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Material properties

Uniaxial deformation and orientation of ethylene–tetrafluoroethylene films

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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.

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® [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 μm. Table 1 reports details of the origins and purchase dates of the films.

Table 1
Origin and nominal dimensions of the ETFE films used in this study.

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

2.2. Calorimetry

For each measurement, one or more circular discs approximately 6 mm in diameter were cut from the rolls 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^{-1} under a N_2 atmosphere, using a PerkinElmer DSC 8000. Melting points, T_m, and crystallisation points, T_c, were determined from the peaks, while heats of fusion, ΔH_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 $\chi = \Delta H_f / \Delta H_{f,0}$ where $\Delta H_{f,0} = 113.4$ 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 × 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 ¼, ½ and ¾ 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^{-1} and 0.1 s^{-1}. Another subset of specimens was loaded to a fixed strain level and, subsequently, unloaded to 0.1 N at the