polymer communications

High effective draw as a route to increased stiffness and electrical response in poly(vinylidene fluoride)

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There has been considerable interest in polyvinylidene fluoride (PVDF), due primarily to the existence of several crystal forms[1], notably the polar Form I[2] which is non-centrosymmetric and may become quite strongly piezoelectric and pyroelectric when the polymer is poled by subjecting it to a high electric field; and the antipolar Form II[3] which is centrosymmetric and only weakly piezoelectric and pyroelectric after poling unless high enough fields are used to produce the polar Form II[4] (still less active than Form I). Subjecting the polymer to various mechanical treatments such as tensile drawing at different temperatures can produce material with different crystal forms[5]. As might be anticipated the materials of different structure show differing piezoelectric and pyroelectric reponses[6-10], although no clear-cut guidelines have emerged which relate these to structure. There is therefore considerable incentive to examine in detail the potential of a wide variety of mechanical forming processes, partly with a view to possible increase in the electrical responses and partly to elucidate the mechanisms of these responses. In this communication we wish to report the interesting and valuable results which have followed from the application to PVDF of ideas on tensile drawing of polymers which have stemmed from recent studies at Leeds University on the production of ultra-high modulus polyethylene and other polymers[11,12].

As a result of these recent studies it has been shown that the concept of a 'natural draw ratio' should be replaced by that of effective draw, i.e. draw which produces enhancement of properties as distinct from flow drawing. Moreover, the natural draw ratio can sometimes be appreciably exceeded through correct choice of polymer molecular weight and drawing conditions. An illustration of the application of these ideas to the tensile drawing of PVDF will now be discussed.

A commercial grade of PVDF (Solvey–Cie, Belgium, Grade Solef XION, $M_n = 171\,000$, $M_w = 351\,000$, typically having 6% defects in stereoregularity) was compression-moulded at 240°C and quenched into water to give an isotropic sheet of thickness 0.6 mm. Dumb-bell samples of 3.8 cm gauge length were cut from this sheet and drawn in an Instron Tensile Testing Machine either at a constant crosshead speed of 0.2 cm min^{-1} or at an initial speed of 10 cm min^{-1} reduced progressively to 0.2 cm min^{-1} at 140°C for a range of draw times up to 80 min. The drawing rates were chosen so as to control the drawing stress in the later stages of the drawing, and were as high as was found practicable without causing fracture. *Figure 1* shows the Young's modulus of the drawn samples, determined from the creep response at 10 s as a function of the draw ratio. It is of particular interest that the 'natural draw ratio' of ~ 4 can be very much exceeded, and that effective draw was obtained so that the Young's modulus increased from 2.1 GPa at $\lambda = 4.1$ to 4.1 GPa at $\lambda = 6.8$. Values as high as 4.6 GPa have been achieved under similar drawing conditions. The drawing behaviour of a similar sample at 80°C is shown in *Figure 2*. In this case the maximum draw ratio before failure was 5.1 and the corresponding value of the Young's modulus was 2.9 GPa, care being taken to produce unvoided samples.

Previous studies of the drawing of PVDF at different temperatures, limiting the draw to the natural draw ratio, have shown that low-temperature draw produces oriented material with Form I crystal structure, whereas high temperature draw produces oriented material with Form II crystal structure. The wide-angle X-ray diffraction patterns of the materials drawn at 80°C in this investigation show the simple low temperature behaviour with formation of oriented Form I structure continuing above the natural draw ratio. The X-ray patterns of the materials produced by drawing at 140°C, however, show that although up to the natural draw ratio of ~ 4, Form II is present, as the draw ratio is increased the proportion of Form II decreases, and there is an increasing proportion of Form I, which by $\lambda \sim 6.7$ exceeds 80% by volume. We believe that production of Form I material could arise from a stress-induced phase transition due to very high drawing stresses at high draw ratios.

Comparison of the pyroelectric and piezoelectric responses of the drawn samples reveals that the high draw ratio samples, in addition to possessing much higher stiffnesses, also show increased electrical responses for the given draw temperature after poling under standard conditions. For example, a sample of draw ratio 6.7 with a Young's modulus of 3.8 GPa, showed a pyroelectric constant λ of 45 $\mu C/m^2/K$ and a hydrostatic piezoelectric
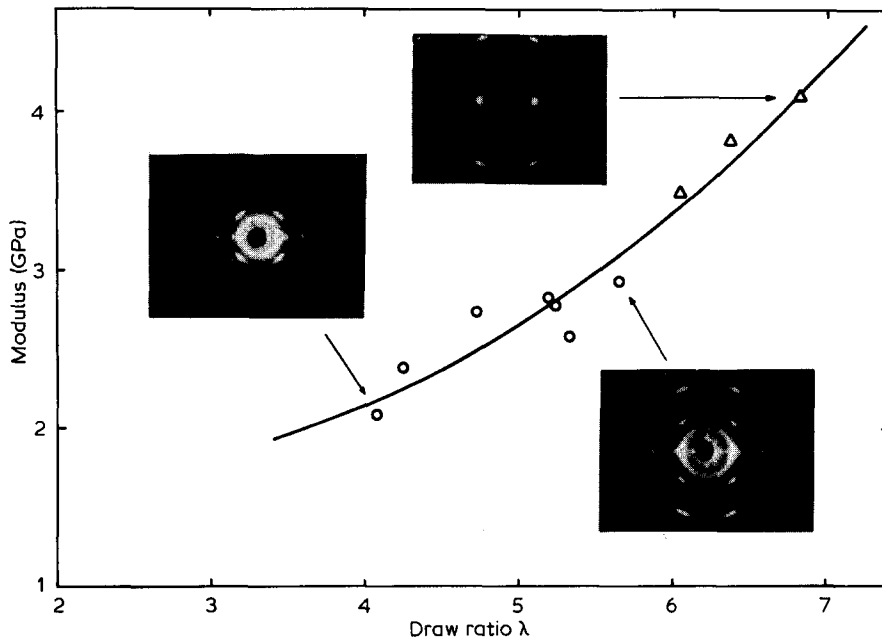
Figure 1 Young's modulus *versus* draw ratio for a draw temperature of 140°C. (Insets are wide-angle X-ray diffraction patterns of indicated samples)
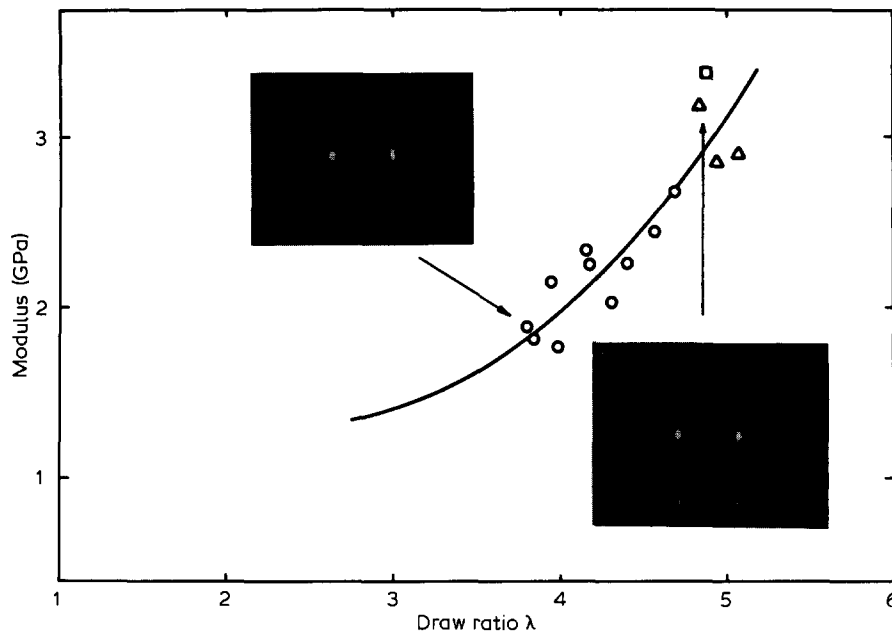

Figure 2 Young's modulus *versus* draw ratio for a draw temperature of 80°C. (Insets as in *Figure 1*)

constant d_h of 15 pC/N (compare with typical values at the natural draw of $\lambda = 25$ μC/m^2/K and $d_h = 8$ pC/N). It is considered that the increases in d_h and λ with effective drawing at a given draw temperature i.e. a doubling of these coefficients for a corresponding doubling of the Young's modulus, are highly significant. First, the magnitude of the coefficients are then already at least as good as values obtained by other methods, including low temperature drawing to the natural draw ratio followed by annealing (an accepted procedure for increasing Form I content). Secondly, we have found no evidence for any saturation of these increases which suggests that further

improvements in d_λ and λ may be achieved by higher effective draw. Such improvement in electric responses coupled with the application of this technique to a wide range of thickness and cross-section (e.g. oriented sheet of thickness greater than 1 mm has been successfully polarized), is likely to have considerable technological significance in a wide variety of applications including hydrophones, ultrasonic medical scanners and infra red or ultrasonic imaging devices.

A full account of this work will be published shortly. It also forms the subject of a patent application [Br. Pat. Appl. 7941419/79 (filed 30.11.79)].

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Slip band formation in polycarbonate under tension

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The effect of thermal history on slip band formation in glassy polymers has been studied extensively. Bowden and Raha[1] discovered that in both polystyrene and poly(methyl methacrylate) under plane strain compression two distinct deformation modes were possible. Yielding took place either along well-defined slip bands or in diffuse yielded zones. As the strain rate decreased the slip bands gradually disappeared. However, it was noticed that it was much easier to form slip bands in thermally aged specimens than in quenched material. Wu and Li[2] obtained similar results in notched compression samples of polystyrene and also found that the diffuse zones were aggregates of fine slip bands around 0.1 μm thick. Various other authors[3-5] have also studied slip band formation in polystyrene under compresion but little work has been done in tension or on other polymers.

During tensile experiments on a 1 mm thick commerical polycarbonate sheet (Makrolon) it was noticed that the propagating neck often appeared to contain an irregular texture. After concluding that the texture was produced by a collection of discrete slip bands, it was decided to investigate the effect of thermal history and neck velocity on the formation of these slip bands.

Firstly, the orientation in the sheet was removed by drying at 120°C for 18 h and then holding at 160°C for 4 h between glass plates. The sheet was then air-cooled and d.s.c. traces showed that it had been effectively quenched. Conventional dumb-bell specimens (narrow section 12.7 × 60 mm) were cut from the sheet. Half of the specimens were then aged by holding at 130°C for 48 h. This treatment provides the maximum degree of aging obtainable in polycarbonate. The specimens were then extended on an Instron Mechanical Testing Machine at crosshead speeds in the range 0.0008 to 0.833 mm s^{-1}. In all experiments the draw ratio was close to 1.7 and therefore the neck velocities lay in the range 0.002 to 2.02 mm s^{-1}.

The appearance of the necks in the aged specimens can be seen in *Figure 1*. When describing the visible features it is convenient to define an orthogonal set of axes xyz with the y axis coincident with the tensile axis and the xy plane lying in the plane of the specimen. The z direction is then normal to the specimen surface. The texture in the necks is easily seen but becomes less pronounced as the neck velocity is decreased. As the neck propagates, 'ripples' are left on the surface of the drawn material. Also visible are groups of slip bands in the xy plane. Evidently the slip bands form at the edge of the specimen and run towards the centre of the specimen as the neck propagates. The specimens in the micrograph are unloaded and elastic relaxation may affect the orientation of the slip bands. However, since they are close to 45° to the tensile axis it is reasonable to assume that they are propagating along the direction of maximum shear stress. The tips of the slip bands remain at a constant distance above the top of the necked region and clearly the presence of the neck is necessary to generate these slip bands. As the neck velocity is reduced the extent of the slip bands increases until at the lowest neck velocity the two sets of slip bands overlap. Possibly a small degree of thermal softening occurring ahead of the neck hinders the formation of the slip bands at the higher neck velocities. Infra-red photography[6] has shown that a neck velocity of 2.02 mm s^{-1} produces a temperature rise of around 15°C. The temperature decreases when moving from the centre of the neck to the edges and perhaps the extent of the slip bands corresponds to some limiting temperature above which they are not produced. At the lowest neck velocity the temperature increase is less than 0.2°C and no significant thermal softening occurs.

In order to learn more about the texture in the necks, sections were taken in the yz plane by cutting with a diamond impregnated slitting wheel. *Figure 2* shows that the texture is produced by a system of slip bands operating in the yz plane. Again the specimen is unloaded and elastic strains would tend to make the slip bands intersect at angles closer to 90°. Nevertheless, it is reasonable to