Polymer Testing 61 (2017) 65–73

Contents lists available at ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytest

Material Properties

Role of PTFE paste fibrillation on Poisson's ratio

Dimitrios Vavlekas [a], Luke Melo [b], Mahmoud Ansari [a], Edward Grant [b], Flavien Fremy [c], Jessica L. McCoy [c], Savvas G. Hatzikiriakos [a, *]

[a] Department of Chemical & Biological Engineering, The University of British Columbia, 2360 East Mall, Vancouver, BC V6T 1Z3, Canada
[b] Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, BC V6T 1Z1, Canada
[c] Northboro R&D Center – Saint-Gobain, 9 Goddard Road, Northborough, MA 01532, USA

ARTICLE INFO

Article history:
Received 27 March 2017
Received in revised form
29 April 2017
Accepted 4 May 2017
Available online 6 May 2017

Keywords:
Polytetrafluoroethylene
Poisson's ratio
Raman Spectroscopy
Fibril orientation
Ultimate strength
Relative density

ABSTRACT

Polytetrafluoroethylene (PTFE) flat profiles were extruded using slit dies, which promoted orientation of fibrils in two directions (2-D). Uniaxial tensile experiments were performed on the collected extrudates using the Sentmanat Extensional Rheometer (SER) at different temperatures and Hencky strain rates to determine the mechanical properties of the material. A nonlinear viscoelastic model developed by Matsuoka was found to describe well the transient tensile results using Poisson's ratio as a parameter. Polarized Raman Spectroscopy was also used to gain additional information on the degree of fibril orientation at different locations both along and across the width and length of the extrudates. Results of the Raman spectra were found to be in agreement with the fibril structure/morphology obtained from SEM micrographs. The compressibility of the extrudates upon stretching was studied by measuring the relative density. The results are modeled using a simple equation including the elastic strain recovery coefficient (κ) and Poisson's ratio.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Polytetrafluoroethylene (PTFE) is a linear highly crystalline polymer with relatively high molecular weight (10^6–10^7 g/mol). These properties yield a very high melting point (342 °C) and melt viscosity (10 GPa s), making it impossible to process using traditional melt processing methods [1,2]. Instead paste extrusion is being used by mixing the PTFE powder with a specific lubricant at concentrations ranging from 16 wt.% to 25 wt.% [3–8].

The production of high mechanical strength PTFE extrudates is possible due to its distinctive phase transition properties. Under ambient pressure conditions, PTFE appears to have two transition temperatures at 19 °C and 30 °C [1,9,10]. Below 19 °C, the PTFE molecule chain segment, changes from a three dimensional order to a less ordered structure by undergoing a slight untwisting [11]. In this temperature range, shearing causes the PTFE particles to slide past each other, retaining their identity. However, above 19 °C, shearing causes the crystallites to unwind and create fibrils, providing extra dimensional stability to the final material. At temperatures above 30 °C, this phenomenon becomes even more apparent and therefore a higher degree of fibrillation oriented in the flow direction can be achieved [3,6].

During the extrusion process, once the compacted resin particles enter the die contraction zone, they are highly compressed. This results in mechanical interlocking. As they experience an accelerated flow at this particular zone, the mechanically locked crystallites are being unwound, creating submicron sized fibrils. Previous scanning electron microscopy (SEM) studies have shown that resin particles retain nearly their original spherical shape even after extrusion [12].

Numerous factors affect the degree of fibrillation as shown by previous studies. These include the type of resin used (molecular weight, level and type of comonomer) [9,13,14], the processing temperature [15,16] as well as the geometrical parameters of the die (reduction ratio, the contraction angle and to some extent the length-to-diameter ratio) [8,12,17].

Post-extrusion conditions such as sintering [18] or stretching can also alter the mechanical properties of the final PTFE product. In previous work [19] we have shown that PTFE is compressible with Poisson's ratio nearly zero. Moreover, a simple model taking Poisson's ratio into account was developed to describe density changes. The extrudates in that case were produced by a cylindrical die with the orientation of the fibrils aligned parallel to extrusion direction (1-D fibrillated samples). Furthermore, the ultimate strength in the

* Corresponding author.
E-mail address: savvas.hatzi@ubc.ca (S.G. Hatzikiriakos).

http://dx.doi.org/10.1016/j.polymertesting.2017.05.004
0142-9418/© 2017 Elsevier Ltd. All rights reserved.

tensile experiments (using the Sentmanat Extensional Rheometer (SER)) were modeled as a function of testing temperature, processing temperature, Hencky strain rate and reduction ratio (RR) of the die [19]. This model was compared with the viscoelastic Matsuoka model [20] (Eq. (1)), where Poisson's ratio appears as a material parameter. It was shown that this model successfully predicts the ultimate strength of our experimental results by considering the Poisson's ratio equal to zero.

$$\sigma_E = E_0 \varepsilon_E (1+\varepsilon_E)^{-2\nu} \exp(-C\varepsilon_E) \exp\left[-\left(\varepsilon_E/\dot{\varepsilon}_E\,\lambda\right)^n\right] \quad (1)$$

where, ν is Poisson's ratio, E_0 is the elastic modulus, λ is the relaxation time, C is the yielding coefficient and n is the relaxation exponent. The first exponential factor involving the parameter C shows the position of the ultimate strength (maximum). In the second exponential factor, the parameter λ is an empirical average value of relaxation time, while n is a width parameter, which vanishes the width of the distribution as it approaches to zero [20].

In this work, the effect of fibrillation on Poisson's ratio for extrudates produced from flat dies, are investigated. Raman Spectroscopy is used to quantitatively describe the degree of fibril orientation in the extrudates. This is achieved by measuring the polarized Stokes-shifted light in the directions parallel and perpendicular to the extrusion directions. The depolarization ratio (ρ) quantitates the preferred fibril orientation in five different extrudate locations. The quality of fibrils can be described in terms of their degree of orientation and continuousness within the extrudate. Previous studies have shown that there is a variation in the scattering intensity at major Raman shifts of 722 cm^{-1} and 1407 cm^{-1} between the two polarization geometries. There is a general agreement that the band at 722 cm^{-1} is due to C-F and C-C stretching while that at 1407 cm^{-1} corresponds to C-C (backbone) stretching, supported by our own density functional theory (DFT) calculations. The depolarization ratio may provide a quantitative measure of preferred fibril orientation [21].

The tensile strength of an extrudate could be used as a macroscopic property indicator of the microstructure. The effect of relative orientation on Poisson's ratio in these samples will be studied in detail. For example, it is desirable to correlate the relative orientation to Poisson's ratio such that samples of preferred expansivity can be produced in various applications (i.e. fabrication of hybrid stents where zero-effective Poisson's ratio is preferred [22] or fabrics of controlled porosity where the Poisson's ratio in the negative range is more ideal [23]).

2. Experimental

2.1. Materials

A homopolymer PTFE powder resin (provided by Saint-Gobain) is mixed with 18 wt% of isoparaffinic lubricant IsoparH® (Exxon-Mobil Chemicals). The paste preparation procedure and aging is described in our previous work [24].

2.2. Extrusion

The paste was placed into a piston driven capillary (Instron Testing model 1123 with a reservoir diameter of 19.5 mm) and subjected to a mild compression pressure of 2 MPa for 60s to produce a preform of uniform density and lubricant concentration. The preform was subsequently extruded at room temperature (25 °C) through a planar die which promotes 2-D fibril orientation in the extrusion and vertically to the extrusion directions (Fig. 1a). The flat samples produced (Fig. 1b) were cut in stripes in the transverse direction for mechanical testing (Fig. 1c).

2.3. Tensile testing

The mechanical properties in tensile have been determined using the Sentmanat Extensional Rheometer (SER) mounted on a MCR502 rheometer (Anton Paar). Measurements are made at three Hencky strain rates (0.6, 1 and 3 s^{-1}) and three testing temperatures (25, 50, 100 °C). The SER fixture consists of two cylindrical drums rotating in opposite directions by means of intermeshing gears [25]. The samples length, which is essentially the gap between the cylinders is fixed (12.7 mm), and upon the constant speed rotation of the drums, an exponential strain will be imposed [25]. Both 1-D (cylindrical or flat) and 2-D flat samples were tested for the sake of comparison.

2.4. Poisson's ratio

The 2-D extrudates were cut into smaller pieces as seen in Fig. 1c. Typical dimensions are 2.1–2.3 mm in width (parallel to the extrusion direction) and 1.3 mm in thickness. These were tested in the SER fixture as discussed above. Changes in the width and thickness of the extrudates were monitored using a digital Nikon D90 camera. These changes were converted into Poisson's ratio values defined as the negative ratio of the transverse strain/extension to the axial strain/extension. The dimensions of the sample in both directions were determined as a function of time and/or different levels of strains using the following equation:

$$1n\left(\frac{D}{D_o}\right) = -\nu \cdot \dot{\varepsilon}_H \cdot t \quad (2)$$

where D is the dimension of the sample at time t, (either W: width or H: thickness), D_o is the initial dimension of the sample and $\dot{\varepsilon}_H$ the Hencky strain rate used for each case. It is noted that Eq. (2) can be used to determine the Poisson's ratio as a function of time/strain/strain rate, provided that tensile tests are done at different strain rates.

2.5. Raman Spectroscopy and chemometrics

Polarized confocal Raman spectroscopy [26] is used to determine the relative orientation of fibrils in both 1-D and 2-D extrudates (see Fig. 2). A 632.8 nm Helium-Neon (HeNe) laser serves as the Raman probe. The laser is linearly polarized in a plane parallel to the surface of the table. Incident light is expanded and collimated, then directed towards an Olympus PLAPON 60x 1.42 NA oil-immersion objective by a 633 nm long-pass filter (lpf) at 633 nm. Backscattered Stokes-shifted light bypasses the lpf as it propagates towards the spectrometer. Confocal light traverses through a 100 μm pinhole. A Glan Thompson polarizer allows the user to select a polarization either parallel or perpendicular that of the incident radiation. Raman light is dispersed by a Princeton Instruments IsoPlane SCT320 spectrograph and recorded using a PIXIS 100B back-illuminated CCD detector. A three-axis piezoelectric drive translates the sample with respect to the microscope objective lens.

Twenty-five spectra are coadded from a 20 × 20 μm area producing a representative spectrum for each region of interest (ROI). This process is repeated three times across separate ROI's for each sample. Background subtraction is applied using an iterative discrete wavelet transform (DWT) algorithm [27] with a symlet-5 basis wavelet and decomposition scale of six over ten iterations.

Download English Version:

https://daneshyari.com/en/article/5205312

Download Persian Version:

https://daneshyari.com/article/5205312

Daneshyari.com