrict ourselves in the following discussion to thermoplastics and glass-fiber reinforced polymers. We may recall that thermoplastic

polymers (uncross-linked linear chains with little or no branches) like polyvinylchloride (PVC) or polymethylmethacrylate (PMMA) show - within the relatively small temperature range between 0 and 200 °C - the behavior of a brittle glass, of a ductile, deformable solid, of a rubber and of a high viscosity fluid.

For illustration we show the well known graph of Retting (Fig. 1) where the positions of the transitions between the different "phases" are depicted in time-temperature space. Depending on these parameters and the state of stress the final failure of an engineering component may occur as brittle fracture, through development of cracks in creep, as yielding and plastic deformation, or through flow. Fracture is only one of many modes of failure.

It need not be emphasized that the failure of a plastic noodle bag, a water pipe or a glassfiber reinforced oil tank is undesirable but even more so if it is unexpected.

Efforts of fracture research are directed, therefore, towards two goals: to understand the cause of failure and to see whether it may be eliminated. If this is not possible one would like to know at least the endurance limit of a part in terms of stress or strain level, number of loading cycles or of loading time. In this paper some of the problems are discussed which are encountered in the interpretation of fracture phenomena and in determination of the endurance limits of thermoplastic and glassfiber reinforced parts.

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FRACTURE PHENOMENA IN THERMOPLASTICS

Fracture at low temperatures

At low temperatures high polymers resemble glasses (Fig. 1) and fracture in a brittle manner. Viewed without magnification their fracture surfaces appear to be smooth but not shining - indicating that the surfaces contain structural irregularities larger than the wavelength of light. This is the case with PE, PVC, PP, and also with PMMA which, however, has an almost shining surface.

Figure 2 shows a notched polyethylen sample fractured by bending at liquid nitrogen temperature. The fracture surface is locally smooth but otherwise full of steps and ridges. The propagation of these cleavage cracks occurs with high speed, normal to the direction of local tensile stress and is strongly affected by elastic waves generated at earlier stages of the crack development. The intersection of wavefronts under different (e.g. right) angles leads to curious patterns as the one shown in the bottom right of Fig. 2 (I). The characteristic properties of thermoplastics, molecular anisotropy and strong rate dependency of deformation, become apparent to a limited extent only. One clearly observes that in the zone of crack initiation (Fig. 2, II) where the rate of crack propagation is small the surface is less smooth than that created later. The irregular shape of the surface also reflects the inhomogeneity of the aggregate of large and anisotropic molecules.

The seemingly smooth cleavage surface deserves further discussion. Figures 3 to 6 show successively higher magnifications of the area III in Fig. 2. Figure 6 reveals that the "smooth" surface has a honeycomb-structure with cells of 1000 to 6000 Å width - in accordance with our

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earlier statement on the size of surface irregularities. The ridges between cells are highly deformed. As their width is comparable to that of the cells a plastic deformation of about 100 % is indicated. This is in view of the test temperature a quite remarkable fact which, however, explains the high values of the crack extension energies of thermoplastics.

For comparison we also show the fracture surface of a (window) glass at identical magnification (Fig. 7) which is quite smooth.

Fracture at room temperature

At room temperature many thermoplastics are tough (HDPE, PVC, PP, PA). Cleavage fracture is difficult to obtain by bending and occurs only in notched specimens of low aspect ratio or if the rate of loading is high (impact loading). In samples of HDPE with extremely high molecular weight ($M_w > 10^6$ g/mole) cleavage fracture does not occur at all. Figures 8 to 10 give an impression of the large plastic deformation of the surface within rosettes and ridges where the walls are drawn by several hundred per cent.

At this temperature the secondary forces between neighbouring molecules are much weaker than at liquid nitrogen temperature. The molecular anisotropy thus becomes much more noticeable. In particular it must be concluded that the axial force acting upon an extended chain segment is transmitted over a distance of more than thousand Ångström units.

Thus any potential stress concentration (at the tip of a crack, in the neighbourhood of inclusions, near extended molecules or reinforcing fibers) is automatically distributed over a large volume element and accordingly decreased.

It is this property which causes the crack extension force G of thermoplastic polymers to assume values which are up to 10^4 times as high as necessary for the breakage of those main chain bonds which are severed by the running crack.

The same property has contributed towards the success of plastic polymers as shock absorbing, energy dissipating packaging material.

Time-dependent strength

The time to failure t_b of a loaded thermoplastic or reinforced sample depends upon the applied load G . Conversely the load level under which a structural component may safely be operated depends upon the length of the service life required. This is clearly observable from the fracture data of PVC tubes presented in Fig. 11. These data again support our statement that - depending on stress and temperature - failure occurs as brittle fracture, through yielding, or in creep. It should be noted that in this logarithmic plot all points belonging to one temperature lie on one line - even if they show different modes of failure. Stress-lifetime diagrams as the one shown in Fig. 11 are most widely used to predict the service life of loaded engineering components. It is the aim of this presentation to point out some of the difficulties involved in interpretation of stress-lifetime diagrams.

In one of the earliest publications on this subject Richard, Gaube, and Diedrich (3) have shown that the stress-lifetime curves of HDPE consist of two parts: an initial linear portion of small slope followed by another linear portion which steeply declines (Fig. 12). The fracture modes observed in both cases are different: ductile failure in the first, development of creep cracks in the second part.

A similar behavior was observed with other semicrystalline thermoplastics. In these cases obviously two deformation processes with different reaction rates are active. This hypothesis is - within experimental accuracy - supported by an Arrhenius plot of the same data (Fig. 13) since $\log t_b$ vs. $1/T$ yields straight lines. If the above hypothesis is valid extrapolation of the straight lines should lead to points which might have been obtained at different temperatures and lifetimes respectively. This method then offers the possibility to extrapolate from high temperature data and short lifetimes (which means short testing times) towards low temperature data with experimentally inaccessible long lifetimes (3, 4). To corroborate the hypothesis that the steeply declining portion of the $\sigma-t_b$ curve is dominated by one process further investigations have been carried out or are still necessary. We would like to mention that with stress and temperature constant t_b increases with the molecular weight of the test sample and is decreased by certain surface active media. Flaws, frozen-in stresses, and chain orientation distributions affect the lifetime. The scatter of lifetimes shows a logarithmic normal distribution (5). The surface of a sample fractured by creep cracks is shown in Fig. 14. The well known "mirror" and the athermal growthzone can be clearly observed. The mirror develops normal to a constant and macroscopically homogeneous stress field. Its surface reveals that a large number of holes have started to grow at about equal rates. Their coalescence leads to the formation of - plastically deformed - ridges. The fracture in creep is strongly determined by the rate of local rearrangement of molecular segments. A number of experiments suggest, however, that the stress-induced scission of main chain bonds might be the key to ensuing breakage of secondary bonds.

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Amorphous thermoplastics behave somewhat differently from semicrystalline ones. Our preparations to prove this point have started 18 years ago when Richard and Diedrich (6) investigated the stress-strain-lifetime behavior of poly-trifluorochlorethylene (PTFCE), Fig. 16. Again we see that the stress-lifetime curve is well represented by one straight line. Some time after load application the so-called crazes (Umordnungszone) can be observed (Fig. 17). A cut through a craze reveals that it consists of a large number of oriented ligaments connecting the two sides of uncrazed material (Fig. 18). Between the time of appearance of crazes and the time of fracture a considerable amount of time may elapse (e.g. 18 years). According to the investigations of Menges (6) crazes will not appear unless the largest strain component is larger than the limiting strain for craze initiation ($\epsilon_{F\infty}$).

PTFCE is an interesting material in as much as it can be obtained in the crystalline or in the amorphous state. Figures 16 to 18 refer to amorphous material. We have also conducted endurance tests with crystalline samples (with loads between 150 and 300 kg/cm²) without obtaining any crazes. The time t_c of craze initiation in amorphous samples is effected by similar parameters as the breaking time. An increase of the molecular weight shifts t_c to larger times, uniaxial orientations (perpendicular to the main stress component), frozen-in stresses, and swelling solvents decrease t_c .

FRACTURE THEORY AND INDUSTRIAL USE OF GLASSFIBER REINFORCED PLASTICS

In this chapter (8) we would like to discuss the interaction between fracture theory and the design and testing

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of glassfiber reinforced plastics (GRP), or, to be more specific, of glass mat and glass roving reinforced resins. It is generally recognized that the gradual deformation of such a composite structure involves the elastic deformation of glass and matrix, the anelastic deformation of the matrix (resin), adhesive failure at the boundary between glass and resin, and the cohesive failures of glass and resin respectively. Uniaxially reinforced laminates are highly anisotropic, they have a large stiffness and strength in the direction of reinforcement, a 10 to 20 times smaller strength and a 3 to 4 times smaller stiffness perpendicular to that. Considerable research effort has been put into solving two problems:

- 1) How can one derive the equivalent of the tensor of elasticity (i.e. the laminate stiffness matrix) for a multiply laminate?
- 2) What are the critical stress or strain conditions which lead to adhesive or cohesive failure respectively?

Access to the present state of knowledge in the problem areas 1 and 2 may be obtained from refs. (9, 10 and 11) respectively.

It is not the aim of our talk to discuss this state of knowledge but rather how this information has been applied in industrial use of glassfiber reinforced resins.

The designer of a load bearing engineering component - like an oil tank for instance - is faced with the problem to combine his knowledge of the strength and fracture behavior of the composite with the necessities of production, testing, transportation, and use of the component. We may state that it is a general principle to design a structure in such a way that no cracks will appear under

service conditions. For given fiber and matrix materials with known strengths the theory of multiply laminates tells exactly how much glass and in what arrangement to use so that even at maximum intended stress level all strains remain below the - theoretically specified - critical level (crack formation by one of the three mentioned processes). From the detailed investigation of the parameters involved in laminate fracture rather practical information has been drawn. One important aspect was the investigation of the relation between glassfiber content and laminate strength in the direction perpendicular to the fiber axis. The strength decreases at higher fiber contents because of the so-called strain magnification of the matrix. The optimum fiber content depends, however, on the adhesive strength of the matrix-fiber bond and on the matrix strength. Another aspect concerns the optimum choice of the resin. Investigations (12) have shown that crack initiation occurs at higher stress levels if a ductile rather than a brittle matrix material is used.

The body of most large tubular components consists of a cross-ply (circumferential windings with axial reinforcements) which is much better to be produced on line than bodies of any other geometry. The technique for testing 90° biaxially wound specimen is also greatly facilitated. In order to protect the unidirectionally reinforced surface layers from crack initiation through unexpected bending moments (2-point support) or impact (transportation) additional layers are applied to the body. So the interior surface - especially of chemical resistant tanks or exhausts - is finished with a (random fiber) glass mat which serves as an excellent crack stopper. Frequently exterior GRP surfaces are protected by thermoplastic coatings - which then also have to be screened from cracks possibly initiated within the GRP by a highly viscous inter-layer.

The present German Standard (AD N 1) for pressure vessels from glassfiber reinforced resins requires that the wall thickness s of the vessel be calculated from the well known vessel formula

$$s = \frac{D_a \cdot p}{CK/SG} \quad (1)$$

where p is the pressure, D_a external diameter, C a constant, K the strength of the composite, and S and G material safety factors. Any time and orientation dependency of the glassfiber laminate is absorbed into K . If the time dependency of K is not known the reducing coefficient G is increased accordingly. Any improvement of laminate strength, however, will be duly reflected in a decrease of s . For the prediction of stress-strain behavior, crack initiation and failure of multiply GRP composites - especially that of high pressure vessels produced by filament winding - special testing techniques and computerized evaluation programs have been developed (13) and successfully applied.

The present understanding of laminate deformation and failure has spurred research on the impregnation and wetting of glassfibers by the resin (14), on improvement of adhesive strengths by glassfiber coating, on fracture initiation in polymeric glasses, and on the effect of isolated cracks on laminate strength.

We have presented many details of fractographic studies and from the theory of fracture development in reinforced and thermoplastic high polymer solids in relation to the two most important industrial problems: investigation of the causes of failure in order to eliminate them and understanding of the kinetics of fracture development in order to put up meaningful, economic, but reliable guide-

lines for the use of load bearing thermoplastic components. The following papers will provide further evidence of molecular mechanisms and of means to utilize stress analysis in polymer fracture. We must admit, however, that we are still some distance apart from a complete, deterministic description of the strength and fracture of high polymer solids.

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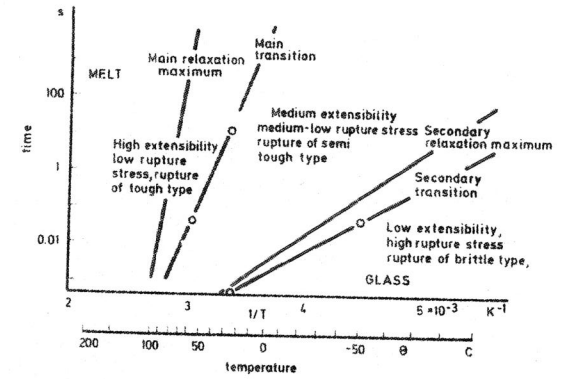


Fig. 1: Ultimate properties of hard PVC as function of time and temperature (after Retting 1966)

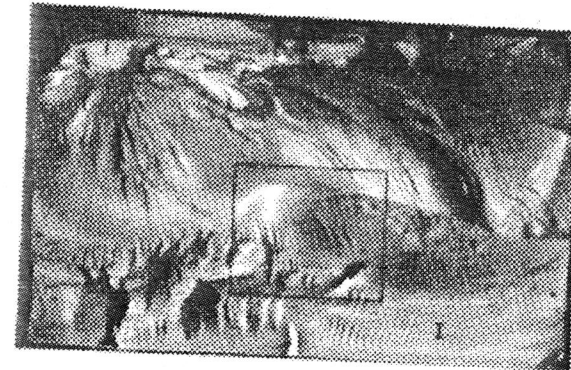
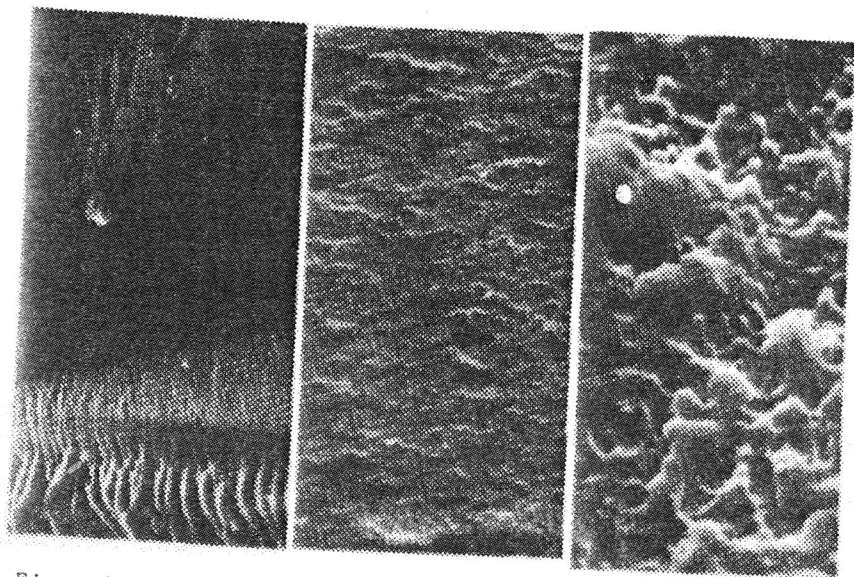


Fig. 2: Impact fracture of notched HDPE at liquid nitrogen temperature (2x)

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Fig. 3: Area III in Fig. 2 (8x)



Figs. 4-6: Details from Fig. 3 (60x) (600x) (12000x)

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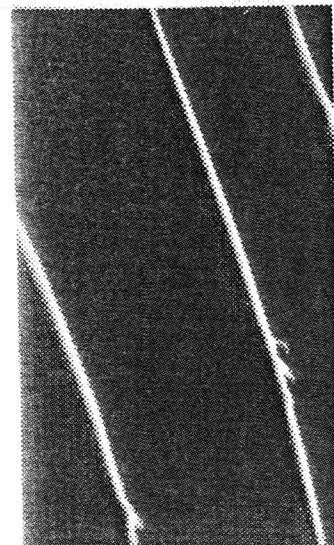


Fig. 7: (Window) Glass (12000x)

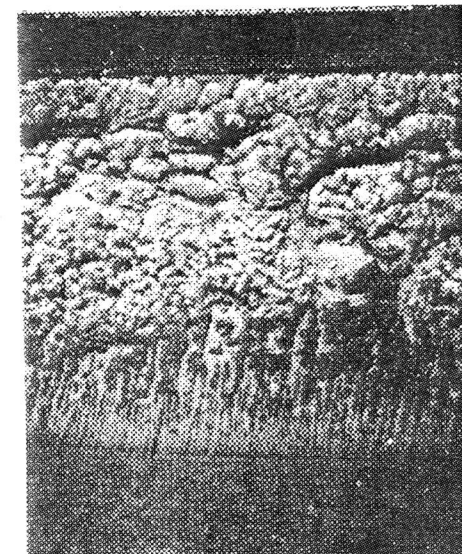


Fig. 8: Impact fracture of notched HDPE at room temperature (10x)

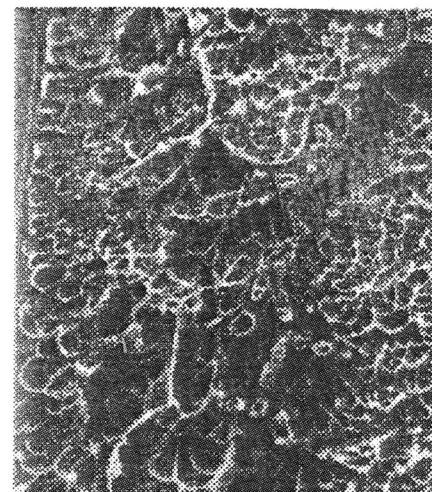


Fig. 9: Detail from Fig. 8 (24x)

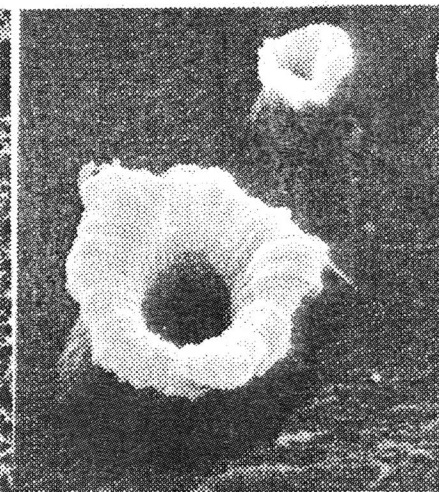
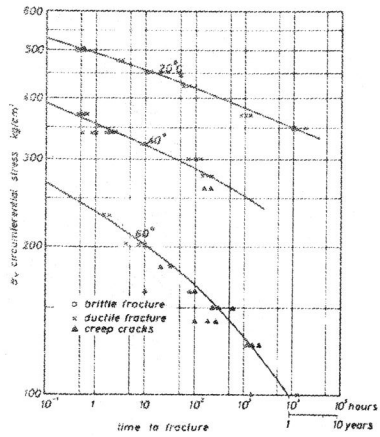


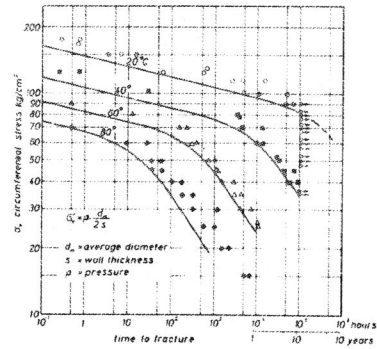
Fig. 10: Detail from Fig. 9 (600x)

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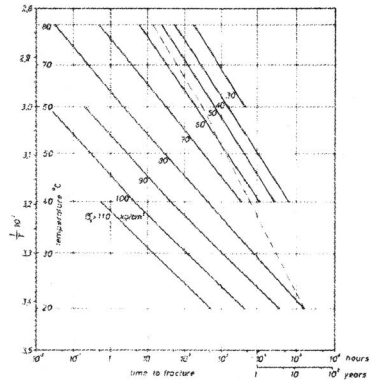
Fracture of PVC tubes under internal pressure

Fig. 11: Time to fracture of PVC tubes (Niklas et al.)



Creep rupture strength of tubes from HDPE

Fig. 12: Time to fracture of HDPE tubes (Richard et al.)



Creep rupture strength of tubes from HDPE

Fig. 13: Arrhenius plot of times to fracture (HDPE tubes, Richard et al.)

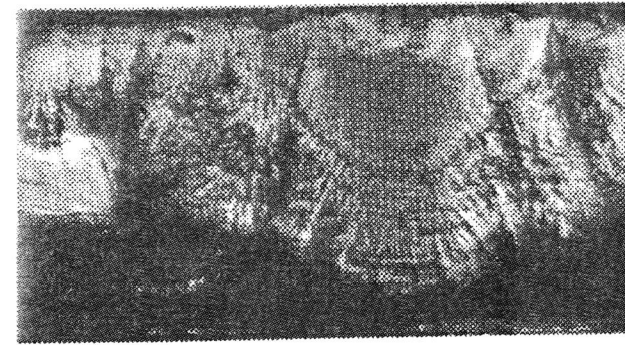


Fig. 14: Surface of a creep crack (10x)

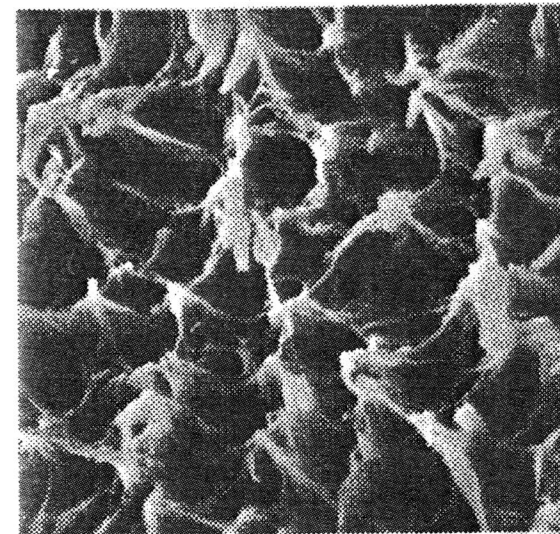
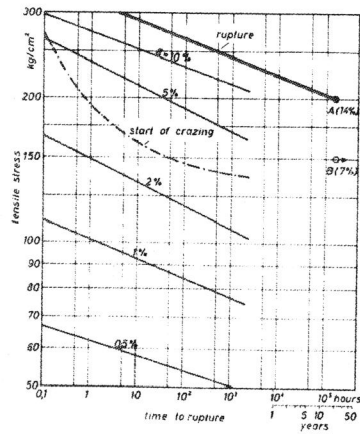


Fig. 15: Details of the "mirror" zone in Fig. 14 (1200x)



Creep rupture strength of PTFCE (20°C)

Fig. 16: Time to fracture of PTFCE
in uniaxial tension
(Richard et al.)

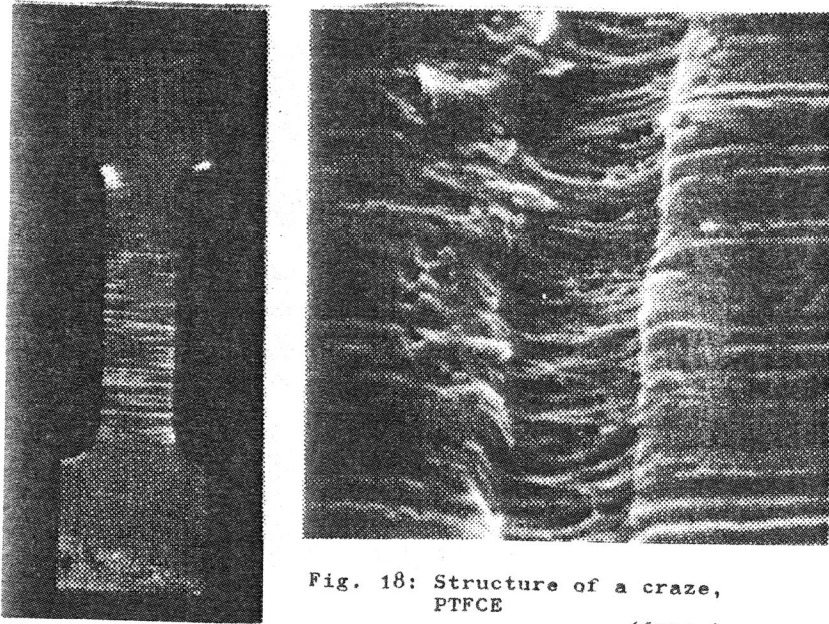


Fig. 18: Structure of a craze,
PTFCE
(6000x)

Fig. 17: Crazed
PTFCE sample
(indicated as B in Fig. 16)