A Study of the Drawing Behavior of Polyvinylidene Fluoride

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Synopsis

The drawing behavior of different molecular weight PVDF grades has been investigated over the temperature range 140–160°C, with particular reference to the production of material with enhanced mechanical and electrical properties. Lower molecular weight grades, which have been subjected to a slow-cooled rather than a quenched moulding procedure yield higher Young's moduli when drawn to a given draw ratio. X-ray diffraction measurements have demonstrated that the crystalline regions of specimens drawn to high draw ratios under these conditions consist predominantly of the piezo- and pyroelectric form I phase. The relationship between the proportion of form I phase and the final drawing stress has been shown to be unique over the temperature range investigated, irrespective of molecular weight and thermal processing history.

INTRODUCTION

The research described in this paper stems from the recognition that the piezoelectric response of polyvinylidene fluoride (PVDF) might be significantly enhanced if this material could be produced in a very highly oriented form. Preliminary studies[1] indicated that this was the case, and the results of this early work have been described in a previous publication[2] and form the basis of a patent application.[3]

In the present paper we give an account of a very extensive investigation of the tensile drawing behavior of PVDF. This work forms part of a wider study of the preparation and properties of oriented PVDF, undertaken jointly by Thorn-EMI Ltd and Leeds University. It relates particularly to previous studies of the drawing behavior of crystalline polymers at Leeds University, where guidelines have been established for the preparation of ultra-high modulus linear polyethylene (LPE),[4–6] polypropylene (PP),[7,8] and polyoxymethylene (POM),[9] and to similar studies in other laboratories.[10–12]

In view of the previous work on polyethylene,[4–6] a natural starting point for the present investigation on PVDF was to examine the influence of molecular weight and initial thermal treatment on the tensile drawing behavior over a range of temperatures and strain rates. In addition to the measurement of the load-elongation characteristics and the maximum draw ratio, the axial Young's modulus has been used as a measure of the effectiveness of the drawing process, following the philosophy of previous work. The draw ratio/time behavior for different molecular weight PVDF grades and thermal processing histories is similar to that for LPE and has been discussed in a previous paper.[2]

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The piezoelectric response of PVDF is influenced by the structure of the crystalline regions, which can take a number of different crystal forms. Our previous studies[1] showed that a transformation occurs in the crystalline regions from the nonpolar form II to the polar form I on drawing to high draw ratios at high temperatures. We have therefore examined the form I content of the oriented samples in relation to the drawing conditions and extent of draw.

EXPERIMENTAL

Material and Sample Preparation

Four commercial PVDF grades from Pennwalt Chemical Industries and Solvay et Cie (Belgium) were investigated. Three of these have been described in a previous paper[2] and were denoted KCF, X10N, and X8N, a nomenclature which will be retained throughout this paper. The fourth material is a lower molecular weight grade from Solvay et Cie which will be referred to as X6N. The molecular weight and the molecular weight distribution for each grade were measured by Dr. C. Booth at the Department of Chemistry, Manchester University using gel permeation chromatography. These are shown in Table I.

To ensure that the thermal history of each PVDF sheet was known, the material supplied was compression moulded using the method described previously.[2] After molding, sheets were (i) quenched in water at room temperature or (ii) slow-cooled in the press down to room temperature or (iii) slow-cooled to below the crystalline melting point and then quenched. An X10N sheet, for example, would be denoted X10N/W, X10N/SC, or X10N/160 depending on whether it had been subjected to procedure (i), (ii), or (iii) respectively. The isotropic sheets, which were typically 0.35 mm thick, were characterized by measurements of density and Young's modulus.

Tensile Drawing

The tensile drawing apparatus and drawing procedures have been fully described in a previous publication.[2] For this work, dumbbell samples (5 mm wide, with 22 mm gauge length) were cut from sheets of different molecular weight grades and morphologies, and drawn at 140, 150, and 160°C. For some materials, two different crosshead speeds (2 and 100 mm/min) were employed. The draw ratio $\overline{D}_R$ was calculated from the ratio, before and after drawing of the spacing of ink-spots marked along the dumb-bell

TABLE I
Molecular Weights of Different PVDF Grades

	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
KCF	171,100	764,200	4.47
X10N	171,000	351,200	2.05
X8N	130,200	275,700	2.12
X6N	75,000	150,000	2.00

gauge length. At the end of each draw run, the final drawing stress was calculated from the final load (measured by the tensile load-cell) and the cross-sectional area of the drawn specimen.

Characterization of the Drawn Material

Mechanical Properties

The extensional modulus parallel to the orientation direction of each drawn specimen was measured at 21°C by a dead-loading creep experiment as described in a previous publication.[2] Dynamic mechanical measurements were made over a range of temperatures from −120 to +20°C on selected drawn specimens. A Solartron 1172 frequency response analyzer (FRA) generated a sinusoidal voltage which drove a generator, producing a sinusoidal variation in uniaxial strain of the clamped sample. This data was processed by the FRA to produce the in-phase and out-of-phase components of the ratio of strain to stress relative to the driving voltage. Values of the modulus, compliance, and tan δ were calculated from these components. A more detailed description of the experimental technique may be found elsewhere.[13]

Crystalline Structure

An X-ray diffractometry technique has been used to determine the relative proportions of form I and form II crystalline phases in the drawn samples. A meridional 2θ scan was performed using a Siemens K-4 X-ray generator equipped with a type F goniometer. The proportions of each crystalline phase were determined from the intensities of the form I (001) and form II (002) reflections using the method of Davies and Singh.[14] The intensities were weighted by a factor calculated from the structure factors for each of the two reflections.

RESULTS AND DISCUSSION

Relationship between Modulus and Draw Ratio

Previous work on LPE,[4-6] PP,[7,8] and POM[9] has shown that the relationship between Young's modulus and draw ratio, for samples drawn under the same conditions, is independent of molecular weight and thermal processing history. It is apparent from Figure 1 that this is not the case for PVDF which shows a pronounced molecular weight effect: The lower molecular weight X10N grade produces a higher modulus at a given draw ratio. In addition, a smaller effect attributable to thermal history is observed for the lower molecular weight grade: A higher modulus at a given draw ratio is obtained if the material has been slow-cooled after compression molding, rather than quenched.

Figure 1 also shows the effect of draw temperature on the modulus/draw ratio relationship, for a given molecular weight and thermal history. A higher Young's modulus is obtained at a given draw ratio for a lower draw

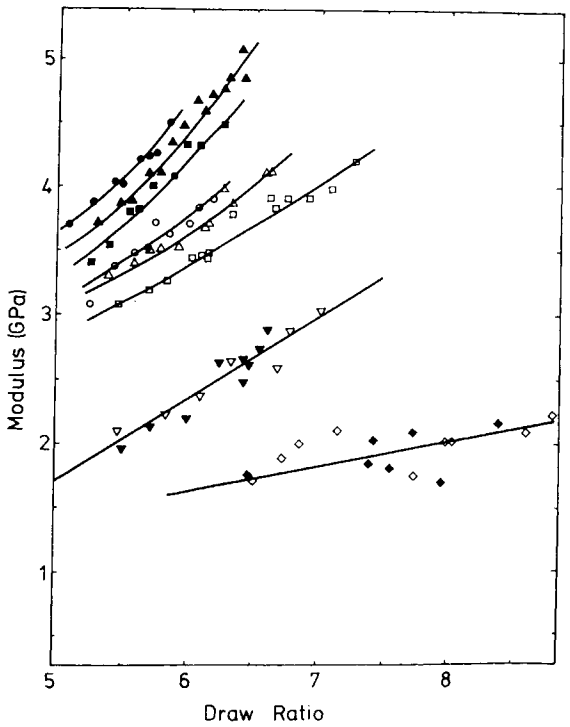

Fig. 1. Modulus as a function of draw ratio for X10N/W drawn at 140°C (○), 150°C (△), and 160°C (□), X10N/160 drawn at 140°C (●), 150°C (▲), and 160°C (■), KCF/W drawn at 150°C (▽) and 160°C (◇), and KCF/140 drawn at 150°C (▼) and 160°C (◆). Crosshead speed = 100 mm/min.

temperature. Similar behavior was observed in the work on POM where it was reported that drawing was most effective at lower temperatures. Increasing the draw temperature, in an attempt to increase the moduli and draw ratios obtainable for high molecular weight grades of LPE, PP, and POM, was unsuccessful. A similar observation was made for the higher molecular weight KCF grade of PVDF where an increased draw temperature produced higher draw ratios, but these were not accompanied by correspondingly high values of modulus. The work on PP showed that the most effective draw temperature was independent of molecular weight, but this was not the case for LPE where the optimum draw temperature was highly molecular weight dependent. If the most effective draw temperature for PVDF were also molecular-weight-dependent, the comparatively low moduli obtained for the KCF grade might be explained: the drawing may have been carried out at the optimum temperature for the X10N grade but not for the KCF.

Figure 2 shows the effect of crosshead speed on the modulus/draw ratio relationship for X10N/W and X10N/SC samples. Although specimens of both morphologies survive to higher draw ratios at a reduced strain rate, there appears to be no advantage in slow-drawing X10N/SC since no significant increase in Young's modulus is obtained. It is suspected that this may be attributable to slight variations between slow-cooled sheets, rather

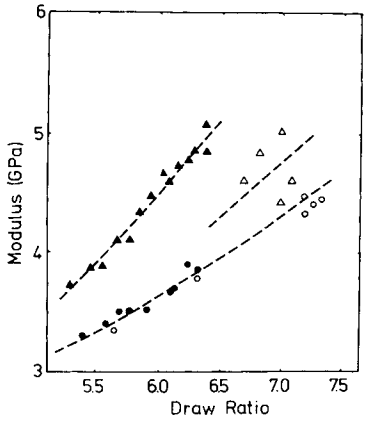

Fig. 2. Modulus as a function of draw ratio for X10N/W drawn at 100 mm/min (●) and 2 mm/min (○) and for X10N/160 drawn at 100 mm/min (▲) and 2 mm/min (△). Draw temperature = 150°C.

than to a strain-rate effect since subsequent drawing work on X8N (discussed below) did show that higher moduli could be obtained by slow-drawing. The quenched morphology data lie on a single line, irrespective of strain-rate so larger draw ratios give correspondingly larger moduli.

In view of the relatively high Young's moduli obtained using X10N polymer, it was anticipated that even stiffer material might result from drawing the lower molecular weight X8N and X6N grades. Maximum moduli of approximately 6 GPa were obtained by drawing these materials at 150°C at 2 mm/min as shown in Figure 3. It was necessary to draw to higher

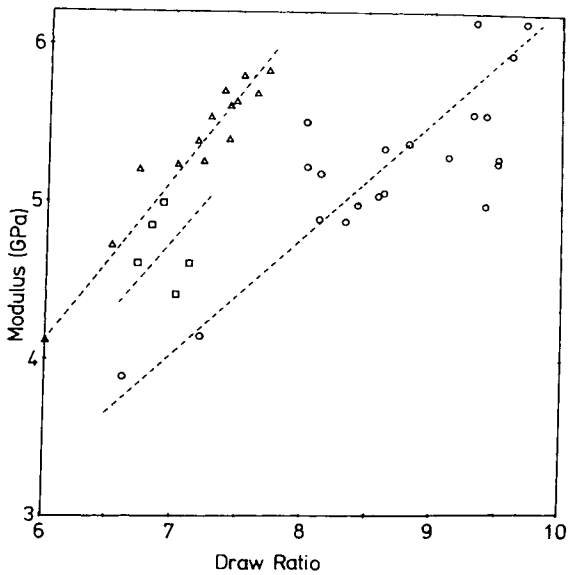

Fig. 3. Modulus as a function of draw ratio for different molecular weight grades: X6N/SC (○), X8N/SC (△), and X10N/SC (□). Draw temperature = 150°C; crosshead speed = 2 mm/min.

draw ratios (up to 9.8) in order to achieve these moduli. A comparatively slow crosshead speed was also required since drawing X8N/SC and X8N/W at 100 mm/min resulted in fracture at approximately 4.5 GPa. Scatter in the data in Figure 3 and the surprisingly low X10N/SC moduli may be attributed to unavoidable variations between slow-cooled compression-molded sheets. The drawing behavior of slow-cooled material is highly dependent on the molding conditions, and a consistent set of data (such as the X8N/SC data in Fig. 3) can only be produced by performing all the drawing on samples from one sheet.

Maximum room temperature Young's moduli of 60, 19, and 40 GPa were obtained for linear PE, PP, and POM, respectively, and at low temperatures the Young's moduli in all cases approached the theoretical chain modulus.[15] The results for PVDF are much less spectacular. The maximum modulus measured at room temperature (i.e., above T_g) for PVDF is approximately 6 GPa. The largest value of dynamic modulus measured at -120°C (i.e., below T_g) using the FRA technique was 33.4 GPa at 10 Hz. This is far short of the theoretical maximum of 237 GPa predicted by Tashiro et al.[16] Figure 4 compares the temperature dependence of the dynamic modulus and tanδ for an X10N/160 specimen, which has a relatively high room temperature Young's modulus (5 GPa) with a low modulus (2 GPa) KCF/W specimen.

The present results therefore differ from those obtained previously for linear PE in two major respects. First, there is not a unique relationship between modulus and draw ratio. Second, the levels of modulus achieved are comparatively low. It seems likely that these two features are related. PVDF is more akin to low density PE than linear PE, and all the samples examined have a comparatively low crystallinity ($\simeq$ 50%). Differences in modulus/draw ratio behavior between samples of different molecular weight and initial thermal treatment can therefore be attributed, at least in part, to the increase in crystallinity with falling molecular weight and, additionally, with slow-cooled initial morphology.

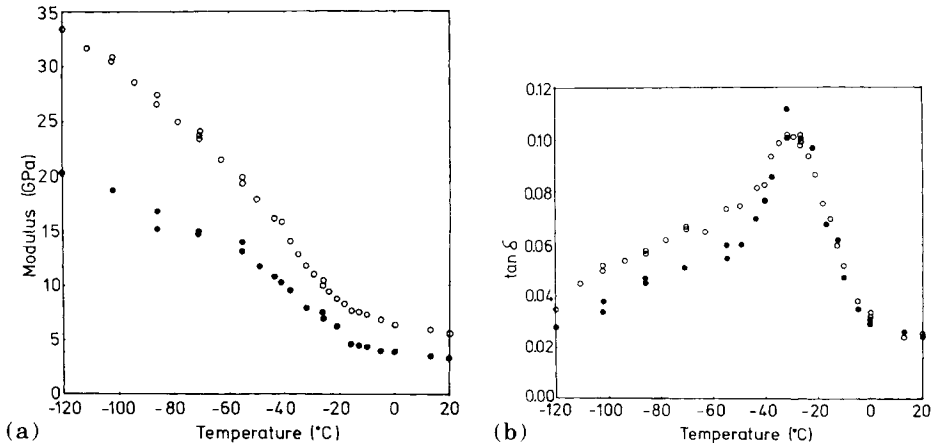

Fig. 4. Comparison of dynamic-mechanical data for high draw (○) and low draw (●) PVDF: (a) Modulus vs. temperature; (b) tan δ vs. temperature.

The degree of crystallinity in the starting materials was assessed by measuring the density and isotropic Young's modulus. These values, which are shown in Table II, display systematic differences attributable to variations in the proportion of crystalline material present. The volume fraction percentage crystallinity was estimated from the relative proportions of form I and form II material assuming densities as follows:

amorphous region = 1680 kg m^{-3}
form I crystalline phase = 1973 kg m^{-3}
form II crystalline phase = 1920 kg m^{-3}

Table III shows how the density and Young's modulus increase with increasing draw ratio, as the degree of crystallinity increases.

Relationship between Form I Content and Draw Ratio

Although optimum drawing conditions for producing relatively high moduli in PVDF have been established, it is the electrical properties of this polymer which are of primary interest. In order to produce the most highly piezoelectric and pyroelectric material in thick film, it is necessary to ensure that a high degree of conversion from form II to form I occurs during the drawing process. The drawing conditions which produce high modulus may not also result in a high form I content. In order to investigate the effect of drawing on the form I content, the drawing parameter which determines the degree of conversion must first be ascertained. Is it simply a matter of obtaining the highest possible draw ratio?

Figure 5 shows that this is not the case because slow-cooled specimens give a more gradual increase in form I content with draw ratio, but yield material with a higher maximum form I content than quenched specimens drawn under the same conditions.

The dependence of form I content on draw ratio for different molecular weight materials (of similar morphology, drawn under identical conditions) was also examined. For each molecular weight grade the maximum form I proportions obtained are in the range 85–88%, but the lower molecular weight materials have to be drawn to significantly higher draw ratios to

TABLE II
Densities and Young's Moduli for Isotropic PVDF

Material	Density (kg m^{-3})	Isotropic Young's modulus (GPa)	Volume[a] crystallinity (%)
X8N/SC	1781.7[b]	2.38	42.4
X8N/W	1778.9	1.80	41.2
X10N/SC	1788.0	2.18	45.0
X10N/W	1773.2	1.78	38.8
KCF/SC	1774.6	1.87	39.4
KCF/W	1763.5	1.52	34.8

[a] Isotropic crystallinities calculated assuming 100% form II.
[b] This low value is a result of microvoiding in the sample.

TABLE III
Densities and Young's Moduli for X10N/W PVDF Drawn at 140°C

Draw ratio	Young's modulus (Gpa)	Density (kg m^{-3})	Form I[a] (%)	Volume crystallinity (%)
Isotropic	1.78	1773.2	0	38.8
4.07	2.09	1787.7	25	42.5
5.23	2.78	1793.0	58	41.7
6.03	3.50	1801.5	74	43.5
6.35	3.83	1804.5	84	43.8
6.80	4.11	1811.0	90	45.5

[a] Estimated from final drawing stress.

reach these form I levels. In particular, a draw ratio of 8.7 is required to produce 86% form I phase in X6N/160 specimens, although prolonged drawing up to a draw ratio of 9.8 did not further increase the proportion of form I. It is clear that a high draw ratio is not the only factor which is important in producing material with a high proportion of form I. Since the conversion from form II to form I is a stress-induced transition, the dependence of form I content on the final drawing stress was also examined.

Relationship between Form I Content and Final Drawing Stress

A unique relationship has been demonstrated between final drawing stress and form I content, irrespective of drawing conditions, initial morphology and the molecular weight of the material. This is illustrated most dramatically by Figure 6, which shows the form I content vs. drawing stress for slow-cooled and quenched X6N grade polymer. There appears to be a virtually unique relationship between form I content and drawing stress for samples drawn under the same conditions, irrespective of thermal processing history. This may be contrasted with the relationship between form I content and draw ratio shown in Figure 5, where samples of different initial thermal treatment, drawn under identical conditions, lie on distinct curves. Figure 7 shows the effect of crosshead speed on the relationship

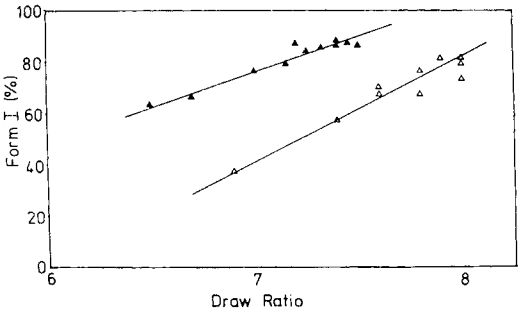

Fig. 5. Form I (%) as a function of draw ratio for X8N/SC (▲) and X8N/W (△) drawn at 150°C, 2 mm/min.

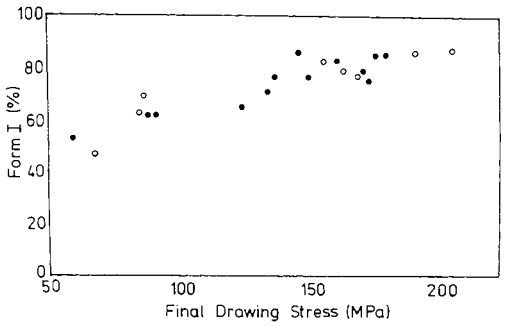

Fig. 6. Form I (%) as a function of final drawing stress for X6N/SC (●) and X6N/W (○) drawn at 150°C and 2 mm/min.

between form I content and final drawing stress. Some measurements on broader X10N/W film drawn at an intermediate strain rate using an "Overload Dynamics" Tensile Tester are included. The majority of the data, which cover a wide range of samples, again lie on a single curve.

Further inspection of the results shows that the relationship between form I content and the drawing stress is independent of sample molecular weight (Figure 8), and, perhaps more surprisingly, is not significantly affected by temperature over the temperature range 140–160°C.

It can be concluded from these results that the limiting draw ratio in PVDF may be associated with the very rapid strain-hardening which occurs when the stress-induced phase transformation from form II to form I nears completion as the available form II crystalline phase becomes exhausted. This is brought out by the comparison between Figures 5 and 6. From Figure 5, it can be seen that much greater draw ratios can be achieved for the quenched material. Comparison with Figure 6 shows that the drawing stress and form I content are then much lower at the same draw ratio, than for slow-cooled material. Young's modulus does not correlate in any obvious way with any single drawing parameter, but depends, at least, on both draw

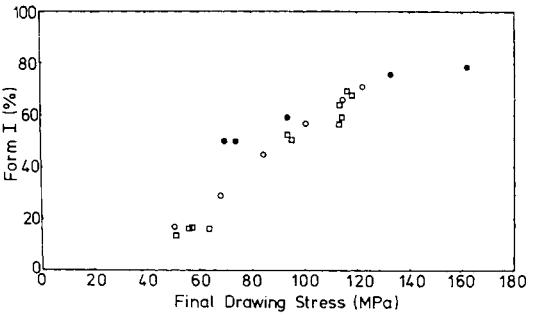

Fig. 7. Form I (%) as a function of final drawing stress for X10N/W narrow tapes drawn at crosshead speeds of 100 mm/min (●) and 2 mm/min (○), and for broad-film samples drawn at an intermediate crosshead speed (□).

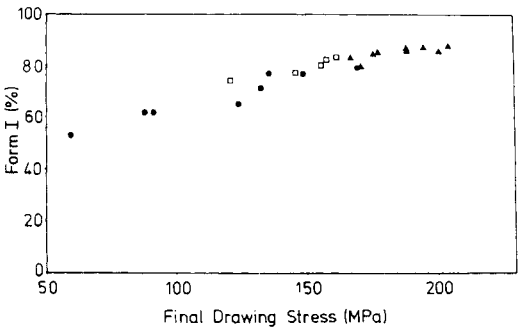

Fig. 8. Form I (%) as a function of final drawing stress for X6N/SC (●), X8N/SC (▲), and X10N/SC (□) grades drawn at 150°C, 2 mm/min.

ratio and drawing stress. NMR measurements currently in progress allow the orientation of the amorphous and crystalline regions to be examined independently and may provide an insight into the Young's modulus/draw ratio behavior.

CONCLUSIONS

1. In contrast to LPE and PP, there is not a unique relationship between Young's modulus and draw ratio for PVDF. Differences are observed between samples of different molecular weight and initial thermal treatment for identical drawing conditions. Higher moduli are observed for drawn samples prepared from polymer which has been slow-cooled rather than quenched. There are also large effects due to molecular weight, and it appears that low molecular weight polymers are mandatory for achieving the highest modulus of about 6 GPa by tensile drawing. These high moduli are most readily achieved by drawing the slow-cooled morphology.

2. The final form I content of the drawn polymer is uniquely related to the drawing stress, irrespective of molecular weight and initial morphology. The rapid rise in drawing stress with increasing draw ratio as form II material becomes exhausted may lead to the observation of a relatively low limiting draw ratio.

3. The modulus of the drawn samples is comparatively low and may relate to orientation of the noncrystalline regions and to the overall crystallinity.

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