Statistical regularities in cellulose triacetate fracture under thermal degradation conditions

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We have experimentally established regularities in the failure of cellulose triacetate at temperatures close to that of its thermal destruction. On the basis of statistical research, two levels of durability are revealed, corresponding to various breaking mechanisms. The mechanism of sample destruction at the first maximum is thermal fluctuation breaking of strained bonds induced by applied mechanical stress. The mechanism of sample destruction at the second maximum is thermal oxidative degradation of a much weakened material.

(Keywords: cellulose acetate; fracture toughness; failure)

INTRODUCTION

At present, the discreteness of polymer durability levels has been demonstrated to depend on the presence of structural defects of various types[1-4]. As shown in the cited works, which mainly deal with quasi-brittle failure of polymers, each type of defect is related to a certain durability level, i.e. to a durability distribution curve maximum. Statistical durability studies are important not only for detecting imperfections but also for elucidating the mechanism of polymer destruction[1,3]. Statistical data on high-temperature polymer destruction are lacking in the literature. Thus an examination of statistical polymer failure patterns near polymer thermal destruction temperatures appears to be of considerable interest.

EXPERIMENTAL

The investigations were carried out on industrial cellulose triacetate films 1.7×10^{-4} m thick and containing 3% dibutyl phthalate and 9% triphenyl phosphate as plasticizers. Statistical data were collected for 100 samples prepared under identical conditions with carefully maintained constant tension, σ, and temperature, T. Durabilities, τ, were measured at tensions of 35, 41, 48 and 54 MPa ($T=443$ K) and 30, 35, 46 and 50 MPa ($T=473$ K). The technique for data processing was described in detail in ref. 4.

X-ray photographs were taken using a URS-501 camera (Cu Kα radiation, Nil filter). The mean angle of disorientation of crystallities, $\Delta\bar{\phi}$, was estimated from equatorial reflection (1 1 0) azimuthal intensity distribution halfwidths.

The kinetics of growth of main-line cracks was monitored visually and by taking photographs on an MKU-1 camera. The crack growth kinetic data and the X-ray and fractographic data given below refer to samples whose durabilities correspond to a maximum of the durability distribution probability density curves, $\rho(\ln\tau)$.

RESULTS AND DISCUSSION

The differential durability distribution curves for cellulose triacetate (CTA) at 433 and 473 K are given in *Figure 1*. One can see that the nature of the distribution of durability values is a function of the tensile stress, σ, applied to the sample. Depending on σ, the differential curves represent spectra containing one or two maxima simultaneously. The first of these ($\ln\tau_{W_1}$) occurs at small durability values and the second is shifted along the time axis to larger τ values. Under tensions approaching the breaking stress and at small σ values, the distribution curves are unimodal. The spread of durability values (R) is then only small. In the intermediate region (30 MPa$<\sigma<$50 MPa), the $\rho(\ln\tau)$ curves have two maxima ($T=473$ K). The appearance of a second maximum when the first one is present enhances the spread in τ values, although, within each peak separately, the R_1 and R_2 values are approximately the same.

It is important to note that the positions of CTA durability levels, $\ln\tau_{W_1}$ and $\ln\tau_{W_2}$, at temperatures near that at which thermal destruction begins, depend on σ and T. With quasi-brittle failure of polymers, on the other hand, the action of external factors is limited to redistributing samples over durability levels without affecting the level positions[2-4]. In addition it was shown[3] that samples 50 μm and more thick are characterized by a unimodal distribution, whereas with CTA, distribution curves can have two as well as one maxima. This difference can in our view be explained as follows.

As is known, durability levels not only are related to sample imperfections but also have a relaxation nature, i.e. they characterize specific features of the structure of a polymer[4,5]. At low temperatures, the structure of a polymer during breaking can be considered to be comparatively stable[6]. As to the conditions under which CTA durabilities were studied, the polymer structure at both the molecular and supermolecular levels underwent substantial changes related to crystallization, orientation and thermal destruction[7]. Also, the nature of these

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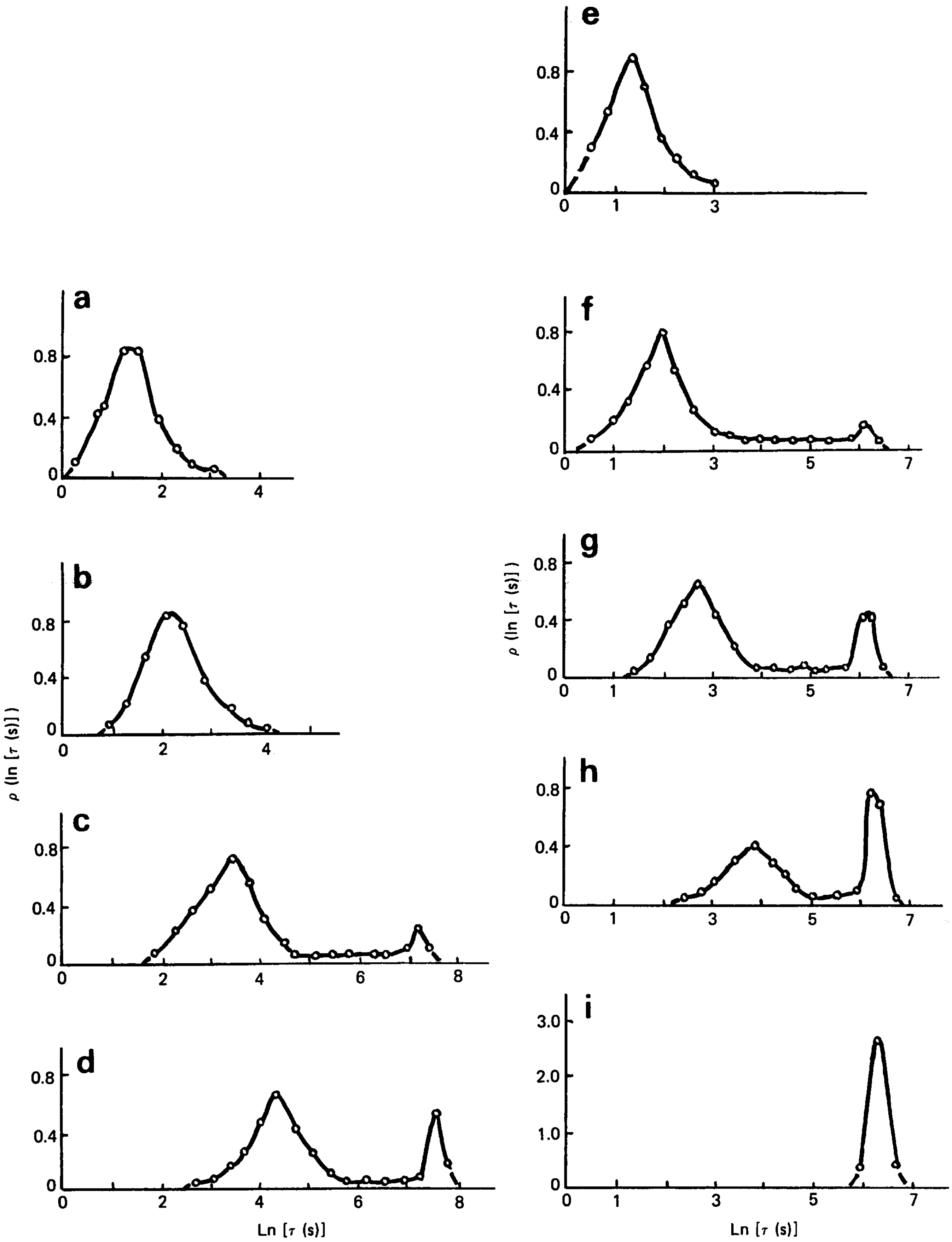

Figure 1 Differential durability distribution curves of CTA at temperatures of 443 K (a–d) and 473 K (e–i) for the following stresses: (a) 54 MPa, (b) 48 MPa, (c) 41 MPa, (d) 35 MPa, (e) 50 MPa, (f) 46 MPa, (g) 41 MPa, (h) 35 MPa and (i) 30 MPa

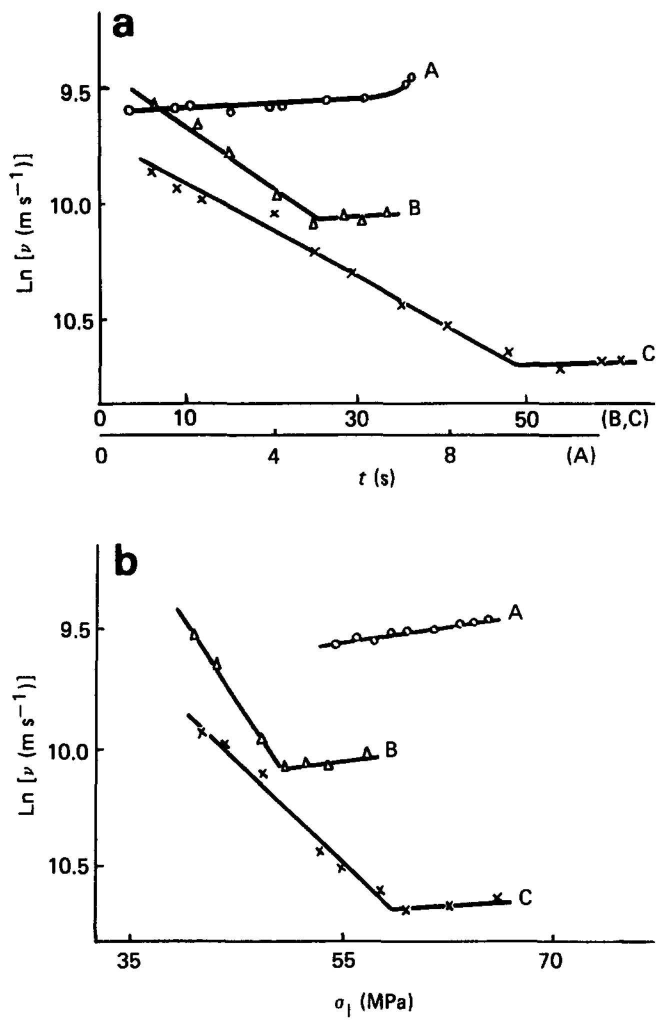

Figure 2 Dependence of logarithm of velocity crack growth rate on (a) time and (b) real stress at a temperature of 473 K: σ_0 (initial stress) = 50 MPa (curve A), 41 MPa (curve B) and 35 MPa (curve C)

changes at a given temperature depends on the applied stress. The occurrence of these processes, which complicate breaking of polymers, and various degrees of polymer structural transformations appear to be responsible for variations in durability levels with varying σ.

It should be noted that the two levels show different dependences on σ and T. The first one is characterized by a high sensitivity to σ variations and only a weak dependence on T. Conversely, the second level depends on σ only insignificantly and shifts strongly with varying T. Different level stress and temperature dependencies are probably indicative of different breaking mechanisms. Let us consider the problem in more detail.

With ductile failure of CTA at high temperature, the durability of a polymer is determined by the ratio of the mechanically induced thermal oxidative destruction rate and the rate of relaxation processes, which depends on $\sigma^{7,8}$. The problem will be analysed by comparing the creep and crack growth curves and using estimates of the degree of polymer destruction and fractographic data on rupture surfaces. As a first approximation, relaxation processes can be monitored by measuring the parameter of orientation of structural elements, $\Delta\phi$.

It has been shown that, for both durability levels, polymer rupture occurred as a result of growth of main-line cracks. The low ($\ln \tau_{w_1}$) and high ($\ln \tau_{w_2}$) level samples, however, differed in that, in the latter, the growth of main-line cracks was influenced considerably by relaxation processes and dependent phenomena, such as the formation of cracks of 'silver', deformation microlamination, surface cracking, etc.

Studying the growth kinetics for artificial cracks has shown the process to involve three steps (*Figures 2* and *3*): (1) retarded growth (growth rate decreases as the crack penetrates into the sample); (2) constant crack growth rate; and (3) fast crack growth, which only makes an insignificant contribution to polymer durabilities (below 0.1τ) and for that reason will not be considered in this work. A different pattern is observed for samples studied near the breaking tensile stress ($t < 10$ s). Step (1) is then lacking. Nor do the corresponding creep and crack growth curves contain steady-state regions. As is seen from *Figure 2* (curve A), cracks then grow with a small acceleration for most of the time ($t > 0.9\tau$), breaking being strongly localized and orientation processes mainly developing near the head of a main-line crack. In spite of a high breaking rate determined by a high σ value, intense relaxation near the crack head maintains a balance between the rates of breaking and rearrangement of macromolecules, which results in a constant crack growth rate. Under high tensions, cracks develop fast to divide a polymer into two parts.

As σ decreases, the ratio of the rates of relaxation and breaking processes shifts progressively to the side of factors causing strengthening of the material, which is manifested by the appearance of a region of deceleration

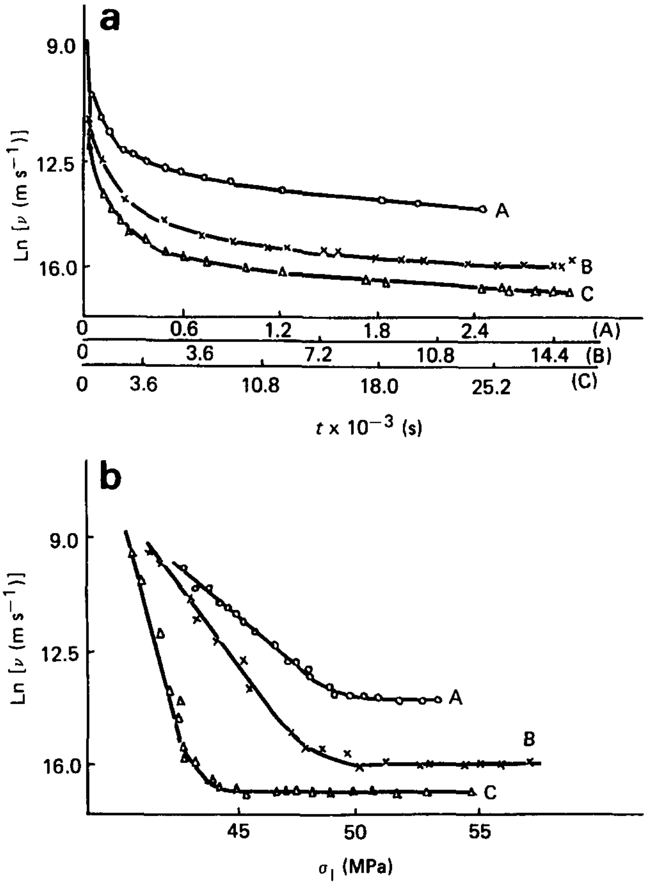

Figure 3 Dependence of logarithm of velocity crack growth rate on (a) time and (b) real stress at a temperature of 473 K: σ = 41 MPa (curve A), 35 MPa (curve B) and 30 MPa (curve C)

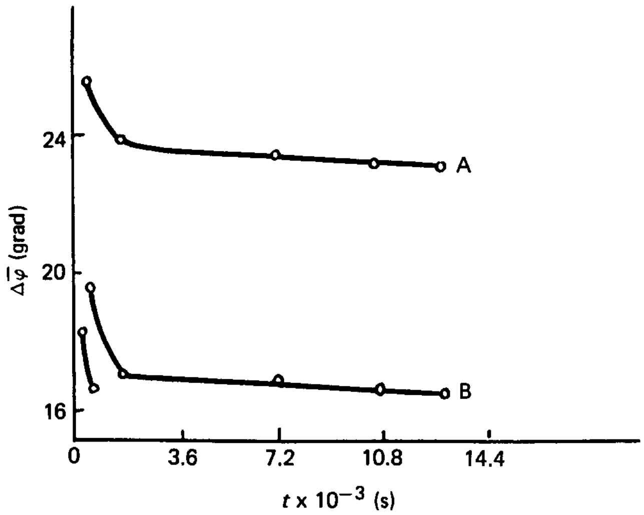

Figure 4 Dependence of mean angle of crystallite disorientation on time ($T = 473$ K) at stresses of 30 MPa (curve A) and 41 MPa (curves B and C); the durability of samples corresponds to the first (C) and the second (B) maximum

in the kinetic curves describing crack growth (*Figure 2*, curves B and C). As a result, $\ln \tau_{W_1}$ maxima of $\rho(\ln \tau)$ curves undergo shifts to higher durabilities (*Figure 1*). In the deceleration region extending to 80–85% of the sample durability, the crack propagation rate decreases by 0.3–0.5 orders of magnitude. This is accompanied by changes in crack shape and head configuration: cracks undergo considerable opening, and their heads become blunt and rounded rather than sharp and wedge-like. It is natural to relate this observation to orientation strengthening of a polymer during stretching. Polymer orientation, however, fails to reach equilibrium because of considerable crack propagation (*Figure 4*, curve C). An increase in stress caused by a decrease in the cross-sectional area, σ_l (*Figure 2b*, curves B and C), results in an increase in the crack growth rate (step (2)) and fast sample rupture.

Edges of torn films (shown in *Figures 5a* and 5b) correspond to samples whose durabilities fit the first $\rho(\ln \tau)$ curve maximum. One can see rupture surfaces either to be uniform across the whole cross-section (*Figure 5a*) or to consist of specular and rough regions (*Figure 5b*). The first type of rupture is most characteristic of samples subjected to near-breaking tensile stress ($\tau < 10$ s). The destruction of samples of $\tau \approx 30$–70 s durabilities is a more complicated phenomenon involving the formation of specular and rough rupture surface regions. A certain widening of the rupture region is observed as a crack penetrates into the sample, which is probably indicative of an increase in the materials's resistance to destruction. A lamellar rupture surface characteristic of a rough region consists of strongly distorted and oriented material.

These observations can be explained as follows. When $\sigma \approx \sigma_r$, samples fail to undergo strengthening under stress, and cracks grow in them at increasing rates. As to samples with longer durabilities, the part of a polymer that lags behind in strengthening requires less energy expenditure to be broken and produces a smooth rupture surface, whereas crack propagation through oriented and ordered regions is a more energy-consuming process and therefore lamellar rough surfaces are formed.

Thus the mechanism of sample destruction at the first $\rho(\ln \tau)$ maximum is the thermal fluctuation breaking of strained bonds induced by applied mechanical stress. Shifting of this maximum along the durability axis with varying σ is caused by the different contributions of relaxation phenomena to the process of mechanically induced polymer destruction.

With the second durability maximum, three crack growth steps are also observed (*Figure 3*). The major processes occurring in stressed CTA samples are crystallization, orientation of structural elements and thermal oxidative destruction. In the first stage of retarded crack growth, the determining factor is rearrangement of macromolecules providing orientation ordering of a polymer. Relaxation processes are then fully realized, and $\Delta\bar{\phi}$ reaches its equilibrium values (*Figure 4*, curves A and B). This causes a substantial decrease in the crack growth rate, by 2–3 orders of magnitude, and the formation of cup-shaped rather than wedge-like cracks. The development of orientation processes results in more

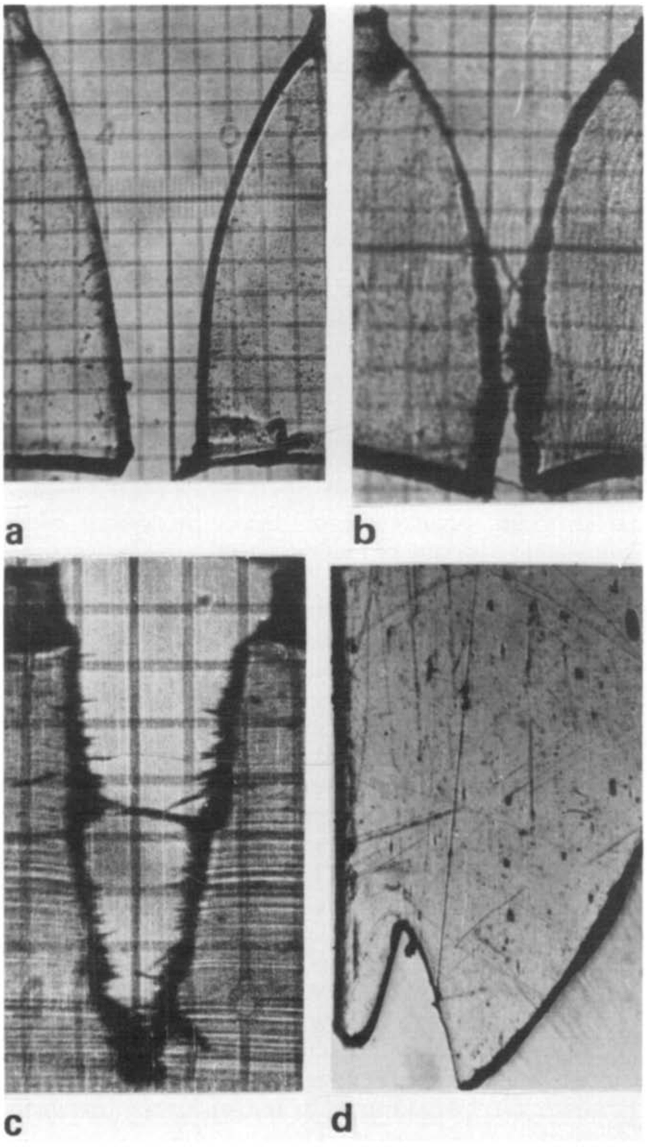

Figure 5 Edges of torn samples tested at a temperature of 473 K: (a) $\sigma = 50$ MPa, $t = 8$ s; (b) $\sigma = 46$ MPa, $t = 68$ s; (c) $\sigma = 41$ MPa, $t = 20400$ s; (d) $\sigma = 30$ MPa, $t = 35450$ s

than 110% increase of polymer strength, and accordingly a considerable shift of sample durabilities towards larger τ values ($\ln \tau_{W_2}$).

At first sight the development of orientation processes causing material strengthening should result in a rapid increase of durabilities and attainment of 'safe' tensions[9]. However, under high-temperature conditions, the decrease in the contribution from mechanically induced destruction is compensated by thermal oxidative destruction of stressed samples. In fact, X-ray and viscosimetry data show that, after strengthening, a considerable loss in sample resistance is caused by the destruction of amorphous intercrystalline regions.

The developments of relaxation processes results in a 'tension-bar' nature of rupture (*Figure 5b*), most fully realized under tensions of 41 MPa $< \sigma <$ 46 MPa. With decreasing σ (35 MPa), rupture surfaces become less rough and the region of rupture undergoes narrowing. At $\sigma = 30$ MPa, the destruction becomes fragmentary and multi-layer in nature (*Figure 5d*). The decrease in CTA destruction energy can be explained by observing that samples are destroyed (loose resistance) mainly because of thermal oxidative processes, while the effect of stress is, probably, reduced to breaking the continuity of a much weakened material. This conclusion is also suppported by only a weak dependence of the position of the second maximum on tensile stress.

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