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### Material properties

# Uniaxial deformation and orientation of ethylene–tetrafluoroethylene films



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#### A R T I C L E I N F O

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#### ABSTRACT

This study concerns the thermal and mechanical response of several commercial grades of ethylene - tetrafluoroethylene copolymer films. Differential scanning calorimetry was used to show that, although films have similar degrees of crystallinity and melting temperature, the melting endotherms and crystallisation exotherms differ between materials, suggesting small changes in composition between manufacturers. Films were deformed in tension at a range of temperatures and rates. Selected films were unloaded immediately after stretching, and measurement of the elastic recovery highlighted further differences between materials. Batches of films were pre-drawn uniaxially above the glass transition and immediately quenched. When these materials were subsequently re-drawn below the glass transition temperature, most of them exhibited much improved yield stress, modulus and tensile strength (improving by factors of 5, 5 and 4, respectively at a draw ratio of 3), but a reduced strain to failure. In most of the films, the pre-drawing, as well as the initial orientation of the films, is accounted for by a simple shift in the true strain axis. This is indicative of a material response dominated by entropic network stretch. It also suggests that, in the cases where strain superposition does not work, a different arrangement of crystalline lamellae may be present, limiting the extent to which improved properties can be achieved in some materials.

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#### 1. Introduction

Poly(ethylene-co-tetrafluoroethylene), known as ETFE, is a copolymer of ethylene and tetrafluoroethylene with a combination of the properties of poly(tetrafluoroethylene) (PTFE) and polyethylene (PE). The polymer was developed and patented by DuPont in the 1940s [1] and later, in combination with NASA, as a melt-processable thermoplastic with properties reminiscent of PTFE. However, it was only in the 1970s that the first products appeared in the market: DuPont and Hoechst exploited its excellent

electrical insulation (derived from the fluorinated part) and its melt processability (derived from the hydrogenated part) to produce ETFE-coated cables [2]. ETFE is still used in this application today, primarily in aircraft and spacecraft wiring.

The 1980s saw the production of ETFE films by Vector Foiltec, first in experimental sail technology, and later as architectural cushions, where two or more ETFE films are sandwiched together and inflated to form a semi-rigid structural element. This is currently the largest application of ETFE films, showcased in the 8 domes of the Eden project in 2001 [3], in the Beijing National Aquatics Center built for the 2008 Olympics [4], and in many other structures [5]. Other applications include filters and linings for the chemical industry (due to the material's chemical stability) [1], convection barriers for solar cells (due to its excellent barrier properties) [6,7], anti graffiti coatings (due

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to its non-stick and self-cleaning properties) and release films for composite manufacture (due to its high temperature resistance) [8].

ETFE films have also been employed for energy conversion applications in hydrogen and methanol fuel cells, primarily by research groups in Japan [9–12], Switzerland [13–16] and the United Kingdom [17–20]. Although the details differ, most applications employ commercial ETFE films tens of microns thick as supporting structures which are irradiated to enable active groups capable of being grafted and, subsequently, functionalised to introduce ion exchange sites. This process renders the resulting film ionically conductive, and in this state the film is referred to as a polymer electrolyte membrane. In case of acidic proton conducting polymers, the materials are referred to as proton exchange membranes (PEM). PEMs that do not require a separate grafting step exist, for example Nafion<sup>®</sup> [21]. The justification for the use of ETFE base films in this way originates from the drive to develop cheaper and longer lasting polymer electrolyte membranes than can currently be achieved with Nafion films [22]. However, as this application is still in its infancy, the production of the ETFE base films has never been tailored or optimised to the requirements of PEM manufacture for fuel cell applications. Very recently, praiseworthy attempts to model the precise states of swelling, temperature and stress that the PEMs are subjected to during fuel cell application have been made (see for example [23-25]), but the process is clearly challenging and unresolved. At the heart of the problem is a limited understanding of how the structure and manufacturing history of the ETFE films and the subsequent stages of treatment influence the final properties [26,27].

In this study, we focus our effort on furthering the understanding of structure-property relationships of ETFE base films, and on if and how properties may be modified by orientation. The thermal and mechanical properties of a range of commercially produced ETFE base films obtained from three different manufacturers are measured and compared. The emphasis is on a temperature range relevant to fuel cell applications. The objective of this study is to identify the origins of the differences in mechanical performance of films of different thickness and from different manufacturers, and to suggest ways in which films may have properties enhanced through molecular orientation. Ultimately, the drive is to produce base films more suited to energy applications.

#### 2. Experimental

#### 2.1. Materials

The materials used in this study are all commercial grades of ETFE ranging in nominal thickness between 25 and 100  $\mu$ m. Table 1 reports details of the origins and purchase dates of the films.

#### 2.2. Calorimetry

For each measurement, one or more circular discs approximately 6 mm in diameter were cut from the rolls

Table 1

Origin and nominal dimensions of the ETFE films used in this study.

Code	Manufacturer	Material	Molecular weight <i>M</i> w (kDa)	Nominal thickness (µm)	Purchase year
S-25	Saint Gobain	Norton ETFE	n/a	25	2013
D-25 D-50	DuPont	Tefzel ETFE 100LZ Tefzel ETFE 200LZ	~1200 [28]	25 50	2006 1997
N-50 N-100	Nowofol	Nowoflon ET-6235	~400 [27]	50 100	1998 1997

using a sharp punch and stacked in order to make up a calorimetry specimen of ~3.5 mg. Each specimen was precisely weighed and secured in a vented aluminium pan. All specimens were subjected to a heating–cooling–heating cycle between 0 °C and 350 °C, at a rate of 20 °C min<sup>-1</sup> under a N<sub>2</sub> atmosphere, using a PerkinElmer DSC 8000. Melting points, *T*<sub>m</sub>, and crystallisation points, *T*<sub>c</sub>, were determined from the peaks, while heats of fusion,  $\Delta H_{\rm f}$ , were determined using a linear baseline and constant integration limits of 220–285 °C and 190–285 °C, respectively, on the first and second heating cycles, using Pyris Manager software. Crystallinity was subsequently determined for both heating cycles as  $\chi = \Delta H_{\rm f}/\Delta H_{\rm f,0}$  where  $\Delta H_{\rm f,0} = 113.4 \ {\rm Jg}^{-1}$  [29]. It was not possible to discern glass transitions in the scans.

#### 2.3. Mechanical testing

Several rectangular specimens with dimensions 100 mm  $\times$  10 mm were cut from the rolls, with the long axis aligned with the machine (MD) and the transverse (TD) directions, using a sharp bladed custom cutter. The thickness of each specimen was measured in three locations along the centreline at approximately 14, 1/2 and 3/4 of the length of the specimen, using a Heidenhain thickness gauge.

Mechanical testing was carried out on a Zwick/Roell Z005 testing machine fitted with climatic chamber and a 200 N load cell. Specimens were clamped in film grips with a fixed distance between the grips of 75 mm. For all tests above room temperature, each specimen was clamped in both grips, after which time the chamber door was closed. A fixed acclimatisation time of 10 minutes was applied prior to the start of each test to allow the chamber to reach a steady temperature. The temperature during each test, *T*, was monitored using a thermocouple located in the air next to the specimen. For all tests below 100 °C, the relative humidity (RH) in the chamber was also recorded, but not controlled. Temperatures and RH values are reported in Table 2.

Each specimen was preloaded with 0.1 N in order to ensure the removal of slack just prior to the test. A subset of specimens was tested to failure or to a maximum nominal strain of 550%, where the limit of travel of the machine was reached. Strain rates were varied between 0.001 s<sup>-1</sup> and 0.1 s<sup>-1</sup>. Another subset of specimens was loaded to a fixed strain level and, subsequently, unloaded to 0.1 N at the

#### Table 2

Temperatures and relative humidities of mechanical tests performed in this study.

Temperature (°C)	Relative humidity (%)	
$25\pm1$	$26\pm3$	
$50\pm1$	$6\pm1$	
$80 \pm 1$	0	
110 ± 1	n/a	

same rate. In the determination of the true stress, the deformation was assumed to be isochoric.

A third subset of specimens was stretched at a fixed temperature of 110 °C and at a fixed strain rate of 0.03 s<sup>-1</sup> to a pre-stretch of  $\lambda_0$ , corresponding to a strain between 100% and 500% as measured by the cross-head displacement, and immediately quenched using a freezer spray obtained from RS supplies. This technique was previously used to freeze in orientation in polystyrene [30]. Each specimen was then removed from the testing machine, allowed to return to room temperature and re-tested at 80 °C. In this specimen subset, a shrinkage stress developed quickly after clamping and, therefore, no preload was necessary.

#### 3. Results

#### 3.1. Calorimetry

Fig. 1(a) illustrates degrees of crystallinity determined from measurements of heat of fusion for all the materials, on first heating (representative of the thermomechanical history of the films), and on second heating (representative of the materials following identical thermal histories and quiescent crystallisation). The differences in crystallinity between the films on first heating are not large; the lowest crystallinity is seen in the S-25 film, and the highest in the D-50 film; on second heating, the DuPont and Nowofol films are able to achieve a marginally greater crystallinity than the Saint Gobain film. All crystallinities are greater on second heating, suggesting that the cooling rate during film manufacture was faster than that used in the DSC, 20 °C min<sup>-1</sup>.

Fig. 2 reproduces the normalised heat flow measurements obtained using DSC. The shapes of the melting and crystallisation peaks suggest that D-25 and D-50, and to some extent S-25, share very similar crystallisation kinetics, with a sharper crystallisation and melting peak, while N-50 and N-100 are also similar to each other, melting and crystallising more gradually and at higher temperatures. Therefore, it is likely that the same (or at least very similar) compounds have been used by DuPont to produce 25 and 50  $\mu$ m films, and by Nowofol to produce both 50 and 100  $\mu$ m films. The Saint Gobain film is similar to the DuPont films in its thermal characteristics, although it does exhibit a lower degree of crystallinity for an equivalent thermal history.

#### 3.2. Temperature and rate effects on the mechanical response

Fig. 3 illustrates the tensile response of D-50 ETFE films at a range of temperatures and strain rates. ETFE is, in many



**Fig. 1.** (a) Crystallinity  $\chi$  on first and second heating obtained using DSC; (b) melting and crystallisation temperatures on first heating, cooling, and second heating.

respects, a typical semicrystalline polymer, exhibiting a linear elastic region over a few % strain, followed by yield and flow, and strain stiffening through to large strains. It also exhibits a pronounced temperature dependence and a limited but not insignificant rate dependence.

On closer inspection, however, it is apparent that the yield phenomenon is somewhat unusual. Fig. 4 illustrates one such example for D-50 ETFE in the machine direction tested at T = 80 °C and  $\dot{e} = 0.03 \text{ s}^{-1}$ , where two distinct yield processes are discernible. Two yield stresses can be identified by drawing three distinct tangents through the stress–strain response. In this way, two yield stresses are identified for each test, defined as the stress values at the intersections of the tangents. The elastic modulus, *E*, was also identified as the gradient of the first tangent.

Fig. 5 reports measurements of yield stress and modulus at T = 80 °C and  $\dot{\epsilon} = 0.03$  s<sup>-1</sup>, for all the ETFE materials



**Fig. 2.** DSC scans obtained from the ETFE films on (a) first heating, (b) first cooling, and (c) second heating. Scans are offset for clarity; endotherm up.

used in this study. There are no significant differences between the first yield stresses in the MD and TD. D-25 and D-50 have marginally lower first yield stresses than the other materials. Second yield stresses are virtually identical across directions and materials except for D-25 in the MD, which occurs at approximately double the stress. Most materials exhibit a marginally higher elastic modulus in the



**Fig. 3.** True stress – nominal strain response of D-50 ETFE in the machine direction, (a) at different temperatures at constant  $\dot{e}$ , and (b) at different rates and constant *T*.



**Fig. 4.** Typical true stress – nominal strain mechanical response of D-50 ETFE at T = 80 °C and  $\dot{e} = 0.03$  s<sup>-1</sup>, illustrating the double-yield phenomenon, and the construction of tangents to obtain the modulus and yield stresses. Inset shows deformation through to failure.



**Fig. 5.** Measurements of (a) first yield stress, (b) second yield stress, and (c) elastic modulus in MD and TD at T = 80 °C and  $\dot{\varepsilon} = 0.03$  s<sup>-1</sup>, for all ETFE materials employed in this study. Error bars indicate standard error based on a minimum of 5 specimens per condition.

MD than in the TD, but differences are not large. D-25 and D-50 also have a lower modulus than the other materials.

Fig. 6 compares the full stress-strain response of all the ETFE films employed in this study from specimens cut in the MD and in the TD, at  $T = 80 \,^{\circ}$ C and  $\dot{\epsilon} = 0.03 \, \text{s}^{-1}$ . Similar behavior was observed at different strain rates (not shown). The largest difference between the responses in the different directions is visible in the thinnest films, in particular in the D-25 and S-25 films. These films also have the most pronounced differences between test direction in the failure strains and in the tensile strengths.

#### 3.3. Load-unload experiments

Fig. 7 illustrates a typical set of load-unload experiments. For each specimen, the recovery strain was determined as the difference between the maximum strain and the strain immediately after unloading.

Fig. 8 reports recovery strain as a function of maximum strain for D-50 ETFE in the MD, at a range of temperatures at fixed deformation rate  $\dot{\varepsilon} = 0.03 \text{ s}^{-1}$ . Recovery increases with temperature throughout the strain range. At the lowest temperatures, recovery remains almost constant with strain; at 80 °C and 110 °C recovery decreases with increasing strain, and at 110 °C only it reaches a minimum at a strain of ~3 before rising again.

Fig. 9 illustrates the recovery strain as a function of the maximum strain for all the ETFE materials used in this study, deformed at T = 80 °C and  $\dot{e} = 0.03$  s<sup>-1</sup>, in the MD and TD. In the MD, recovery is low for all materials except D-50, which exhibits substantially higher recovery, particularly at low maximum strains. Recovery in the TD is higher for all materials. A minimum recovery occurs at an intermediate value of strain in the TD.

#### 3.4. Redrawing experiments

Fig. 10 illustrates a typical set of true stress–nominal strain curves at T = 80 °C and  $\dot{\varepsilon} = 0.03$  s<sup>-1</sup> of specimens of D–50 cut in the MD and pre-stretched to varying stretch ratios  $\lambda_0$  at T = 110 °C and  $\dot{\varepsilon} = 0.03$  s<sup>-1</sup>. The pre-stretching and quenching locks in orientation, and the effect can be seen on the yield region as an increase in yield stress, and on the strain stiffening region as an earlier onset of strain stiffening.

Fig. 11 reports the effect of pre-stretching on the yield stress, the elastic modulus, the failure strain and the ultimate tensile strength, on specimens of D–50 cut in the MD and pre-stretched to varying stretch ratios. Both the first and second yield stress rise significantly, the first yield stress by a factor of 10 and the second by a factor of 5. Both yield stresses rise with pre-stretching by a similar amount. The elastic modulus also rises, by as much as a factor of 5. Failure strain falls with increasing pre-stretch, from around 4.4 for unstretched specimens to 0.6 for specimens prestretched to a draw ratio of 3. The ultimate tensile strength, or the maximum nominal stress at failure, increases by as much as a factor of 4.

Very similar effects of orientation as those shown for D-50 MD in Fig. 11 are found in the TD specimens of D-50, and in D-100 and N-50 in both directions. D-25, shown in



**Fig. 6.** True stress – nominal strain response of (a) S-25, (b) D-25, (c) D-50, (d) N-50, and (e) N-100 ETFE films, in the machine direction (MD, solid lines), and transverse direction (TD, dashed lines), at T = 80 °C and  $\dot{e} = 0.03$  s<sup>-1</sup>.

Fig. 12, and to some extent S-25 (not shown), show marked differences between the MD and the TD. In these materials, pre-stretch in the TD has a much reduced effect on all of the parameters recorded except strain to failure.

#### 4. Discussion

#### 4.1. Structure of ETFE

At first sight it can appear from the crystallinity and melting temperatures shown in Fig. 1 as if there is little difference between ETFE materials sourced from the different suppliers. Closer inspection of the DSC traces in



**Fig. 7.** A typical set of load-unload experiments, carried out on D-50 in the MD at T = 80 °C and  $\dot{e} = 0.03$  s<sup>-1</sup> (lines). For one experiment, carried out to a maximum strain of 2 (shown as circles), the determination of the recovery strain is displayed.

Fig. 2 reveals more systematic differences in the shapes of the endotherms and exotherms. For instance, it is hard to distinguish between the shapes of the exotherms of D-25 and D-50, and between those of N-50 and N-100, suggesting that the same raw material is used in both pairs of films. The shape of the S-25 exotherm is similar but not identical to that of the DuPont materials. The differences between the DuPont and Nowofol materials are noticeable, with the Nowofol films crystallising much earlier on cooling, but exhibiting a broader crystallisation exotherm. Films from the same supplier extruded at different thickness exhibit lower crystallinity at smaller thickness – this is consistent with a faster cooling rate, as might be expected, but the differences are not large.



**Fig. 8.** Recovery as a function of maximum strain, for D-50 at a range of temperatures in the MD, deformed at  $\dot{e} = 0.03 \text{ s}^{-1}$ . Lines are a guide to the eye.



```
TD SR=0.03 s<sup>-1</sup>
Load-unload
```

**Fig. 9.** Recovery as a function of maximum strain, in the (a) MD and the (b) TD, at  $T = 80 \degree C$  and  $\dot{e} = 0.03 \ s^{-1}$ , for all the ETFE materials employed in this study. Lines are a guide to the eye.

There are a number of possible molecular causes for the observed differences in crystallisation behaviour between manufacturers:

- 1) A different molecular weight or distribution [31] higher molecular weight polymers typically have higher crystallisation temperatures, although the effects at the high molecular weights of ETFE are not expected to be significant. The observed differences in  $T_{\rm m}$  and  $T_{\rm c}$  between the DuPont and Nowofol materials follow the opposite trend, suggesting that this is not the cause.
- 2) A different alternating sequential fraction of ethylene monomer to tetrafluoroethylene monomer, or the presence of defects in the sequence [32] – this is known to have an effect on both the melting and glass transition temperatures [33].



**Fig. 10.** True stress – nominal strain response of D-50 ETFE MD specimens at T = 80 °C and  $\dot{e} = 0.03 \text{ s}^{-1}$  following pre-stretching and quenching at T = 110 °C and  $\dot{e} = 0.03 \text{ s}^{-1}$  to stretch levels  $\lambda = 1 - 3$  as marked.

- 3) A different overall ratio of ethylene monomer to tetrafluoroethylene monomer – experimental evidence suggests that this is unlikely to have a significant effect on crystallinity [34].
- 4) The presence of a third monomer [35,36] this is often added in commercial materials to increase the resistance to thermal stress cracking and to improve elongation at break at higher temperatures [34,37], this can have a large effect on crystallinity. This is the most likely source of the differences between materials.
- 5) The presence of non-copolymerised additives acting as nucleation sites or crystallisation suppressants [38].

#### 4.2. Deformation of ETFE

The double yield stress shown in Fig. 4 and visible in all the ETFE stress–strain curves has been observed before by several authors, in ETFE [39,40] and in its parent polymer polyethylene [41–44]. In the case of polyethylene, the first yield stress is linked to a martensitic transformation within the crystalline lamellae leading to lamellar stack rotation, whereas the second yield stress is associated with fragmentation of individual crystalline lamellae [41,45]. The application of this picture to ETFE is consistent with the experiments of Kawabata, who was able to effectively remove  $\sigma_{y1}$  in ETFE films by cyclic extension up to  $\sigma_{y2}$ , thus achieving elastic behaviour through to  $\sigma_{y2}$  [39]. In this work,  $\sigma_{y1}$  occurred between 1–2.5% strain, while  $\sigma_{y2}$ occurred between 1.5–40% strain, depending on the film type, direction, temperature and strain rate.

#### 4.3. Anisotropy in as-received films

The as-received extruded films are undoubtedly anisotropic as a result of the extrusion process. The anisotropy can manifest itself through a number of microstructural



**Fig. 11.** The effect of pre-stretching and quenching at T = 110 °C and  $\dot{e} = 0.03$  s<sup>-1</sup> to stretch levels  $\lambda = 1 - 3$  on D-50 ETFE MD specimens re-tested at T = 80 °C and  $\dot{e} = 0.03$  s<sup>-1</sup>, on (a) the first and second yield stress, (b) the elastic modulus, (c) the failure strain, and (d) the ultimate tensile strength. Lines are a guide to the eye.



**Fig. 12.** The effect of pre-stretching and quenching at T = 110 °C and  $\dot{e} = 0.03 \text{ s}^{-1}$  to stretch levels  $\lambda = 1 - 3$  on D-25 ETFE in both MD and TD specimens re-tested at T = 80 °C and  $\dot{e} = 0.03 \text{ s}^{-1}$ , on (a) the first and second yield stress, (b) the elastic modulus, (c) the failure strain, and (d) the ultimate tensile strength. Lines are a guide to the eye.

features, such as oriented crystal domains, anisotropy in the length scale of the crystalline lamellae, and network stretch in the amorphous tie-molecule domains, frozen-in by crystalline lamellae acting as cross-links.

To a first approximation, the anisotropy can be described by an additional amount of in-plane network stretch between the MD and TD. This is demonstrated by overlaying a plot of true stress-true strain for a material in the TD on top of the same plot in the MD by simply shifting the data along the true strain axis. This procedure is shown for D-50 in Fig. 13, and implies that the anisotropy can be represented by a pre-stretch  $\lambda_{\perp}$ such that  $\sigma_{TD}(\lambda) = \sigma_{MD}(\lambda_{\perp}\lambda)$ , with  $\ln(\lambda_{\perp})$  the horizontal shift along the true strain axis. There is no way of knowing the degree of network stretch frozen in along the through-thickness direction and, therefore, it is only possible to identify this as a *relative* degree of stretch between the MD and the TD. The procedure was applied to all the materials deformed at  $T = 80 \,^{\circ}\text{C}$  and  $\dot{\epsilon} = 0.03 \,^{\text{s}-1}$ , and Table 3 reports values of the relative pre-stretch identified by a manual overlap of the stress-strain responses, and a qualitative assessment of the quality of the overlap.

It is interesting to note that, as the relative degree of pre-stretch increases, so the quality of the overlap decreases. This suggests that, in materials with a high degree of initial anisotropy, there is not only anisotropy in the network but also in the nature and orientation of the crystalline domains, eventually rendering the simple picture of an increasingly stretched amorphous network invalid in the case of the D-25 films. In particular, the unusually anisotropic second yield stress recorded only in D-25 suggests that there is also a greater resistance to the slippage of crystalline lamellae in this material. This might suggest that the constraints on deformation of the polymer chain network imposed by the crystalline domains are not of the same nature as those of the other materials. Nevertheless, the procedure works remarkably well in D-50, N-50 and N-100 films, and reasonably well in S-25 films.

Brack et al. [27] reported measurements of shrinkage in the machine direction only, carried out for 5 minutes at



**Fig. 13.** Plot of true stress vs true strain for D-50 at T = 80 °C and  $\dot{\varepsilon} = 0.03 \text{ s}^{-1}$ , illustrating that the curves superpose if a horizontal shift is applied to one of the curves. The same data is shown unshifted, on a nominal strain axis, in Fig. 6c.

#### Table 3

Degree of relative pre-stretch obtained by a manual overlap of the true stress – true strain curves at T = 80 °C and  $\dot{e} = 0.03$  s<sup>-1</sup>, and qualitative assessment of the quality of the overlap; shrinkage in the MD obtained by Brack et al [27] after 5 minutes at 150 °C.

Material	Relative pre-stretch $\lambda_{\perp}$ (–)	Quality of overlap	Shrinkage in MD (%) [27]
S-25	1.55	Good	n/a
D-25	1.82	Very poor	0-1.2
D-50	1.08	Very good	0-1.6
N-50	1.23	Very good	-0.1-5.5
N-100	1.12	Excellent	-0.3-8.2

150 °C, shown in Table 3. The two measurements reported refer to the range obtained between shrinkage experiments performed at the edge and in the middle of a roll of film, respectively. The greater shrinkage observed by Brack in the Nowofol films could be interpreted as a greater degree of frozen-in orientation. However, for shrinkage to occur as a result of frozen-in orientation of the amorphous phase, there must be sufficient mobility of the crystalline phase. One possible explanation for the much reduced shrinkage in the DuPont materials relative to the Nowofol materials is that the crystalline domains have a greater degree of interconnectivity, which may only be lost upon partial melting of the crystallites.

#### 4.4. Deformation of pre-oriented ETFE

Figs. 10–12 have shown the considerable potential for property enhancement arising from pre-orientation of ETFE films. It is possible to account for much of the change in properties by considering the pre-orientation step as a deformation of the network, which manifests itself as a horizontal shift of stress-strain data along the true strain axis. This is shown for each material, including specimens oriented in both MD and TD, re-drawn at T = 80 °C and  $\dot{\varepsilon} = 0.03 \text{ s}^{-1}$ , in Fig. 14. In these plots, all curves are shifted back to the reference undrawn curve in the TD; thus, for every material, each stress measurement  $\sigma_{\text{dir}}^{\lambda_0}(\lambda)$  from an experiment pre-stretched to  $\lambda_0$  is shifted as follows:

$$\sigma_{TD}^{\lambda_0=1}(\lambda) = \sigma_{dir}^{\lambda_0}(\lambda_p \lambda) \tag{1}$$

where dir is the direction of testing, MD or TD. In the case of MD data, the shift  $\lambda_p$  includes a shift due to the preorientation stage alone  $\lambda_{\lambda_0}$  (relative to the unstretched MD experiment) and a shift correcting for the initial MD-TD anisotropy  $\lambda_{\perp}$ , so that  $\lambda_p = \lambda_{\lambda_0} \lambda_{\perp}$ . For TD experiments,  $\lambda_p = \lambda_{\lambda_0}$ .

It is possible to achieve excellent overlap between all the curves in both directions for S-25, D-50 and N-100; the N-50 curves overlap well if only MD or TD experiments are considered; in D-25 it is impossible to achieve consistent overlap of the curves. There are small variations between the applied  $\lambda_0$  and the shift  $\lambda_{\lambda_0}$ . These arise from inhomogeneity of stretching due to constraints from the film grips and, in some cases, due to the material's propensity to necking, as well as from the quenching operation.

The physical explanation for an overlap of this type is that an underlying elastic network of chains dominates the



**Fig. 14.** Plot of true stress vs true strain for as-received and pre-oriented (a) S-25, (b) D-50, (c) D-50, (d) N-50, and (e) N-100 ETFE films, re-drawn at  $T = 110 \degree C$  and  $\dot{e} = 0.03 \degree s^{-1}$ , illustrating the best attempt at superposition of the curves using a horizontal shift along the true strain axis. The inset shows the applied pre-stretch shift  $\lambda_s$  as a function of the nominal pre-stretch  $\lambda$ .

response and, to a first approximation, the material may be modelled in the classical way as an entropic spring in parallel with a viscoelastic Maxwell element [46]. At 80 °C the material is close to its glass transition, and crystalline domains act as physical cross-links between relatively mobile chains within amorphous domains. In these materials under the conditions examined in Fig. 14 a quantitative fit would require a neo-Hookean spring with shear modulus of  $\sim$  5 MPa for all the materials. This is around an order of magnitude larger than the plateau modulus determined from linear rheology by Chen and co-workers: 412 kPa. This discrepancy is well known and still somewhat unresolved in the modelling of large deformations in polymer glasses, where the analogy with rubber elasticity is made by considering entanglements as cross-links (see [30,47] for more detailed discussions). In semicrystalline polymers close to the glass transition, however, the effective density of physical cross-links will be increased beyond that of melt entanglements alone, since a number of chains will be trapped within crystalline lamellae. In addition, there may also be strain amplification around the more rigid crystalline domains. Whatever the precise physical reason for such a density of cross-links, it is apparent that such a model would go a long way to explaining the superposition observed, and hence the significant changes in material response that can be achieved with preorientation in most of the materials.

## 4.5. Improvements in base film properties for energy applications

This preliminary study has considered only a single orientation condition: T = 110 °C and  $\dot{\epsilon} = 0.03$  s<sup>-1</sup>, and only uniaxial orientation of films. Clearly, if films with enhanced performance are to be produced for energy applications, the orientation state would need to be biaxial. By small variations in the residual orientations of the two axes it is probable that manufacturing anisotropy could be erased, thus eliminating the so-called weak direction. In addition, if properties at operating conditions are to be optimised, there is considerable scope for exploring orientation over a wider range of rates and temperatures in order to achieve complementary effects on both the amorphous network and the crystalline domains. For example, Ono and co-workers recently demonstrated that the room-temperature tensile strength of ETFE films rises more quickly with drawing at 80 °C, but that a larger increase can be obtained with drawing at 150 °C [48], and attributed this to the formation of unusually extended crystalline domains.

In order to contribute to the production of cost-effective and long-lasting PEM for energy applications, at least three other aspects need to be considered. Firstly, a major outstanding challenge is precisely how failure of ETFEbased fuel cell membranes relates to mechanical performance, and in turn to easily measured parameters. Accelerated testing often consists of membrane swelling and deswelling cycles, whose influence is primarily on the grafted portions of the film. Grafts, in turn, are primarily found on the amorphous fractions of the film [49]. Grafting, cross-linking, and sulfonation are known to affect the crystallinity of the ETFE as well as the viscoelastic properties [50]. It is not known how pre-orientation may influence these processes. Secondly, in order to avoid a weak direction in the oriented films, the orientation needs to be biaxial. There are challenges in achieving uniform biaxial deformation of ETFE films, as a fall in stress after yield can lead to strain localisation, and as a different failure mode may be encountered under biaxial tension [40]. It is possible that this may be overcome if the biaxial orientation stage is carried out at a combination of rate and temperature where the deformation is homogeneous, such as is the case with many varieties of packaging films. Thirdly, cost-effectiveness of PEMs is a complex function of the parameters affecting the various stages involved in transforming a base film into a PEM. Orientation may play a positive or negative role in one or more of these aspects. For example, Brack and co-workers identified a negative effect of orientation on graft kinetics [27]. Thus, it is only through a thorough and complete understanding of the many interacting parameters involved, that performance improvements may be made without penalty.

#### 5. Conclusions

This study has investigated the thermal and mechanical response of ETFE films of different thicknesses and from several manufacturers. Thermal analysis demonstrated that, although films have similar degrees of crystallinity and melting temperatures, there are visible differences in the melting endotherms and crystallisation exotherms. Possible reasons for these differences have been discussed. Films cut both parallel and perpendicular to the machine direction were stretched under tension at a range of temperatures and rates. All films exhibited a double yield stress followed by flow and strain hardening. The yield stress is rate and temperature dependent. Selected films were loaded and unloaded during stretching, and the recovery recorded. This demonstrated further differences between materials.

A range of film specimens were pre-drawn uniaxially just above the glass transition, and subsequently quenched with a cold spray. These were then re-drawn just below the glass transition, at a temperature of relevance to energy applications. The pre-oriented films exhibited considerable improvements in both yield stress and elastic modulus (up to a factor of 5), and in tensile strength (up to a factor of 4), but reduced strain to failure.

It was demonstrated that the pre-orientation can be accounted for in most of the films by a simple shift in the true strain axis. The initial anisotropy due to the orientation of the film relative to the machine direction can also be accounted for in this way. This suggests that the material response is dominated by entropic network stretch, and may be modelled using the concepts proposed long ago by Haward and Thackray. The failure of superposition along the true strain axis, primarily in one of the materials, is also informative as it suggests that superposition does not work because of a possibly interconnected arrangement of crystalline lamellae. This is supported by an unusually large second yield stress in the machine direction of the same material. Finally, ways in which biaxial stretching could lead to improvements in properties across the plane of the film are suggested, and discussed within the context of the production of polymer electrolyte membranes for energy applications.

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