

Melt-state shear flow and elasticity of a thermoplastic fluorosulphonated—PTFE copolymer

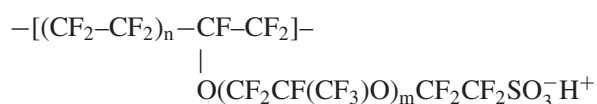
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Some rheological properties of a perfluorosulphonated PTFE copolymer have been measured in order to characterise the melt-state viscous and elastic behaviour of a thermoplastic precursor of Nafion[®], an ion-selective membrane used in the electrochemical industry. Steady-state shear viscosity measurements show conventional pseudoplastic flow behaviour over a wide temperature range, under high shear conditions. These data have been modelled to a high level of accuracy using polynomial simulations to obtain Carreau model coefficients and flow activation energies. Using an orifice die in a capillary rheometer, calculated extensional viscosity data are shown to decrease with stress and are more temperature-sensitive than shear viscosity. Although die swell increases with shear rate in a conventional manner, unusual and complex die swell data (at a fixed shear stress) have been obtained in response to an increase in process temperature. This behaviour is attributed to the breakdown of a small-scale network of domains and ordered crystalline material in the amorphous matrix of the precursor, as exemplified by a very broad melting endotherm. Different modes of deformation have been proposed to explain the rheological data observed across the process temperature range. The observed changes to the flow mechanism and elastic character of the melt carry practical implications for the extrusion processes and developed microstructure of film products manufactured from this precursor copolymer. © 2005 Springer Science + Business Media, Inc.

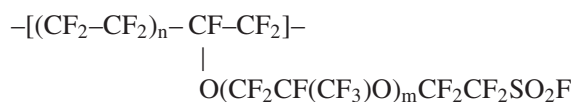
1. Introduction

Perfluorinated ionomer membranes have been developed and commercialised by the DuPont company [1] for applications in chlor-alkali cells, as an ion-sensitive separator. These membranes function during electrolysis by allowing the passage of Na⁺ ions whilst restricting the passage of OH⁻ and Cl⁻ ions. The membrane is cation-selective, preventing the passage of negatively charged ions, a property known as permselectivity. Other applications include use in fuel cells, biological sensors and as a superacid catalyst in organic synthesis. The commercial name for the DuPont membranes is Nafion[®], which has a molecular structure and repeat unit as follows:



Typically, the value of m is 1 and n is in the range 6–13; the hydrogen ion may be partially or fully exchanged by other cations or cationic groups. The chain structure consists of a linear fluorocarbon backbone similar

to PTFE, with perfluorinated vinyl ether side chains terminated with a sulphonic acid functional group. Therefore the structure shown above is in its 'ionic sulphonic acid' form. This structure is produced by an ionic conversion process of precursor sheet material (see below), using a hot aqueous solution of NaOH or KOH to convert the SO₂F group to the ionic form. The membrane sheets (of typical thickness range 0.1–0.3 mm) are formed previously by an extrusion process carried out on the precursor material, whose non-ionic, sulphonyl fluoride chain structure (prior to the ionising conversion process) is as follows:



Integers m and n are as shown in the repeat unit for ionised Nafion; n -values of 6 and 12 (for example) would predict the existence of one side branch per 14 or 26 backbone carbon atoms, respectively, in the precursor [2]. The concentration of sulphonated side-groups is usually characterised by an 'equivalent

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weight' (EW) parameter, defined as the mass (in grams) of sulphonic acid form Nafion required to neutralise one mole of base and ranges from around 1000–2000. In this way, EW and molecular weight are both important characteristics of the copolymers that can be controlled according to the properties required for processing and for end-use applications. Precursor material is a conventional thermoplastic and may be melt processed, whilst the ionic interactions in the converted membranes act as physical crosslinks, preventing flow.

Once converted into ionic form, the properties of the membrane are very different from the precursor polymer. Water molecules are attracted to the membranes and aqueous regions are incompatible with the hydrophobic nature of the fluorocarbon chain backbone. Conversely, water is attracted to the ionic (hydrophilic) sites, so that phase separation occurs within the overall structure of the polymer. A so-called 'cluster-network' model [3] has been proposed to describe how the ionic groups and water form in small-scale clusters, connected by narrow channels within a fluorocarbon matrix. It is the water content, together with the equivalent weight of the polymer that determine the ion-selectivity of the membrane and its conductivity in electrochemical cells.

Since it is the ionised form of the material that is available commercially, much more is known and has been published regarding its structure and physio-chemical properties [1, 2, 4, 5]. However, relatively little has been published previously regarding the microstructure and processing characteristics of the precursor copolymer, not least because it is not generally available commercially. This has led to a number of studies carried out to determine the processing behaviour, structure and electro-physical properties of the polymer in its ionic form [6–10].

Research from dynamic mechanical analysis (DMA) reported by Kyu *et al.* [11] has demonstrated a primary relaxation (α -transition) temperature of around 0°C, for the precursor material, confirming that at ambient temperatures, the amorphous phase is in its rubbery state. A more recent publication has confirmed the existence of crystalline order in the precursor, imperfect domains which melt over a wide endothermic range (130–160°C). The degree of crystallinity may be modified by mechanical and thermal history within this temperature range, thereby providing the basis for enhanced properties to be achieved as a result of molecular orientation [12].

On the basis of the relatively limited knowledge of the SO₂F-form precursor material, investigations have been carried out to characterise its flow behaviour, by researching the properties relevant to film or sheet extrusion processes, together with the influence of some important variables, including temperature and flow rate. Overall, the objectives of the research reported in this paper are to:

- measure the practical rheological properties governing shear and extensional flow characteristics of precursor
- determine model coefficients for the shear viscosity as a function of apparent shear rate and tem-

perature, to provide the basis for extrusion process simulation

- evaluate the elastic properties of precursor using practical measurements of die swell and melt fracture
- interpret the melt-state flow properties and their dependence upon process conditions, with reference to the changes in crystalline structure known to exist at elevated temperatures

2. Experimental techniques

2.1. Materials

Samples were supplied by DuPont as part of their involvement in the ongoing research and development of regenerative fuel cells being carried out by Regenesys Technologies Ltd. Materials were obtained both in SO₂F-precursor form (as thermoplastic granules) and in 'reaction-converted' SO₃H⁺ form as ion-exchange, film-based membranes. Only the precursor material is considered in this paper, which had an equivalent weight (EW) of 1100 g · mol⁻¹ and is normally extruded into films of appropriate thickness before being chemically converted into ionic form. The precursor form of the copolymer material is not available commercially, so there are no published physical property data available from standard tests.

2.2. Thermal analysis

Extrudate samples were characterised by thermal analysis to examine the effect of processing (thermo-mechanical history) on the precursor material. A DuPont 910 Thermal Analyser fitted with a DSC cell was used for this purpose. Specimen weights used were usually between 10–15 mg and a heating rate of 10°C min⁻¹ was generally specified, across a temperature range from ambient up to 300°C. DuPont General Analysis (version 4.0D) software was used to analyse the plots to obtain crystalline endotherm onset temperatures and heat of fusion data.

2.3. Rheological analysis

The nominal melt flow rate (MFR) of precursor was measured using a Davenport Melt Flow Indexer, according to the test conditions given in Table I, which are based upon BS2782: Part 7 (Method 720A). Since raw data of this type have not been published previously and standard MFR test conditions are not available for the

TABLE I Specified melt flow rate (MFR) test conditions for precursor material

Description	BS2782: Part 7, Method 720A	
	4	6
Condition	4	6
Die bore diameter (mm)	2.095 ± 0.005	2.095 ± 0.005
Mass of weight & piston (kg)	2.16 ± 0.01	10.0 ± 0.04
Nominal force (N)	21.2 ± 0.1	98.0 ± 0.2
Test temperature (°C)	190 ± 0.5	190 ± 0.5
Reference time (s)	600	600

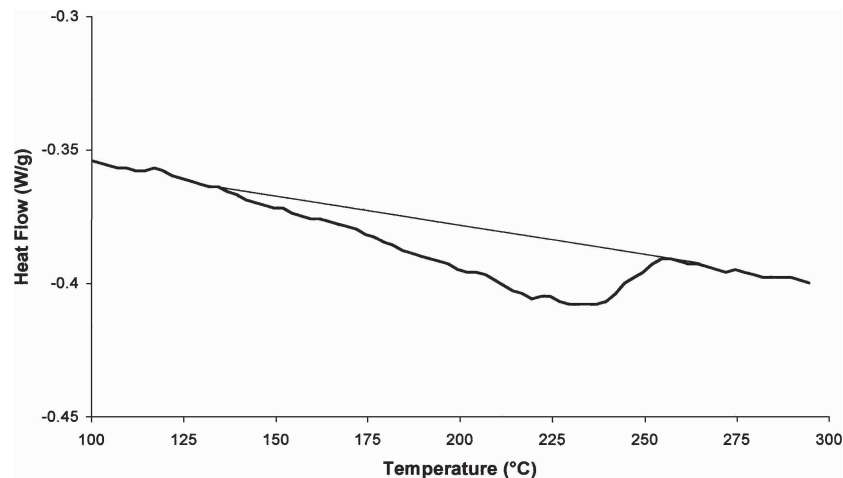


Figure 1 Thermal analysis scan for the fluorosulphonated copolymer (in precursor form) showing a broad melting endotherm.

fluorosulphonated copolymer, a wide range of analytical conditions was initially used. Dead-weight masses of 2.16, 5.0 and 10.0 kg were each used at test temperatures between 220 and 270°C (using intervals of 10°C), these conditions being defined on the basis of thermal analysis data reported previously [12]. The results are expressed as a nominal melt flow rate (MFR) in g/10 mins. (dg min^{-1}).

More detailed analysis of shear flow properties and elasticity was carried out by a series of capillary rheometry experiments, using a Davenport capillary rheometer fitted with capillary dies of diameter 1 mm. One of these was a long die (length 16 mm, hence length-diameter ratio of 16) and the other was an orifice die with zero land length, used to obtain both end-corrected shear flow data and also, extensional flow characteristics according to the method developed by Cogswell [13]. The equipment has a barrel diameter of 19 mm; piston speeds were varied to produce apparent shear rate values in the range $50\text{--}5000\text{ s}^{-1}$, across a test temperature range between 205 and 265°C. Pressure data were computed from a transducer fitted at the die entrance and these measurements were used to compute all subsequent rheological data. Samples were cut from the extrudate and cooled normally to measure die swell and saved for further examination to note surface defects attributable to melt fracture. In all cases, the piston velocity (hence apparent shear rate) at which melt fracture first became evident was noted.

2.4. Rheology: Data processing

Rheological data were analysed according to the well known power law model of pseudoplasticity, in order to evaluate flow coefficients (consistency index (k) and power law index, n), at each processing temperature. For this purpose, a flow analysis software programme [14] was used to provide the linear regression coefficients from bilogarithmic shear flow plots. Also, the data were exported into 'Flow 2000', an extrusion software programme developed by Compuplast, to determine flow constants from a modified Carreau analysis. This is a more exact, non-linear and multi-parameter model that is able to determine the limiting, zero-shear

viscosity of polymer melts, in addition to the coefficients in the pseudoplastic, high shear region. Results were subsequently verified using standard regression software; solutions to the non-linear, 3-parameter Carreau model were obtained by data convergence using the Hooke-Jeeves & Quasi-Newton numerical method.

3. Results and discussion

3.1. Thermal analysis

Technical literature and scientific information on the precursor form of the fluorosulphonated copolymer is not widely available, so that some introductory experiments were carried out to investigate its thermal behaviour and physical properties [12]. Although the polymer is substantially amorphous with a glass transition around 0°C, [11] strong evidence has been obtained for the existence of crystalline order, with a very broad melting endotherm existing between 130 and 255°C, indicative of imperfect crystallites within the amorphous matrix (Fig. 1). The degree of crystallinity is dependent upon the equivalent weight (EW) of the polymer and its development on cooling from the melt-state is likely to be restricted by the frequency of side groups along the polymer chain [3]. The endotherm was found to be strongly dependent upon process history: if the polymer is heated to, or processed at a temperature below the endotherm maximum, separate and distinctive 'A' and 'B' endotherms are then detectable. In this way, the annealing (or processing) temperatures can be detected retrospectively [15]. Typically, the heat of fusion is normally around $4\text{--}10\text{ Jg}^{-1}$ and the degree of crystallinity is in the range 4.2–10.5% (since the heat of fusion for full crystallinity is 94 Jg^{-1}), although this is influenced by thermal and mechanical history.

An equivalent, broad melting endotherm is well known to exist in PVC compounds and its sensitivity to thermal history has been well documented in the literature [16–18]. This effect is known to have a strong influence upon the subsequent polymer microstructure and physical properties of manufactured PVC products. Therefore, to provide a more complete understanding of these relationships in Nafion precursor, it is essential to

characterise flow behaviour so that the influence of processing conditions can be determined more precisely.

3.2. Shear flow analysis

3.2.1. MFR testing

Fig. 2 shows the melt flow rate of the precursor as a function of temperature, for tests carried out using a series of different piston weights, in the pressure-imposed viscometer. MFR increases systematically with temperature and at any given temperature, MFR is highest for the largest weight of 10 kg. During tests carried out at and below temperatures of 230°C, the extruded melt had an irregular, 'grainy' appearance on a macroscopic scale. This suggests a localised rupture effect associated with incomplete melting of crystalline order, a result that is consistent with the thermal analysis data for this precursor material presented elsewhere [15]. Clearly, if processing temperatures are within the melting endotherm range, the more perfect crystallites will be annealed rather than melted, and will remain in the microstructure of products formed by cooling from the melt state.

Although appreciable shear flow may take place at temperatures below the melting endotherm maximum (typically around 250°C), the flow mechanism will be modified by the presence of unmelted crystalline regions. This likely to produce a heterogeneous melt and a flow mechanism influenced by the presence of discrete flow units within the continuous polymer melt matrix. It is the gradual destruction of these ordered flow units that accounts for the establishment of more uniform shear flow behaviour at temperatures of 240°C and above in true melt-state conditions, resulting in the increases in gradient observed in Fig. 2.

The magnitude of the data in Fig. 2 is notable, since the typical MFR values for polymers used in extruded film applications is relatively low, usually significantly below (say) 5 g/10 min, when using a mass of 2.16 kg at a 'typical' process temperature. Therefore, on the basis of the melting behaviour determined by thermal analysis, the processing temperatures required to obtain such low values of MFR would be below 230°C, at which the melting of ordered crystalline domains

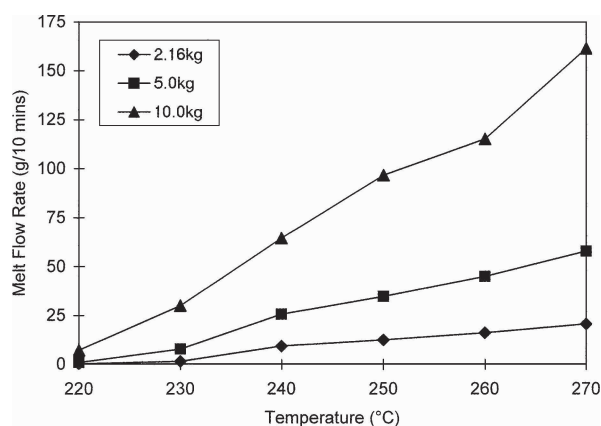


Figure 2 Variation of melt flow rate (MFR) of precursor, as a function of temperature, for pressure-imposed experiments carried out using different masses (see legend).

would not be completed. The prediction would then be for extruded film products to assume crystalline superstructures consisting of annealed crystallites (that melt only at temperatures higher than the processing temperature) and also, recrystallised regions formed during the post-forming cooling stage.

Equivalent processing conditions for PVC that do not fully eliminate all crystalline order can be detected by thermal analysis and are known to subsequently influence the solid-state physical properties of extruded products [16–18]. Consequently, it is reasonable to anticipate similar behaviour for extruded Nafion precursor. For the studies reported here, the previous thermal history of the precursor material (at the compounding/granule production stage) is not known.

3.2.2. Capillary rheometry

Raw data from the capillary rheometer were processed to investigate the dependence of shear viscosity upon shear strain rate and process temperature. The shear rate range chosen was relatively high (50–5000 s⁻¹) in order to generate viscosity data appropriate to a high output, film extrusion process. The bilogarithmic shear flow curves presented in Fig. 3 illustrate these physical relationships quite clearly. At all temperatures, the precursor melt is pseudoplastic in nature, with shear viscosity decreasing with increasing shear rate. A departure from power law behaviour is most marked at low shear rates and notably at high temperatures (265°C). This suggests that if 'zero-shear' viscosity data could be evaluated by further manipulation of the test data, this rheological parameter would be more discriminating, in terms of the effect of process temperature.

The flow curves converge to some extent in the high shear region, so that changes in melt processing temperature become less significant if the imposed deformation rate is relatively high. Across the entire temperature range, all shear viscosity data for precursor lie between 100–600 Nsm⁻² for apparent shear rates exceeding 10³ s⁻¹, and become gradually less temperature-sensitive, as shear rates increase further. This is consistent with pseudoplastic flow characteristics of many high polymers and represents conventional shear flow behaviour.

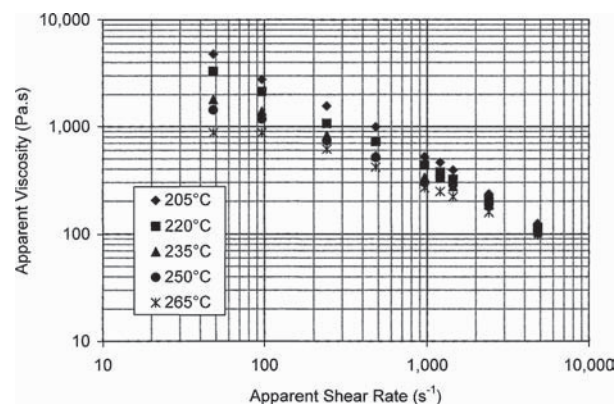


Figure 3 Capillary rheometry data for Nafion precursor: apparent viscosity versus apparent shear rate, for different process temperatures between 205–265°C.

However, in the low shear rate regime, there is some evidence to suggest that the flow mechanisms are different, either side of the trendlines corresponding to melt process temperatures of 220 and 235°C. The flow curves determined at temperatures above this range tend towards limiting shear viscosity values (within the range investigated) much more than those determined at 205 and 220°C, suggesting once again that a change in flow mechanism takes place in this critical temperature range. It is proposed that residual domains associated with crystalline order (at temperatures at or below 230°C) account for the observed differences in behaviour at low shear rates. Rheological model coefficients that illustrate this differential flow behaviour are presented in the next sub-section.

3.3. Modelling and simulation—power law

Fig. 4 shows a comparison of flow curves generated by the conventional power law model [14], effectively a linear regression analysis, for a bilogarithmic plot (fitted to the experimental data shown in Fig. 3), so that shear viscosity (η) is expressed as a function of apparent shear rate ($\dot{\gamma}$):

$$\eta = k(\dot{\gamma})^{n-1}$$

$$\text{hence: } \log(\eta) = \log(k) + (n - 1) \cdot \log(\dot{\gamma})$$

where k = consistency index and n is the power law index of pseudoplasticity.

At a given shear rate and temperature, viscosity is given by:

$$\eta(\dot{\gamma}, T) = \eta_T(T)\dot{\gamma}^{(n-1)}$$

For clarity, data from only three temperatures are shown in Fig. 4; power law coefficients from all melt temperatures investigated are presented in Table II. Although the model fits the data reasonably well over part of the shear rate range at 235°C, the measured data deviate from the power law prediction at both high and low shear rates.

The power law model does not allow for variations in power law index (n) with temperature, so that the

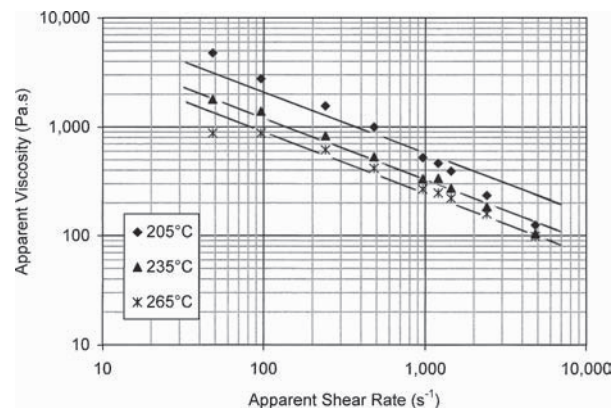


Figure 4 Shear viscosity/shear rate flow curves (as a function of melt temperature) showing experimental data points fitted to the power law model.

TABLE II Power law model coefficients for shear flow behaviour of fluorosulphonated copolymer, between 205–265°C

Temperature (°C)	Power Law model coefficients	
	$k (\times 10^3)$	n
205	77	0.28
220	46	0.32
235	15	0.46
250	9.6	0.52
265	4.6	0.60

model can only fit the data closely at a single reference temperature. From Fig. 4, it is clear that the power law does not give an adequate representation of the data, especially at high temperatures, where the flow curves become progressively more non-linear in the low shear rate region. Consequently, the degree of correlation is lower as temperature increases and the values of Power Law index (n), although adequate at 205 and 220°C, are also misleading.

3.4. Modelling and simulation—Carreau model

A more accurate representation can be obtained from the Carreau model, which provides a fundamental basis to allow for non-linear behaviour and variation in curve shape according to temperature. A generalised form of this model can be used to express viscosity as a function of shear rate and temperature:

$$\eta(\dot{\gamma}, T) = \eta_T(T)[1 + (\eta_T(T)\dot{\gamma}/\tau_c)^2]^{(n-1)/2}$$

where τ_c is a critical shear stress. A more specific form of this expression, using three parameters to describe individual flow characteristics, can be utilised to model the shear flow behaviour to take account of the non-linear effects of shear rate:

$$\eta(\dot{\gamma}) = \eta_0[1 + (t_1 \cdot \dot{\gamma})^2]^{(n-1)/2}$$

Fig. 5 shows the shear flow data and the overall correlation with the predictions made by the Carreau model, to fit the data points obtained at each test temperature.

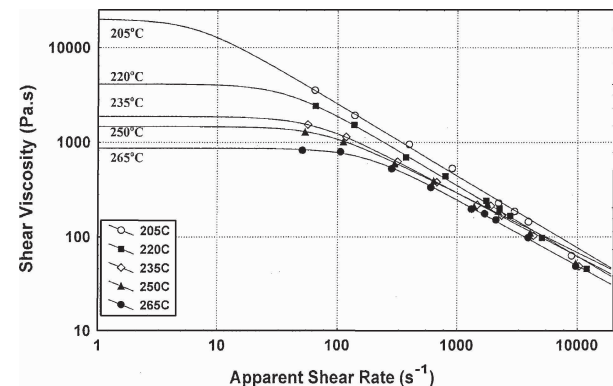


Figure 5 Shear viscosity/shear rate flow curves (as a function of melt temperature) with experimental data fitted to the three-parameter Carreau model.

TABLE III Carreau model coefficients for shear flow behaviour of precursor copolymer, as a function of process temperature

Temperature (°C)	Carreau 3-parameter model coefficients		
	η_0 (Pa.s) ($\times 10^3$)	t_1 (s)	n
205	425	10.7	0.28
	<i>20.0</i>	<i>0.151</i>	<i>0.24</i>
220	6.4	0.049	0.30
	<i>4.1</i>	<i>0.027</i>	<i>0.25</i>
235	2.1	0.017	0.36
	<i>1.9</i>	<i>0.016</i>	<i>0.33</i>
250	1.6	0.014	0.40
	<i>1.5</i>	<i>0.013</i>	<i>0.37</i>
265	0.9	0.006	0.33
	<i>0.9</i>	<i>0.006</i>	<i>0.30</i>

The model coefficients (zero shear viscosity η_0 , time constant t_1 and pseudoplasticity index, n) are tabulated in Table III.

At 205°C, coefficients η_0 and t_1 are very different to those derived at other temperatures, partly due to a lack of data points at low shear rate, which will compromise accuracy, to some extent. Therefore, a Rabinowitsch correction procedure was carried out on the shear rate data and the modelling routine was repeated, resulting in the coefficient data presented in italic print, in Table III. These data points are illustrated by the open symbols in Fig. 6.

Zero-shear viscosity is the limiting deformation resistance of a polymer system at infinitely low shear rates, a fundamental flow property that may be related to a number of process and material-related variables, including temperature. Since flow is a thermally activated process, its temperature dependence can be investigated using a conventional Arrhenius relationship of the type:

$$\eta_0 = A \cdot \exp(E_a/RT)$$

where A is a material constant, R is the universal gas constant and E_a is the activation energy for flow. A plot of log-viscosity versus the reciprocal of absolute tem-

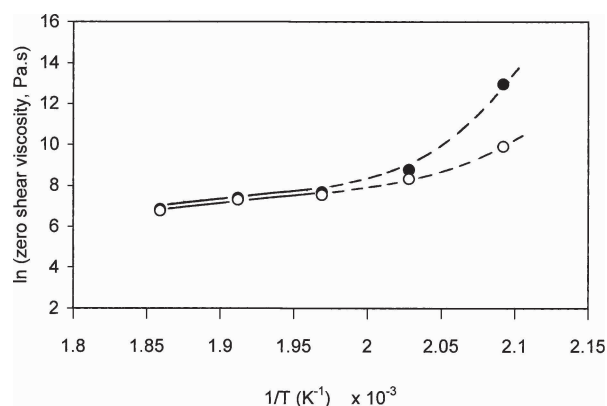


Figure 6 Arrhenius plot of zero shear viscosity (predicted by the three-parameter Carreau model) versus reciprocal temperature, for shear viscosity data of copolymer between 205 and 265°C. (Open symbols represent shear rate data corrected by the Rabinowitsch method, whilst closed symbols represent uncorrected data).

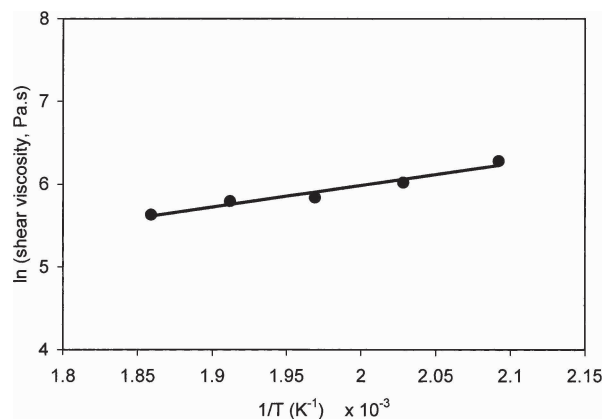


Figure 7 Arrhenius plot of shear viscosity (natural log) at shear rate 1000 s^{-1} versus reciprocal temperature; shear viscosity data of copolymer between 205 and 265°C.

perature can then be used to evaluate E_a . Fig. 6 shows a good correlation at process temperatures exceeding 220°C and the value for E_a based upon the high temperature data is 63.4 kJmol^{-1} . This value clearly does not apply at lower process temperatures, where the linear correlation in Fig. 6 is lost, regardless of the correction routine. It is proposed that a different flow mechanism is evident within the low temperature region, due to the presence of the residual regions of molecular order referred to earlier and defined more exactly in a later section of this paper.

A similar approach has been used to calculate the activation energy for flow based on shear viscosity (as predicted by the Carreau model coefficients in Table III) at an arbitrary shear rate of 1000 s^{-1} . In this case, Fig. 7 demonstrates a more precise and clear dependence of viscosity on temperature, with a predicted activation energy (E_a) of $21.8 \text{ kJ} \cdot \text{mol}^{-1}$, across the range studied. This result demonstrates that at high shear rate in a stress-activated flow field, the energy requirements for flow are more closely related to the applied temperature, so that the existence of residual molecular order is less critical. The derived values for flow activation energy are similar to those published elsewhere for other polymers, although it has been recognised that the activation energy for polymers (such as LLDPE) containing short chain branching sequences tends to increase with the length of the side-chains [19].

3.5. Extensional flow analysis

An advantage of using a ‘zero land length’ die in capillary rheometers is the ability to transform the orifice pressure readings into data that describe the elongational flow characteristics in constrained flows between fixed flow boundaries, according to the method first attributed to Cogswell [13]. It is acknowledged that there is some debate regarding the applicability of an elongational viscosity parameter generated from this type of analysis [20]. However, there is little doubt that the technique is an effective way of producing material data that distinguishes polymers/process conditions and is immediately applicable to the analysis of processes such as constrained, converging flows in extrusion dies.

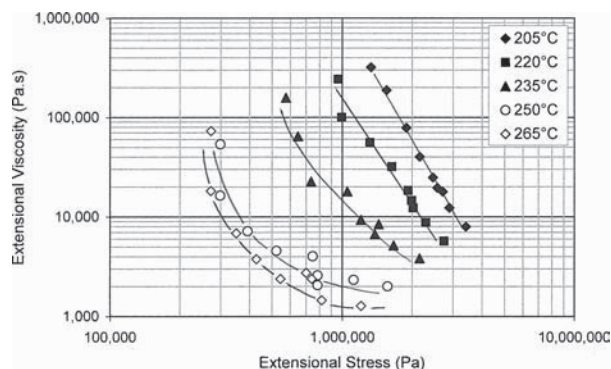


Figure 8 Extensional viscosity/stress flow curves, obtained from orifice die pressure data in capillary rheometry, as a function of melt temperature.

Fig. 8 shows the relationship between extensional viscosity and stress, for each of the process temperatures considered in the previous section. Viscosity decreases with increasing stress in a classical ‘tension-thinning’ response, across the entire processing range chosen for study. In spite of the relatively low pressures that are measured when operating the rheometer with the orifice die, the technique is able to generate a relatively high level of discrimination between the viscosity data measured at the temperatures selected. Only at the highest temperatures do the observed levels of scatter become more significant. Extensional viscosity data derived from zero-length dies is less frequently available relative to shear flow curves, in terms of both fundamental material behaviour and also the modelling techniques used to describe trends. However, the potential value of the data is apparent since the respective influences of both extensional stress and temperature are clear. As was proposed in the previous section, it is suggested that the residual crystalline order in the precursor contributes to a better discrimination of data points (hence, a greater dependence of extensional viscosity on temperature), for the analyses carried out between 205 and 235°C.

The calculated viscosity range carries across more than two decades, with the magnitude varying between 1000 and 300,000 Pa.s (1–300 kPa.s). Extensional viscosity values clearly exceed shear viscosity values by a large factor (typically between 20 and 60) at equivalent test conditions, emphasising the potential importance and contribution of this parameter to the practical design of equipment, operation of extrusion processes and prediction of pressures required to achieve specific process requirements. Research has subsequently been carried out on practical film blowing of this copolymer, a process involving large extensional deformations to achieve molecular orientation, the results from which will be reported separately.

Although the precursor polymer contains short chain branches, it is evident that these are not of sufficient length to induce significant strain hardening behaviour in the melt, under an extensional stress system. An analogy in this respect might be polyethylene (PE), for which highly long-chain branched low density (LDPE) polymers show clear strain hardening at intermediate deformation rates in free-surface experiments, thus en-

hancing processability in situations where free-surface flows are dominant. This is often defined by an upturn in extensional viscosity above the linear viscoelastic start-up asymptote [21]. However, linear low density (LLDPE) polymers, with short chain branches, do not show the same degree of enhanced strain hardening when under extensional stress in the melt state. It is suggested that a substantial increase in the concentration of vinyl ether groups (higher value of ‘*m*’, for the fluorosulphonated copolymer) might provide a basis to create rheological behaviour (strain hardening and higher melt strength) more akin to branched PE.

3.6. Melt elasticity—die swell

In all capillary rheometry experiments carried out to investigate shear flow behaviour using the high aspect ratio die, the equilibrium diameter of extrudates was measured in order to compute die swell (expressed as a simple diametric ratio) as a function of process variables. Typical behaviour is shown in Fig. 9, for swell data derived from measurements between 190 and 265°C. At these temperatures, die swell ratio generally increases with increasing shear rate, as is observed in virtually all high polymer systems, due to the recovery of the elastic component of strain, predominantly a shear strain when using dies of finite length with high length-diameter (*L/D*) ratio. However, the most significant point to note is the relatively low values of die swell ratio obtained across the range of investigation, which rise to a limiting level of around 1.25 (25%), at the maximum shear rates investigated.

In Fig. 9, the effect of temperature in the upper part of the range is not clear. More meaningful trends are evident in Fig. 10, which shows the temperature-sensitivity more clearly, at two reference shear rates of 50 and 2500 s⁻¹. Initially, swell ratio is temperature-insensitive, but appears to rise to a maximum at around 250°C and then becomes a decreasing function of temperature at melt temperatures higher than 250°C. This type of behaviour is most unusual in thermoplastics, many of which show reduced elasticity and swell (at any given shear stress) as temperature is increased. In effect, the responses displayed in Fig. 10 represent two distinct mechanisms (separated by the discontinuous lines) that

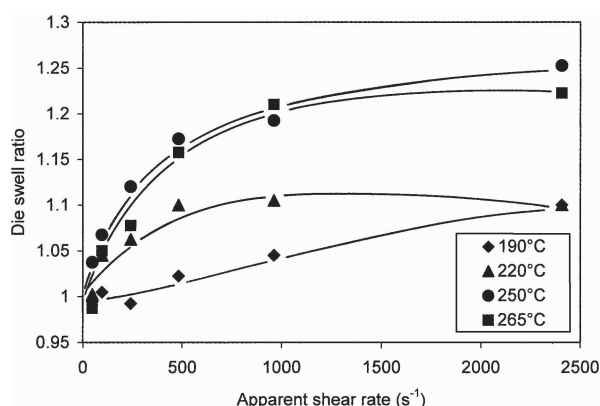


Figure 9 Die swell ratio of precursor copolymer versus apparent shear rate, at various temperatures (190–265°C).

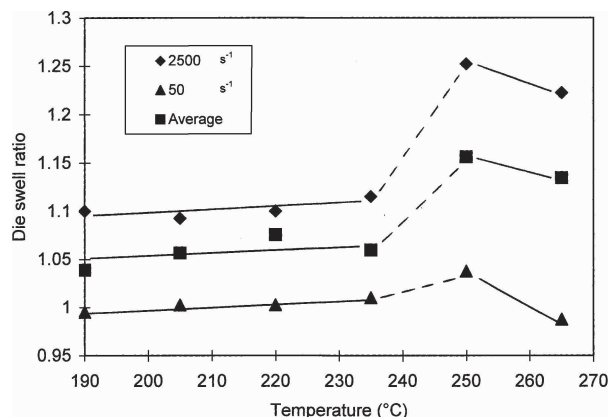


Figure 10 Die swell ratio of precursor versus temperature, at shear rates of 50 and 2500 s⁻¹.

contribute to relaxation and die swell, in terms of their dependence upon temperature. The precise deformation mechanisms responsible for these observations are discussed following the melt fracture data.

3.7. Melt flow instability—melt fracture

The establishment of a super-critical stress, whether shear or tensile, in an extrusion die can lead to elastic instability, unsteady flow and ultimately, to poor quality extrudates, a condition often loosely referred to as melt fracture. More particularly, very high tensile stress might exist at the die entrance due to the converging flow field and also at the die exit, where the surface layers of the melt accelerate from the zero velocity condition at the die wall to the nominal extrudate velocity outside the die. These effects are often the cause of elastic instability when a critical flow condition is achieved.

Fig. 11 shows the apparent shear rate at which two types of flow instability were achieved, plotted as a function of melt temperature. The lower curve was defined by noting the piston speed in the rheometer (corresponding to the apparent shear rates quoted) at which the surface of the extrudate became rough, on a macroscopic scale, whereas the upper curve corresponds to the shear rates at which the pressure recorded at the die entrance became unsteady. These effects are differ-

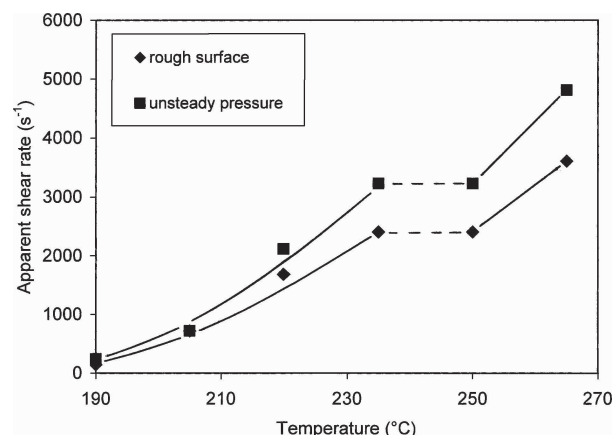


Figure 11 Elastic instability phenomena: onset of melt fracture for precursor, as a function of melt temperature.

ent but the overall trends are similar, showing stable flow up to higher shear rates, as process temperature is increased. Note that on this plot, the lowest process temperature investigated was 190°C, at which the flow instabilities were detectable even at very low flow rates, corresponding to apparent shear rates below 200 s⁻¹. At temperatures above 240–250°C, the critical flow rate for elastic instability increases with temperature. Qualitatively, this form of result might be anticipated for a thermoplastic showing conventional flow behaviour, as a result of the deformation of a macromolecular continuum. Figs 10 and 11 have been plotted with a discontinuity, to emphasise the difference in deformation behaviour that is evident when the crystalline order is destroyed.

3.8. Temperature-sensitivity and flow mechanisms

For the specific case of the precursor copolymer, the evidence gained from the flow analysis and elasticity data requires more detailed interpretation. It is proposed that the response of the fluorosulphonated copolymer can be explained with reference to some fundamental differences in small-scale structure, so that distinctive deformation and flow mechanisms are now defined to account for the changes observed.

3.8.1. Mode 1 deformation—Viscous flow

At temperatures higher than 250°C, conventional shear and extensional flow behaviour occurs, as observed in predominantly viscous high polymer melts. Macroscopic flow is by molecular deformation, described by a continuum of molecular species that interact, according to the precise flow conditions used. All the crystalline domains in the precursor have been eliminated by melting [12], leading to simple viscous behaviour overall, where viscosity parameters are described by an Arrhenius-type model (Figs 6 and 7) and swelling is reduced on increasing temperature (Fig. 10). These are well established effects, whereby shear viscosity and the developed stress each decrease with temperature under rate-imposed flow conditions, leading to reduced recoverable (elastic) strain, hence reduced swelling.

3.8.2. Mode 2 deformation—Particulate sub-units

At lower processing temperatures below 250°C, the residual molecular order and crystallinity in the fluorosulphonated copolymer determined previously by thermal analysis (Fig. 1 and Ref. [12]) acts as a form of reinforcement, with small and imperfect ordered regions acting as physical crosslinks in the amorphous network structure. This contributes to some high values of zero-shear viscosity (Table III) and non-conventional flow behaviour more generally (Fig. 6). As the temperature is increased across the broad melting endotherm (Fig. 1), the amorphous phase passes through a gradual, indiscrete change from rubbery-state to a conventional, predominantly viscous polymer melt. It is more easily

deformed in the regions of high stress, without permanent deformation taking place. Thus when the deforming stress is released at the die exit, elastic recovery occurs, resulting in die swell.

In Mode 2 deformation, the degree of elastic recovery is very low, especially at the low-temperature end of the processing window. Die swell then increases with temperature since there is sufficient crystalline material existing in a pseudo-network structure to restrict the viscous flow of melt. This promotes entropic recoil effects that occur around the constraining influence of the physical crosslinks in the network structure, to enable elastic recovery. The crystalline order is gradually eliminated at higher temperatures within the Mode 2 deformation regime, so that the shear modulus of the precursor 'melt' (the physical property governing elastic strain recovery at a given stress level), would be expected to decrease, consistent with the results shown in Fig. 11.

Similar behaviour to the Mode 2 deformation is known to exist in PVC melts, for which 'flow units' exist, which are formed at the polymerisation stage. These spherical domains of around 100 nm diameter control the overall deformation, producing a particulate, rather than molecular-based flow mechanism [16], up to the point where the broad melting endotherm terminates. Within these domains, smaller structures are also thought to exist, held together by ordered regions that represent the crystalline order detectable by thermal analysis [17]. The crystallites of different size and perfection arise from the different lengths of syndiotactic sequences, which are the predominant configuration for crystallites in PVC. Similar conclusions have also been made regarding the structures of low crystallinity grades of ethylene vinyl acetate [22] and ethylene-propylene copolymers [23]. Whilst there has been no evidence published regarding the distribution of side-chains in the precursor, it is likely that a random distribution of these could produce crystallisable sequences of different length, along the fluorocarbon chain backbone. Since the side-groups are bulky and therefore unlikely to crystallise, this would be consistent with the evidence obtained on the precursor from thermal analysis.

In consequence, the rheological response is controlled by the two mechanisms: particulate flow at relatively low temperatures and molecular deformation at temperatures above the endotherm maximum. For PVC, the importance of these respective mechanisms has been shown to be dependent upon molecular weight and domain particle size, together with primary flow parameters such as temperature and the imposed shear rate [18]. As a result, minimum die swell is obtained in PVC at low temperatures (where particulate flow dominates), elasticity and swell then increase with temperature and optimum physical properties are most likely when processing in the molecular deformation regime at high temperatures [18].

Observation of a very similar deformation mechanism for the fluorosulphonated copolymer, together with the evidence that melting is not complete until above 250°C, reinforces the conclusion concerning the

melting behaviour and physical structure of the copolymer. It is proposed that analogous to the physical behaviour of PVC, two distinct flow mechanisms exist over the temperature range studied. However, further work is required to elucidate the precise structures of the domains and ordered regions that are responsible for the different flow mechanisms on a macroscopic scale.

4. Conclusions

The perfluorinated-PTFE copolymer has a wide melting endotherm with an onset temperature at 130°C and an end temperature around 255°C. This is due to the existence of residual crystalline order, with a range of crystallite sizes (attributed to the existence of crystallisable sequences of various lengths) and degrees of perfection. The existence of these structural domains is responsible for changes in both viscous flow and elastic behaviour, at typical processing temperatures.

Steady-state shear flow properties are temperature-dependent. More significantly, melt temperature also modifies the dominant flow mechanism, once the majority of crystalline order is destroyed at temperatures above 230°C. Although the precursor is a pseudoplastic polymer, a simple power law is insufficient to model shear flow data with sufficient accuracy. Instead, a 3-parameter, non-linear Carreau model analysis has been used to obtain suitable rheological model coefficients, enabling a full characterisation of temperature-dependent shear flow behaviour. Flow activation energy of 63 kJmol⁻¹ has been obtained, for zero-shear viscosity at temperatures of 235°C and above. Below this temperature, there is a discontinuity in the Arrhenius plot, as a result of a change in deformation mechanism. Extensional viscosity data have demonstrated that viscosity decreases with both extensional stress and process temperature. The magnitude of extensional viscosity is significantly higher than in shear, partly due to the influence of crystalline order when analysed in the lower range of the temperature span investigated.

The existence of ordered, super-molecular units also gives rise to some unusual elastic effects in the copolymer. Generally, die swell ratios are very low in magnitude, and tend to increase with process temperature up to an apparent maximum at 250°C. Different modes of deformation behaviour have been defined (Mode 1 and Mode 2, respectively) according to whether particulate flow units (and crystalline sub-structure) has been eliminated, or remains in the network structure to some extent. Experimental observations of melt fracture and elastic instability are consistent with these proposed deformation mechanisms: the process window for high output manufacturing is expanded significantly when temperatures are increased above the melting endotherm maximum.

In summary, both process temperature and the residual particulate domain structure are shown to influence conventional melt flow behaviour of the copolymer. Subsequent products will have a complex microstructure that is sensitive to the thermo-mechanical history during the manufacturing process, an effect that is

also likely to influence the physical properties of melt-processed products.

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