

# Die Swell of Thermoplastic Polyurethanes: A Peculiar Behavior

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**ABSTRACT:** The instantaneous and equilibrium isothermal die swell ratios of thermoplastic polyurethanes have been measured by two methods. The incidence of some structural, geometrical, and processing parameters has been analyzed. The experimentation reveals the atypical behavior of these polymers related to a structural evolution during processing that greatly depends on the residence time in temperature under shearing and that probably results from the cumulated effects of multiple recombinations and chain cuts. This thermo-mechanical degradation affects the rheological properties of these polymers. The maximal behavior variations are observed for short times and stabilize above a specific critical time. Taking into account the effect of these rheological alterations on the generating mechanisms of die swell allows us to interpret all the experimental results (atypical or not) in terms of magnitude and direction of variation of the phenomenon. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1710–1724, 2001

## INTRODUCTION

The control of the thermoplastic die swell phenomenon is of the greatest industrial interest, for extrusion as well as for extrusion blow molding processing. Indeed, it determines the control of the dimensional accuracy and stability of manufactured products.

It is well established now that the die swell phenomenon results from three fundamental mechanisms, two of them being directly related to the viscoelastic properties of molten polymers: the recombination of the velocity field at the end of the die (which generates only limited swelling of about 10%), the elastic recovery of the elongational strain and thus of the elongational stress imposed at the entrance of the die (which can be partially relaxed during the flow through the die),

and the relaxation of the first normal stress difference induced by the simple shear flow through the die.

Although the exceptional magnitude of the die swelling of thermoplastic polymers is directly related to their viscoelasticity, no direct correlation has been established by now, between the rheological parameters and the die swell ratio.<sup>1–4</sup> Nevertheless, most studies conclude that, at fixed shear rate, a high first normal stress difference, characteristic of a high elasticity, leads to a high swell magnitude.

In the same way, numerous works have shown the high sensitivity of the die swell to structural parameters. The incidence of the molecular weight on the die swell ratio is much-debated.<sup>3,5,6</sup> It seems that more than the molecular weight itself, its distribution (and notably the degree of very high and very low molecular weights) complexly determines the die swell magnitude.<sup>3,7–13</sup>

Moreover, the die swell ratio increases with the degree of long branching<sup>14</sup> and the addition of

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fillers reduces, even breaks down, the magnitude of the phenomenon, by blocking of the deformation and relaxation processes.<sup>15,16</sup> Nevertheless, here again, it has been impossible to establish strict correlations between structural parameters and die swell ratio.<sup>2,4,14</sup>

The process parameters affect the die swell magnitude by their incidence on the stresses imposed on the material. Indeed, an increase of the shear rate into the die induces an increase of the die swell ratio attributed to an increase of the recoverable deformation.<sup>17-25</sup> In contrast, for a fixed share rate, an increase of the melt temperature corresponds to a decrease of the die swell magnitude, related to a decrease of the stresses generated into the die.<sup>22,26,27</sup> Nevertheless, the magnitude of die swell variations, obtained in an industrial context and reducible to a change in the processing parameters, are generally lower than those generated by a change in the structural parameters.

Finally, the geometrical parameters greatly affect the die swell magnitude. Indeed, the use of short dies,<sup>23,24</sup> small tank diameters,<sup>28,29</sup> or small entrance angles<sup>17,25,29,30</sup> allows reducing it, in very large proportions. On the other hand, by comparison with straight dies, the use of divergent dies reduces (by about 10%) the die swell magnitude and the use of convergent ones greatly increases it (by about 30%).

These different tendencies of the evolution of the die swell magnitude with the structural, geometrical, and processing parameters have all been determined with standard thermoplastic polymers, the structure of which is simple and stable (notably polyethylene and polystyrene).

But nowadays, the diversification of the application fields of the extruded products needs the use of new polymers, which are far more complex and which have some specific properties. In particular, the properties of the thermoplastic polyurethanes (mechanical strength, elasticity, transparency, biocompatibility with human tissues and human blood) have progressively imposed themselves for numerous bio-medical applications (pacemakers, catheters, delivery tubes, etc.).<sup>31</sup> Nevertheless, the thermal stability of the biphasic linear structure of these materials is much lower than the one of polyethylene.<sup>32,33</sup> Indeed, there are absorbent and hydrolizable under the combined action of heat and high moisture level.<sup>34-37</sup> The control of the die swell phenomenon remains essential for these applications, and it is needed to verify that the tendencies obtained

with standard polymers can be transposed to the extrusion process of these specific polymers. This is the aim of the present study.

## EXPERIMENTAL

### Materials

#### *Nature of the Materials*

The thermoplastic polyurethanes selected here have been specifically formulated for bio-medical applications and are used to manufacture tubes of very small dimensions. Their commercial references are: Tecothane 1085A (aromatic) and Tecoflex EG93A (aliphatic) and they are marketed by the Termedix company. Both have a good compatibility with human tissues and blood, but the Tecoflex EG93A's transparency allows a better control of the fluid flows. The density at room temperature of the Tecothane 1085A is 1.12. The Tecoflex EG93A one is 1.08. They have to be dried  $3\frac{1}{2}$  hours before processing or testing.

#### *Characterization Equipment and Procedures*

Molecular weight distributions (in styrene equivalence) are determined by gel permeation chromatography, in solution in tetrahydrofurane. The equipment is a Water 150C model.

The transition and melting temperatures have been measured by mechanical spectrometry with a Polymer Laboratory device. The frequency and the bending are fixed at respectively 1 Hz and 64  $\mu\text{m}$ . The heating rate is fixed at 5°C/min.

Before and after treatments, representative of different processing conditions, the infra-red spectrum of the materials are determined with a Perkin Elmer 1720 equipment.

Their melt flow indexes have been measured following the ISO1133 standard with a Gottfert 001 device, at 190°C, under a 5 kg loading.

The viscosity indexes of these polymers have been determined by viscosimetry in solution in tetrahydrofurane, following the NFT 51-061 standard, at 60°C.

The flow curves have been obtained by capillary rheometry following the procedures fixed by the ISO11443 standard, taking into account Rabinovitch's and Bagley's corrections, using a Gottfert 2001 equipment. The die diameters are fixed at 1 mm. Their lengths are fixed at 10, 20, and 30 mm. The testing temperatures are set up at the

**Table I** Main Characteristics of the Two Thermoplastic Polyurethanes

	$T_m$ (°C)	$T_g$ (°C)	MFI (g/10 min)	$M_w$	$M_n$	$DP$
Tecothane 1085A	110	-12	3	304000	118200	2,57
Tecoflex EG93A	100	37	120	143300	94500	1,51

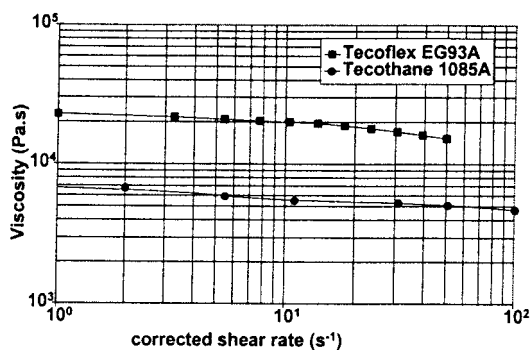
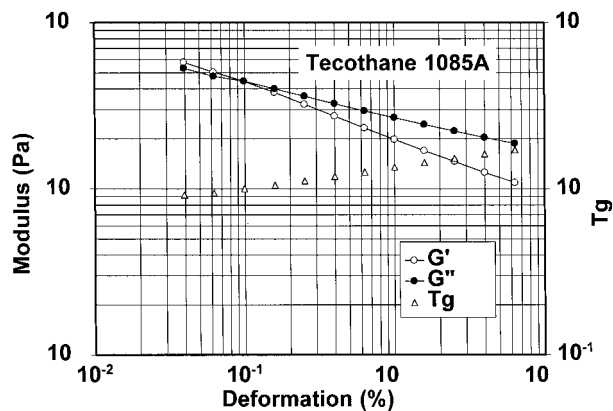
processing ones (205°C for the Tecothane 1085A and 160°C for the Tecoflex EG93A).

The viscoelastic characterisation of these polymers at the molten state has been achieved with a rotational Ares (Rheometric Scientific) rheometer, with plane-plane tools for the measurement of the viscous and elastic modules (the plate diameter is 25 mm) and with cone-plane tools for the determination of the first normal stress difference (the plate diameter is 25 mm, the cone apex angle is 4°, the gap is fixed at 0.005 mm). The test temperatures are equal to the extrusion temperatures. The frequency of the shearing deformation is equal to 1 rad/s. The experimental procedure has been adapted so that each measurement was made at controlled thermo-mechanical history.<sup>38</sup>

### Characterization Results

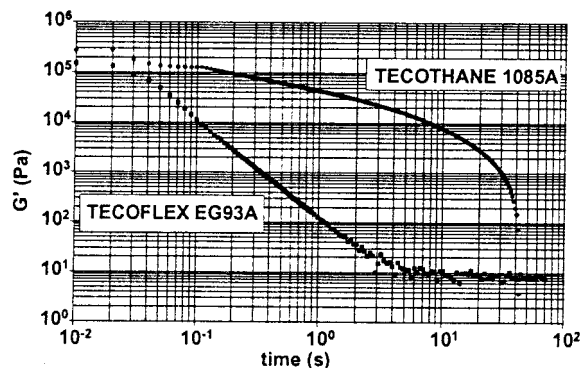
The main physical, chemical, and rheological characteristics of the two polymers are listed in Table I and in Figures 1–3.

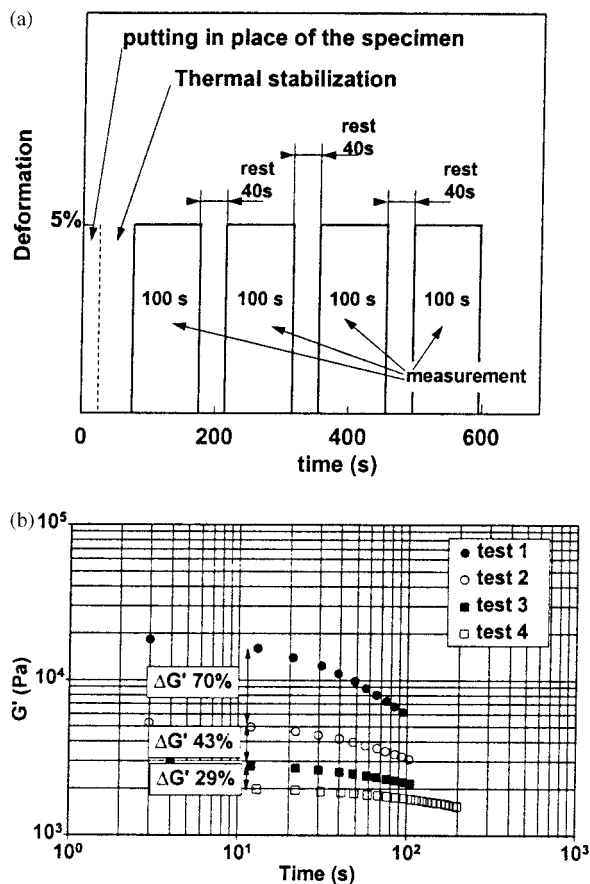
The molecular weight and the polydispersity of the Tecothane 1085A are clearly higher than those of the Tecoflex EG93A; its die swell values should then also be higher, all other parameters

**Figure 1** Flow curves of the two polymers at extrusion temperature.**Figure 2** Evolution of the moduli and of the loss angle of the two polymers with the amplitude of the deformation.

being kept constant, taking into account the tendencies reported in the literature. The glass transition temperature of the Tecoflex EG93A is clearly higher than the room temperature, whereas the one of the Tecothane 1085A is negative. In contrast, their melting temperatures are very close, ranging from 100 to 110°C. At 190°C, their melt flow index values show that the Tecothane 1085A is much more viscous than the Tecoflex EG93A at very low shear rate.

In contrast, at extrusion temperature (205°C for the Tecothane 1085A and 160°C for the Tecoflex EG93A) over the shear rate tested domain, the shear viscosity of the Tecoflex EG93A is clearly higher than the one of the Tecothane 1085A. Their flow indexes are quite similar. It is interesting here to note that the scattering associated with the capillary characterization of the Tecothane 1085A is high. That can lead us to

**Figure 3** Relaxation of the elastic modulus of the Tecothane 1085A vs. the shearing time (frequency 1 rad/s).

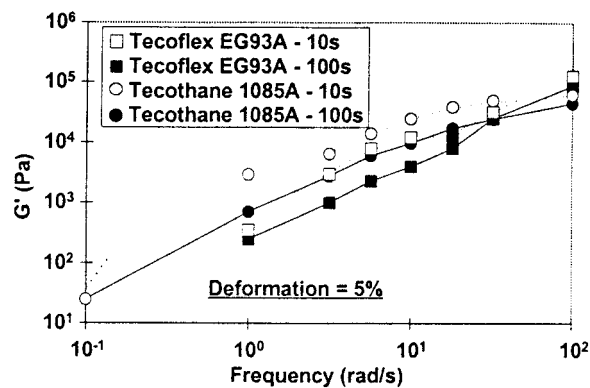


**Figure 4** (a) Procedure used to observe the change in the elastic modulus of the Tecothane 1085A with the residence time at extrusion temperature under shearing, at fixed frequency. (b) Effect of the residence time at extrusion temperature under shearing on the elastic modulus of the Tecothane 1085A (frequency 1 rad/s).

assume that the thermo-mechanical stability of this polymer is low (cf. Fig. 1).

This seems to be confirmed by rotational rheometry measurements, because, by a standard procedure of deformation scanning, it is not possible to observe the existence of a linear domain. The viscous and elastic modules as well as the loss angle values always vary with a significant magnitude, and this is observed even for very low deformations, close to 0.01% (Fig. 2). In addition, at fixed deformation frequency and magnitude, the elastic modulus of each polymer decreases dramatically (notably for the Tecoflex EG93A) when the shearing time increases, even at the very first beginning of the test (cf. Fig. 3).

This tendency has been verified over long time scale for the Tecothane 1085A, following the procedure described on Figure 4a. Indeed, a dramatic



**Figure 5** Comparison of the elastic modules of the two thermoplastic polyurethanes at extrusion temperature and fixed thermo-mechanical history.

decrease of the elastic modulus values, varying from 30 to 70%, as well as dramatic fall of the other viscoelastic characteristics (loss modulus, loss angle and first normal stress difference) are observed (Fig. 4b) between two measurement series.

All these results show that the rheological behavior of the two thermoplastic polyurethanes varies during the test; this means that this behavior is sensitive to the residence time in temperature under shearing.

The objective comparison of the rheological behavior of the two polymers can then be made only at fixed thermo-mechanical history (that means for the same residence time at extrusion temperature under shearing, frequency, and deformation). In this case, it appears that the elastic modulus and the first normal stress difference of the Tecothane 1085A are higher than those of the Tecoflex EG93A (Fig. 5 & Fig. 6). This reveals its higher elasticity and allows us to predict a higher die swell magnitude.

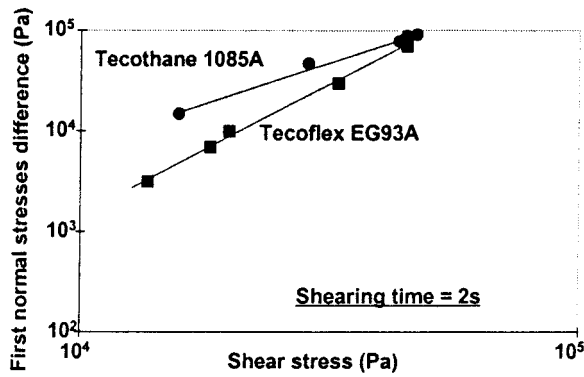
## Processing Conditions and Die Swell Measurements

### Processing Conditions

The processing equipment is constituted by a single screw extruder Rheomex 254 (diameter: 19

**Table II** Optimized Processing Temperatures for the Two Thermoplastic Polyurethanes

	Zone 1 (°C)	Zone 2 (°C)	Zone 3 (°C)	Zone 4 (°C)
Tecothane 1085A	170	180	190	205
Tecoflex EG93A	145	150	155	160



**Figure 6** Comparison of the first normal stress differences of the two thermoplastic polyurethanes at extrusion temperature and fixed thermo-mechanical history.

mm, L/D ratio: 25) associated with a crosshead die and regulated by a Haake Buchler Rheocord System 40 system. The thermal regulation is made over 4 zones. The optimal processing temperatures have been determined for each polymer and are listed in Table II.

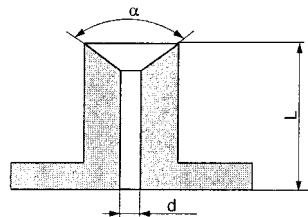
Different cylindrical dies were used in order to study the effect the flow geometry on the die swell magnitude. Their general shape and their dimensions are shown on Figure 7.

Different extrusion volume flow rates have been tested, the objective being to scan, for each die and each polymer, corrected wall shear rates varying between 1 and 100 s<sup>-1</sup>.

**Die Swell Measurement**

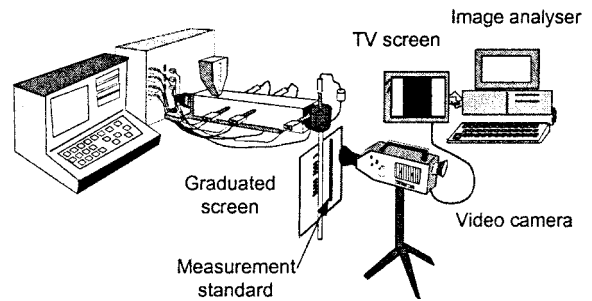
The die swell magnitude is defined as the ratio between the profile diameter and the die diameter (D/d).

The instantaneous diametrical die swell measurement, in air at 6 mm from the end of the die, is achieved by a laser-scanning micrometer.<sup>39,40</sup> The experimental device is shown Figure 8. It is a Zumbach (type OEM0.5R ODAC 81 CMK) device,



L = 33, 43 and 53 mm, α = 60, 90, 120 and 150°  
d = 1, 2, 3, 5.7 and 7 mm

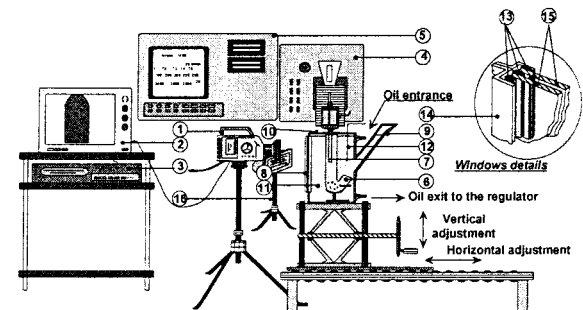
**Figure 7** Geometrical characteristics of the dies.



**Figure 8** Experimental device used for the measurement of the instantaneous diametrical die swell ratio in air by laser scanning micrometer.

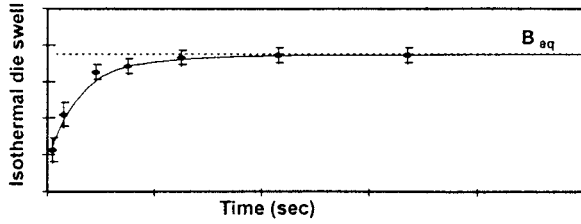
equipped with a helium-neon laser. The dynamic measurement accuracy is equal to 0.02 mm with a resolution of 0.01 mm for diameters varying between 1 and 78 mm. The details of the experimental procedure are described in Dufrancatel-Veiller.<sup>38</sup> It is important to underline that this measurement is affected by the perturbing effects of gravity and cooling.

The measurement of the diametrical die swell ratio, without the perturbing effects described above, of profile relaxed from all the stresses generated by the processing, is made in an oil bath regulated at extrusion temperature, on the experimental device built by Koopmans<sup>12,13</sup> and modified in order to improve its accuracy and its reliability (Fig. 9). The heat exchanging fluid is silicone oil Dow Corning 550. The details of the experimental procedure are presented in Dufrancatel-Veiller.<sup>38</sup> In this case, the evolution in time of the diameter of the profile is filmed. The record is then examined by an image analyzing system.



1-Video camera 2-TV screen 3-Video recorder 4-Extruder 5-control device 6-J Tube 7-Extrudat 8-Window 9-Arm 10-Hole cover 11-Oil 12-Temperature sensor 13-Seal 14-Holding device 15-Borosilicated glass 16- 800 Watt Spot

**Figure 9** Experimental device used for the measurement of the equilibrium isothermal diametrical die swell ratio by camera recording.



**Figure 10** Determination of the equilibrium isothermal die swell.

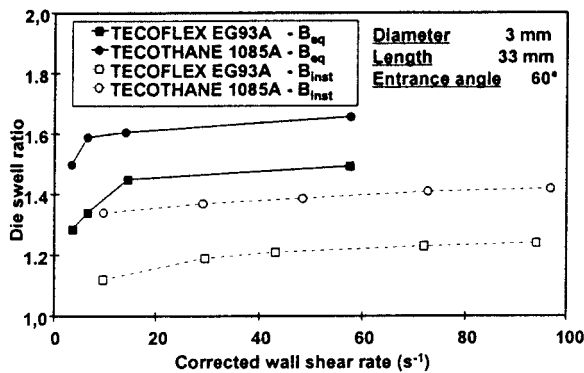
An example of the experimental results is presented in Figure 10. At short times the extruded diameter increases quickly, then ends to an asymptotically value, qualified as equilibrium isothermal die swell and noted as  $B_{eq}$ .

**RESULTS**

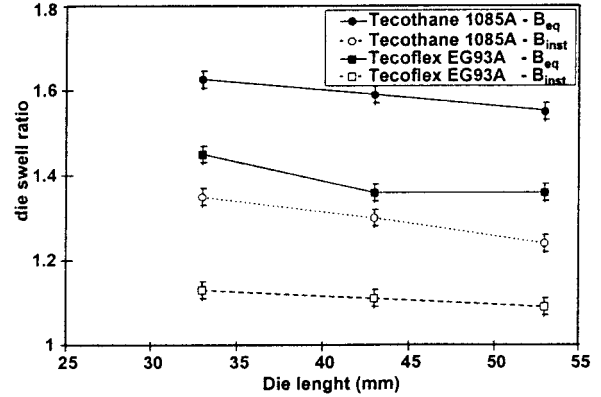
The objective is first to compare, for each material, the dies swell values measured in air and in isothermal and steady conditions. Then, for each measurement, the problem is to compare the die swell ratios associated with the two polymers; all other conditions being kept constant. Furthermore, the effect of two types of parameters (related to the flow geometry and to the extrusion process) on the die swell magnitude is determined.

**Comparison between Instantaneous Die Swell Ratio in Air-Equilibrium Isothermal Die Swell Ratio**

Figures 11 to 14 compare the values of instantaneous die swell ratio in air and of equilibrium isothermal die swell ratio obtained for the two polymers, for different combinations of process and geometrical parameters. As expected, the



**Figure 11** Effect of the corrected wall shear rate on the die swell of the two polymers.

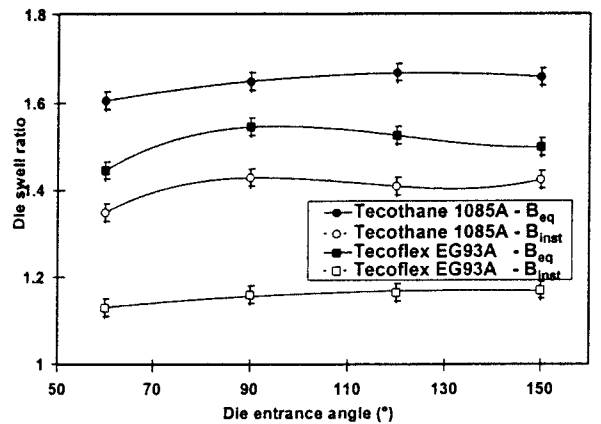


**Figure 12** Effect of the die length on the die swell ratios for the two polyurethanes (diameter 3 mm, entrance angle 60°, shear rate 10 s<sup>-1</sup>).

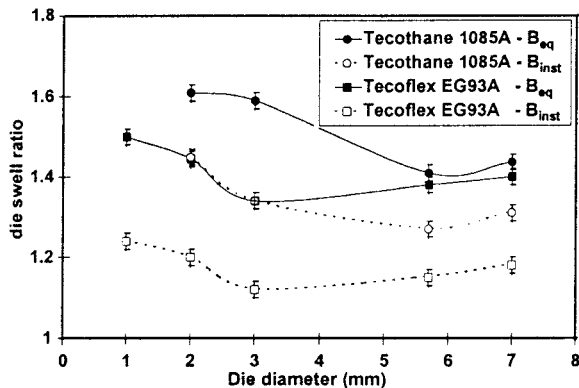
equilibrium isothermal die swell ratio is always higher than the instantaneous die swell ratio; i.e.: instantaneous die swell ratio, integrating gravity and cooling effects (which oppose the die swell phenomenon) and being measured on non completely relaxed profiles. In addition, these two quantities are affected in the same way by the different studied parameters.

**Effect of the Structure and of the Rheology on the Die Swell Ratio**

In other respects, it can be noted that the die swell values measured with the Tecothane 1085A are about 10% higher than the ones measured with the Tecoflex EG93A. This is to relate to the structure of this polymer (its molecular weight



**Figure 13** Incidence of the die entrance angle on the die swell ratios of the two polyurethanes (length = 33 mm, diameter = 3 mm, corrected wall shear rate = 10 s<sup>-1</sup>).



**Figure 14** Effect of the die diameter on the die swell ratio for the two polyurethanes (die length = 33 mm, entrance angle = 60°, wall shear rate = 10 s<sup>-1</sup>).

and its polydispersity are higher) and to its elasticity (its first normal stress difference is also higher). In addition, the die swell ratios of the two polymers, measured at extrusion temperature, are affected in the same way by the process and geometrical parameters, even if the magnitude of variation can be more or less pronounced or/and shifted depending on the observed polymer or the considered parameter.

#### Effect of the Process Parameters on the Die Swell Ratio

For the two materials, Figure 11 shows that, at fixed diameter, length, and entrance angle, the die swell (instantaneous in air and isothermal at equilibrium) increases with the corrected wall shear rate. This tendency, in accordance with the one reported in the literature, is generally related to an increase in the first normal stress difference and thus to an increase of the recoverable deformation, generated by the simple shear flow through the die. The magnitudes of die swell variations are limited here (between 6 and 16%) and equivalent to those corresponding for other polymers.<sup>11,13,23</sup>

#### Effect of the Geometrical Parameters on the Die Swell Ratio

Figures 12 to 14 present the effect of the length, the entrance angle, and the diameter of the die on the instantaneous in air and equilibrium isothermal die swell ratio, the fixed parameters being the process conditions, namely the extrusion temperature and the corrected wall shear rate.

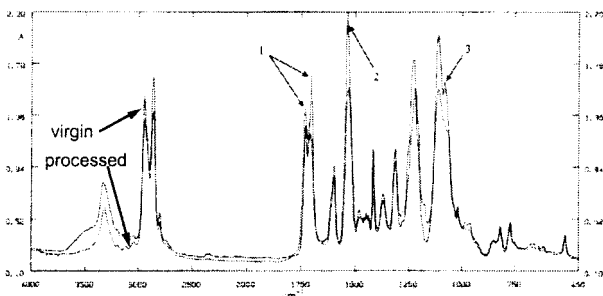
The evolution of these two quantities with the length and the entrance angle of the die are in accordance with tendencies reported in the literature. (i) An increase of the die length (at a fixed diameter) corresponds to a reduction of the die swell ratio, related to a more complete relaxation of the entrance elongational stress, due to an increase of the residence and conformation times. For an identical length variation of 61%, the relative change of the die swell ratio remains low and similar for the two polyurethanes and the two measured quantities (the die swell ratio drop is ranged from 3.5 to 7.5%). (ii) Above a critical angle, close to 90° for the two polymers, the flow at the entrance of the die is controlled by a vortex, and the die swell ratios are practically constant. In contrast, below this critical angle, the smaller the entrance angle, the lower the die swell ratio, because the elongational deformation is then more progressively applied. Over the entrance angle range tested (from 60 to 150°), the changes in die swell ratio are very low (from 4 to 7%).

In contrast, the change of the die swell ratio of the two polymers with the die diameter (the other parameters being fixed) is peculiar. Indeed, below a critical die diameter, higher for the Tecothane 1085A than for the Tecoflex EG93A, but identical for the two die swell ratios, an increase of the die diameter induces a decrease of die swell ratio. This behavior is generally related to a decrease of the elongational stress at the entrance of the die. But the tendency is reversed above this critical die diameter. To our knowledge, this peculiar behavior has not been reported in the literature yet. It is to be noted here, taking into account the experimental procedure, that the tests carried out at increasing die diameter and constant corrected wall shear rate, mean the use of increasing volume flow rates, thus decreasing residence times. So, we assume that this peculiar behavior is then linked to a structural change during the flow, which would perturb the classical effect of the decrease of the elongation stress at the entrance of the die.

## DISCUSSION

### Confirmation of the Structural Change

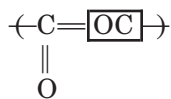
In order to confirm the possible structural modifications due to the residence of the polymers at processing temperature, some Tecothane 1085A samples have been analyzed by infra-red spec-



**Figure 15** Infra-red spectra of the virgin and processed Tecothane 1085A.

trometry. The pellets have been dried during  $3\frac{1}{2}$  hours at  $80^{\circ}\text{C}$ ; sheared for 3 min at  $10\text{ s}^{-1}$  (in the rotational rheometer) at  $205^{\circ}\text{C}$ , and then dissolved in tetrahydrofurane (THF). The final product has then been placed in an oven at  $50^{\circ}\text{C}$ . The evaporation of the solvent gives a thin film (the thickness is equal to 0.2 mm), which is then dried at  $180^{\circ}\text{C}$  for different times (2 to 24 hours). The sample can then be analyzed. Figure 15 compares the spectra obtained with original Tecothane 1085A pellets (it means pellets which have only been dried for  $3\frac{1}{2}$  hours at  $80^{\circ}\text{C}$ ) with a sample which has been sheared and then dried for 24 hours at  $180^{\circ}\text{C}$ . Some alterations reveal structural changes. Indeed, we observe:

1. an inversion of the peak at 1700 and  $1730\text{ cm}^{-1}$  (marker 1 on Fig. 15), the first one being characteristic of the linked  $\text{C}=\text{O}$  bond and the second one being characteristic of the free  $\text{C}=\text{O}$  bond.<sup>41</sup> The residence of the polyurethane at processing temperature seems to induce the cut of hydrogen bonds allowing the molecular cohesion in the hard domain. The processed material contains more free  $\text{C}=\text{O}$  bonds (peak at  $1730\text{ cm}^{-1}$ ) than the pellets;
2. a clear reduction of the peak at  $1600\text{ cm}^{-1}$ , characteristic of the  $\text{N}-\text{H}$  bond (mark 2 on figure 15);
3. the vanishing of the shoulder at  $1080\text{ cm}^{-1}$  (mark 3 on figure 15), characteristic of the  $\text{C}-\text{O}$  bond in the hard sequence.



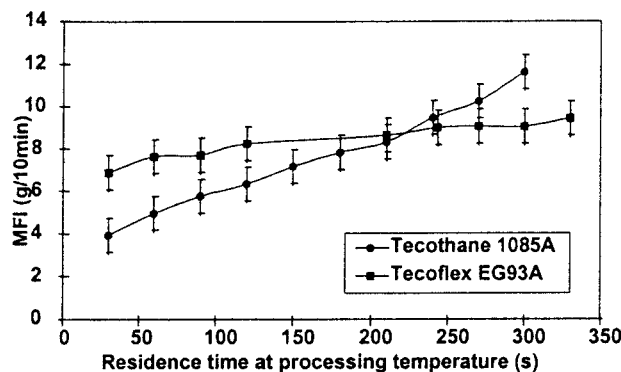
The infra-red spectroscopy cannot certainly reveal the nature of the molecular modifications. Indeed, the multiple possible recombinations of

the polymer with small molecules ( $\text{NH}_2$ ,  $\text{OH}$ , amide) cannot be observed, because the spectrum of the virgin polyurethane already contains the lines that should appear at equivalent wavelengths. But nevertheless, this technique allows confirmation that the residence of the polymer at processing temperature under shearing leads to a molecular change, the latter being capable of significantly affecting the physical, chemical, and rheological properties of the material.

The sensitivity of this polyurethane to the temperature and/or the shearing can also be confirmed by different indirect measurements.

So, the melt flow indexes of the two polymers at extrusion temperature ( $205^{\circ}\text{C}$  for the Tecothane 1085A and  $160^{\circ}\text{C}$  for the Tecoflex EG93A), under a loading of 5 kg have been measured. The pellets have been dried for  $3\frac{1}{2}$  hours at  $80^{\circ}\text{C}$ , then have been placed in the melt flow index device during different times (characteristic of the actual residence times in the industrial process) before measurement. The changes in flow index of the Tecothane 1085A are higher than those of the Tecoflex EG93A. However, whatever the material, a simple residence at processing temperature leads to a structural modification which is rapidly initiated and continuous (Fig. 16).

The actual nature of this modification remains unknown, but it is not a simple hydrolysis. In order to prove it, the viscosity index has been measured on some Tecothane 1085A samples, which had undergone different pre-conditioning and processing on an open mixer (Table III). Only the extreme treatment, which is poorly representative of the industrial process, and which consists of letting the pellets in water for 16 hours, leads to significant change in viscosity index (Fig.



**Figure 16** Effect of the residence time at processing temperature on the melt flow index of the two polyurethanes.



**Table III Parameters of the Viscosity Index Evolution Analysis**

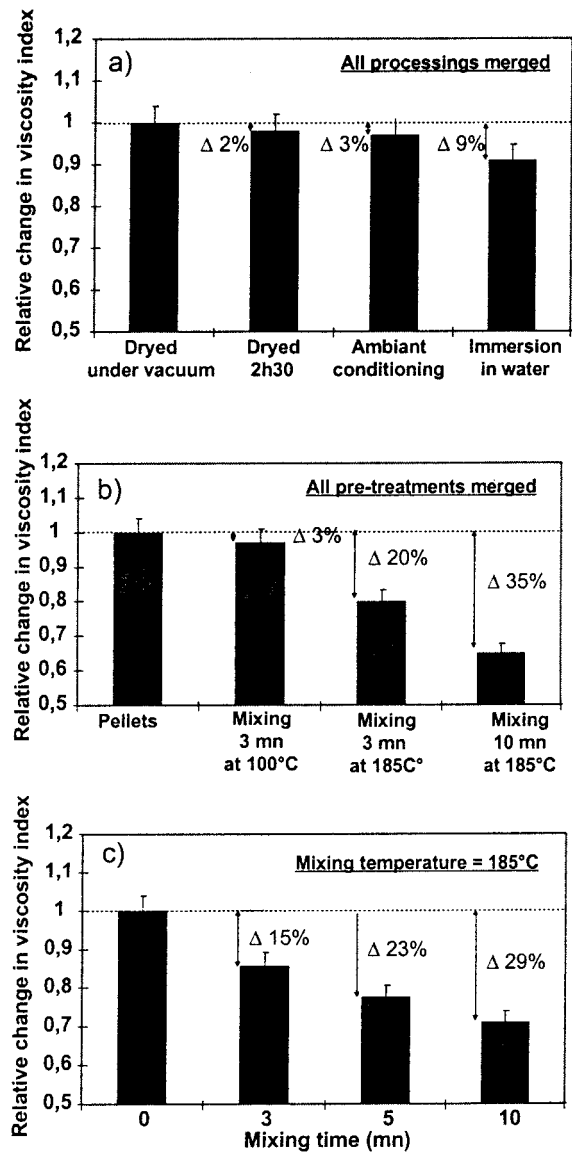
Pre-treatment	Mixing Conditions
• 16 hours in water at 25°C	• 3 min at 100°C
• 16 hours in air (atmospheric conditions)	• 3 min at 185°C
• 3½ hours in oven at 80°C	• 5 min 20 at 185°C
• 3 hours in oven under vacuum at 60°C	• 10 min at 185°C

17a). The mixing alone (at low temperature of 100°C) generates only a small change in this index, and thus in the polymer structure. In contrast, the combination of a temperature higher than 100°C and of a shearing, characteristic of the industrial process, have major effects (Fig. 17b). On the other hand, the change in viscosity index with the mixing time is continuous, thus confirming that the change in the polymer structure is also fast and continuous (Fig. 17c).

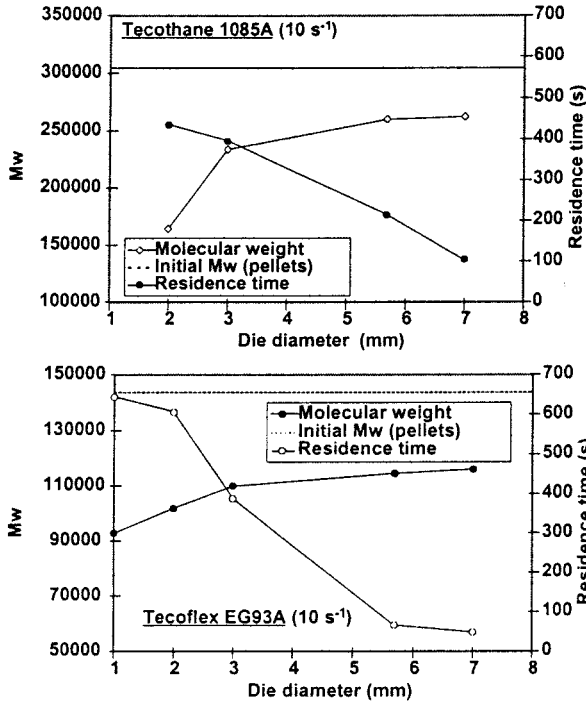
Finally, measurements of the molecular distribution after extrusion should allow us to judge on the effect of the actual processing conditions on the magnitude of the structural change. A first series of tests has been carried out on samples that had flown at fixed corrected wall shear rate, equal to  $10 \text{ s}^{-1}$ , through dies the diameter of that ranged from 1 to 7 mm. The processing conditions and the residence times in the process are listed in Table IV. The change in the molecular weight with the die diameter is shown on Figure 18.

Whatever the polyurethane and the processing conditions, the molecular weight of the extruded material is always lower than the one of the initial pellets. At fixed shear rate, a decrease in die diameter induces an increase of the residence time and a decrease of the molecular weight. The highest relative changes in molecular weight are obtained for the lowest die diameters, corresponding to the longest residence times. They are high and fast at the beginning and then stabilize themselves for die diameters comprised between 3 and 5.69 mm for the two polymers. However, the magnitudes of variation between 2 and 7 mm are more pronounced for the Tecothane 1085A (30%) than for the Tecoflex AG93A (10%).

A second series of tests has been carried out on samples, which had flown at different corrected wall shear rates (from 3 to  $300 \text{ s}^{-1}$ ) through the 2

**Figure 17** Effect of the thermo-mechanical history on the viscosity index.**Table IV Residence Time in the Process at a Corrected Wall Shear Rate of  $10 \text{ s}^{-1}$  and Different Die Diameters**

Die diameter (mm)	1	2	3	5,69	7
Tecothane 1085A		7'15"	6'35"	3'34"	1'45"
Tecoflex EG93A	10'44"	10'06"	6'28"	1'07"	49"



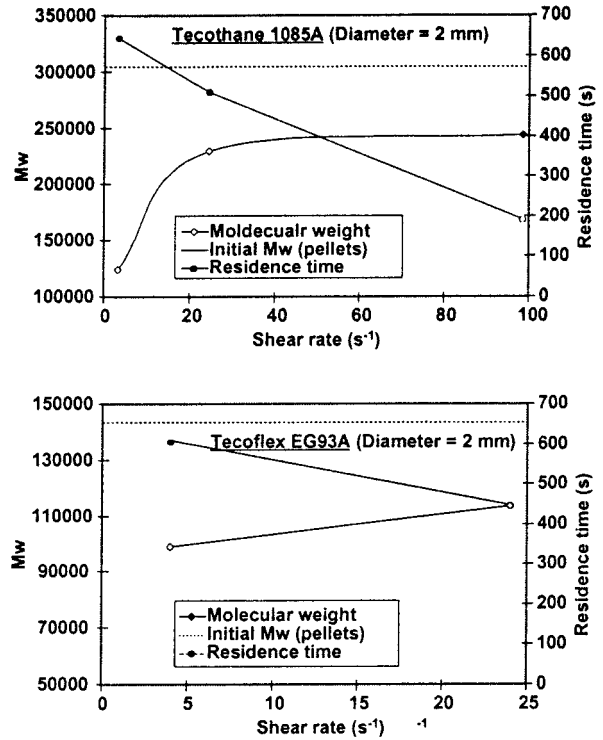
**Figure 18** Effect of the residence time in the process on the molecular weight of the two polyurethanes for a corrected wall shear rate of  $10 \text{ s}^{-1}$  and different die diameters.

mm in diameter die. The processing conditions and the residence times in the process are listed in Table V. The change in the molecular weight (in styrene equivalent) with the die wall shear rate is shown on Figure 19.

At fixed die diameter, an increase in the shear rate corresponds to a decrease in the residence time and thus to a reduction in structural modification. The maximal molecular weight changes are obtained for the lowest corrected wall shear rates, it means for the longest times. For the Tecothane 1085A, the changes are high and fast at the beginning and then stabilize above a shear

**Table V** Residence Times in the Process for a 2 mm in Diameter Die and Different Corrected Wall Shear Rates

	Tecothane 1085A			Tecoflex EG93A	
Shear rate ( $\text{s}^{-1}$ )	3,3	24,6	98,5	6,5	40
Residence time (s)	10'44"	8'30"	3'10"	10'06"	7'25"

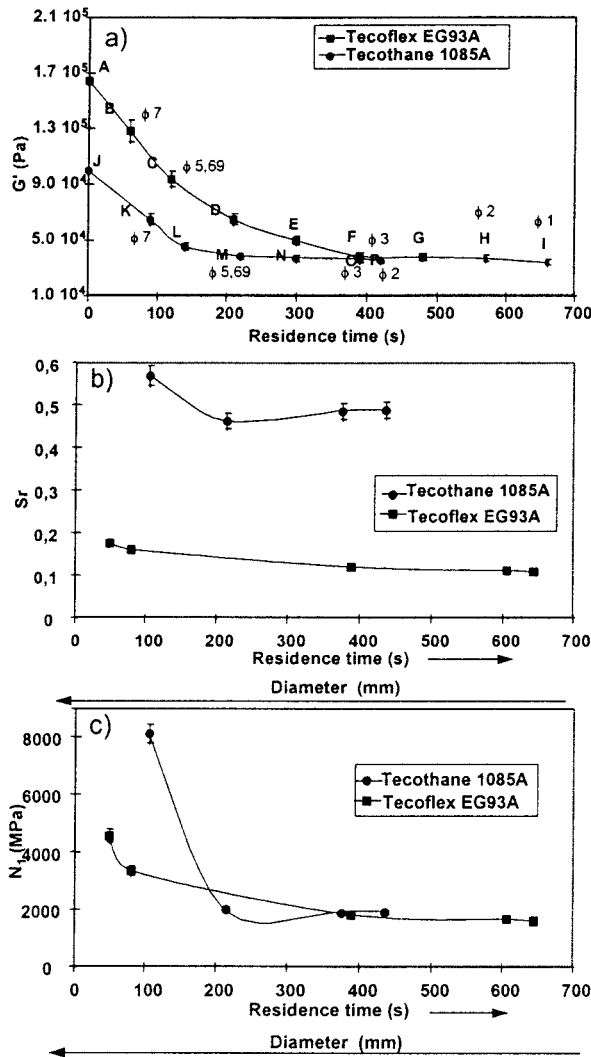


**Figure 19** Effect of the wall shear rate during processing on the molecular weight of the two polyurethanes.

rate around  $25 \text{ s}^{-1}$ . The tested shear rates in the case of the Tecoflex EG93A do not allow us to conclude on the possible stabilization of the structural evolution above  $25 \text{ s}^{-1}$ .

**Effect on the Rheological Behavior**

The structural evolution of the materials during processing having been proved, its consequences on their rheological behavior must be quantified now. In order to do so, the elastic modulus, the first normal stress difference and the recoverable deformation (evaluated as the first normal stress difference to two times the corresponding shear rate ratio) of the two polymers have been measured at processing conditions that are coherent with the thermochemical history that they undergo in the different studied extrusion configurations. So, the tests have been carried out at processing temperature. The samples have been pre-sheared in the rotational rheometer at fixed shear rate ( $10 \text{ s}^{-1}$ ) for times corresponding to the actual residence times in the industrial process (platification and flow through the die) for die diameters varying between 1 and 7 mm. After, they have been submitted to a multifrequency



**Figure 20** Incidence of the residence time in the extrusion process on some viscoelastic characteristics of the two polyurethanes.

test. Figure 20 shows the incidence of the residence time on these characteristic quantities for a frequency of 10 rad/s.

Whatever the viscoelastic characteristic, it decreases dramatically at short times (AF and JM segments on Fig. 20a), and then more progressively at long times (FI and MP segments on Fig. 20a). The critical times, above which the rheological properties remain approximately stable do not depend on the considered property and are close to 210 s for the Tecothane 1085A and to 390 s for the Tecoflex EG93A. But in fact, a short residence time in the process corresponds to the use of a large die diameter (at fixed wall shear rate) or to the processing at high shear rate (at fixed die diameter), and vice versa. In other words, it can

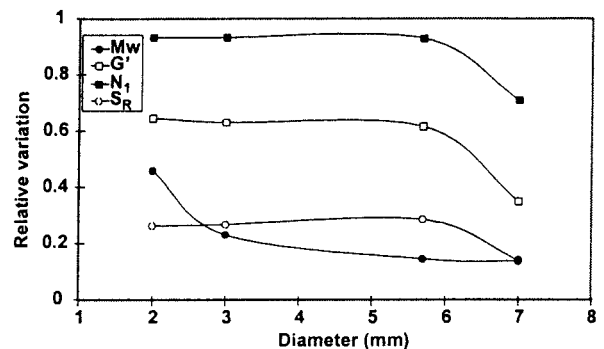
be assumed that the residence time of the polymer in the extruder is inversely proportional to the die diameter. So, the rheological behavior will be more affected by the processing through dies with small diameter (or by the use of low shear rates); the critical diameters (for a fixed shear rate of  $10 \text{ s}^{-1}$ ) being respectively equal to 3 mm for the Tecoflex EG93A and to 6 mm for the Tecothane 1085A. It can also be noted, that all the measured evolutions with the increase of the residence time correspond to a reduction of the elasticity of the polyurethanes.

Moreover, it can be seen that the magnitude of the molecular weight change, characteristic of a structural evolution, is not proportional to the rheological behavior variation that it generates (Fig. 21). A low change in molecular weight at short times, induces a large variation of the rheological behavior, whereas large structure evolution at long times corresponds to low alterations of the rheological behavior.

### Effect on the Die Swell Ratio

It is generally admitted that the die swelling of the macromolecular materials results from three elementary mechanisms.

*The recombination of the velocity profile*, purely a mechanical mechanism, generates diameter variations of approximately 10%, practically independent of the nature of the polymer as well as of the technological and geometrical parameters of the process. Thus, one can expect that the structural and rheological modifications induced by the processing will have very little effect on the die swell magnitude; they will not be considered here.



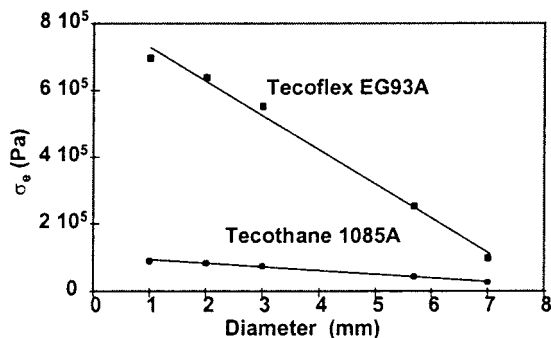
**Figure 21** Comparison of the evolution of the molecular weight and of the viscoelastic properties of the Tecothane 1085A with the die diameter (wall shear rate =  $10 \text{ s}^{-1}$ , die length = 33 mm, entrance angle =  $60^\circ$ ).

The magnitude of the swell reliable to the elastic recovery of the *entrance elongational deformation* associated with the corresponding entrance normal stress can be significant for specific geometrical configurations (entrance angles or tank diameter that do not lead to the creation of recirculations, dies with an insufficient length for the relaxation of the entrance phenomena). Moreover, the general mechanism can be perturbed by a possible structural and rheological evolution during processing. The reasoning is similar for the part of the die swelling reliable to the *relaxation of the first normal stress difference* generated by the simple shear flow through the die.

Thus, the objective here consists in determining the consequences of the structural and of the rheological evolution on the die swell ratio generated by these last two mechanisms. Only the experimental results obtained in isothermal conditions will be considered because the tendencies obtained in air are similar, differing only by their magnitudes.

The entrance elongational stress has been estimated by Gibson's model,<sup>42</sup> from experimental measurements of the pressure loss (partially integrating the structural change) corresponding to the extrusion processing of the two polymers at a corrected wall shear rate of  $10 \text{ s}^{-1}$ , through dies with different diameters and lengths (the diameter varied from 2 to 7 mm and the length ranged from 33 to 53 mm). It has been assumed that this elongational stress is instantaneously established at the entrance of the die, and that it does not relax during the flow through the die. It has been indeed experimentally shown that the die swell ratio always decreases if the die length increases, and that proves that the entrance normal stress is never entirely relaxed at the end of the die. Thus, as first approximation, and for the study of the incidence of the die diameter on the die swell ratio, it has been assumed that this stress does not relax at all, whatever the die diameter. The analysis is only qualitative, and the objective is not to calculate the exact value of the normal stress at the end the die, but only to estimate its direction of variation with the considered geometrical parameter.

It can be noted that  $\sigma_e$  is higher and more sensitive to the die diameter for the Tecoflex EG93A than for the Tecothane 1085A (Fig. 22). For the two polymers, it decreases if the die diameter increases. This behavior is identical to the one observed with polymers whose structure is not evolutive. The structural changes generated



**Figure 22** Incidence of the die diameter (entrance angle =  $60^\circ$ , wall shear rate =  $10 \text{ s}^{-1}$ ) on the magnitude of the entrance normal stress.

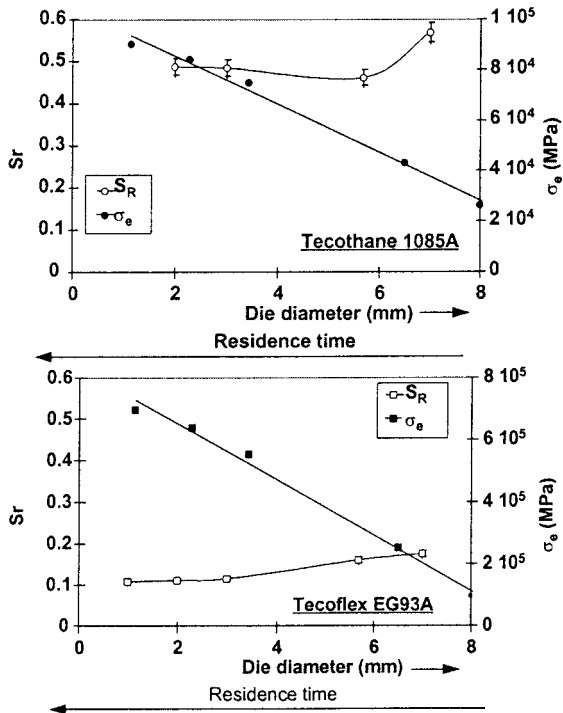
by the processing, affect perhaps the magnitude of  $\sigma_e$ , but not its direction of variation with the die diameter.

The effect of the die length and of the die entrance angle on the entrance normal stress has not been experimentally determined. However, all other geometrical and technological parameters being kept constant, and taking into account the calculation hypotheses, the structural evolution does not affect the direction of variation of  $\sigma_e$  with respect to the die length. In the same way, over the domain where the flow is not perturbed by recirculations, an increase of the die entrance angle leads to an increase of the entrance normal stress, even if there is a structural evolution.

The effect of the corrected wall shear rate on the entrance normal stress, at fixed die diameter, has not been measured either. However, its increase induces a reduction of the residence time in the process, and thus a decrease of the effect of the structural change possibly capable of perturbing the classical increase of  $\sigma_e$ .

Taking into account all these statements (effect of the die diameter, the die length, the die entrance angle, and the wall shear rate on  $\sigma_e$ ), it can be assumed that only the direction of variation of the entrance normal stress with the die diameter could be affected by the structural evolution, as it has been shown that is not the case. Thus, the direction of variation of equilibrium isothermal diametrical die swell ratio with the die diameter can be interpreted in the following way.

A change in die diameter introduces two antagonistic phenomena (Fig. 23). The first one corresponds to the evolution of the entrance elongational stress; the second one is linked to the variation of the first normal stress difference generated by the simple shear flow through the



**Figure 23** Comparative changes of the entrance normal stress and the recoverable deformation with the die diameter, taking into account the structural modification due to the processing.

die, which can be related to the recoverable deformation. Qualitatively, it is experimentally observed that up to a critical diameter, which is characteristic of the polymer (3 mm for the Tecoflex EG93A and 6 mm for the Tecothane 1085A), the entrance normal stress progressively decreases whereas the recoverable deformation remains approximately constant, if the die diameter increases. So, the change in die swell ratio with the die diameter is mainly reducible to the decrease of the entrance normal stress, which induces a decrease of the die swell ratio. That corresponds to the classical behavior of stable molten polymers. Above this critical diameter, the entrance normal stress always decreases linearly, but the recoverable deformation sharply increases, due to the structural change. The variation of the die swell ratio is then reducible to the last phenomenon. Then, the die swell ratio increases with the die diameter, in contrast with what is observed with more classic polymers.

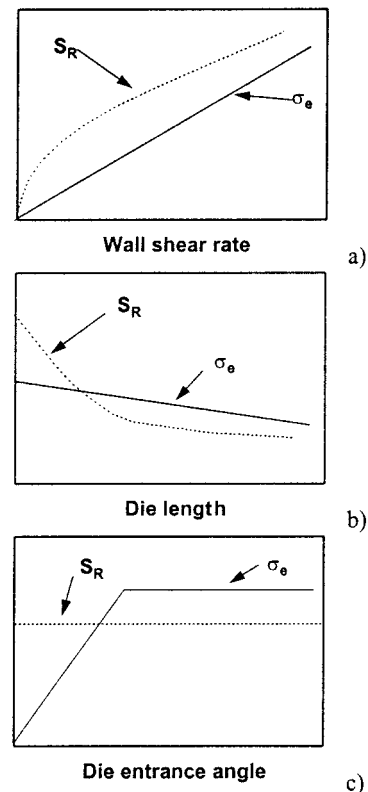
For all the other parameters (die length, die entrance angle, wall shear rate), the two phenomena act in the same direction. A skeleton diagram is presented in Figure 24. Indeed, an increase of

the wall shear rate always induces an increase of the entrance elongational stress<sup>25</sup> and also an increase of the recoverable deformation (Fig. 24a), both leading to an increase of the die swell ratio.

It can be noted that an increase of the wall shear rate, corresponding to a reduction of the residence time, minimizes the structural change.

In the same way, an increase of the die length induces a higher relaxation of the entrance elongational stress and a lower recoverable deformation (which includes the structural change: an increase of the die length generates an increase of the residence time, maximizes the structural evolution, reducing the die swell ratio). The two mechanisms induce a reduction of the die swell ratio (Fig. 24b).

Finally, an increase of the die entrance angle (in the domain, which is not perturbed by the recirculations), induces an increase of the entrance normal stress, but no change in the recoverable deformation (and no variation of the structural effect). Thus, it generates an increase of the die swell ratio (Fig. 24c).



**Figure 24** Comparative changes in the entrance elongational stress and in the recoverable deformation with the variation of the wall shear rate, the die length, and the die entrance angle, taking into account the structural evolution during processing.

## CONCLUSION

Two experimental techniques have been developed in order to quantify the effect of different geometrical and technological parameters on the die swell ratio of two thermoplastic polyurethanes, specifically formulated for bio-medical applications. The results clearly reveal the peculiar behavior of these polymers, which was reduced to a structural change during processing.

The latter has been confirmed by infra-red spectroscopy measurements, but its exact nature could not be explained and probably results from cumulated effects of complex cuts and recombinations of molecular bonds. It induces a change in the melt flow index and in the viscosity index as well as in the molecular weight. It is not a simple hydrolysis. The structural evolution is rapidly initiated and spreads without discontinuity all over the duration of the processing. The maximal changes in molecular weight are obtained at longest residence times in the extrusion process.

This structural evolution leads to a notable reduction of the elasticity of the materials during processing. However, the maximal changes in rheological properties are obtained at shortest residence times, that is to say, taking into account the experimental procedure, with highest die diameters and highest wall shear rates.

Taking into account the consequences of these rheological alterations on the main mechanisms generating the die swell phenomenon allows to explain all the experimental results, in terms of magnitude and direction of variation of the die swell ratio.

In particular, it is confirmed that the atypical incidence of the die diameter on the die swell ratio is directly correlated to the structural evolution on the coupling of the elastic recovery of the entrance normal stress and the relaxation of the first normal stress difference generated by the simple shear flow through the die mechanisms.

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## REFERENCES

1. Miller, J. C. A Rheological Product Problem in Blow Molding. *The Society of Rheology*; 1975, p. 341-350.
2. Garcia-Rejon, A.; Alvarez, C. ANTEC '89, 1986, p. 480-485.
3. Racin, R.; Bogue, D. C. *J Rheol Report no. 115*, 1979, 23, 263-280.
4. Orbey, N. Sag and swell of extrudate from annular dies; Ph.D. Thesis Mc Gill University Montreal, 1983.
5. Leblanc J. *Rhéologie expérimentale des polymères à l'état fondu*, Ed. Cebedoc, Liège, 1974.
6. Wissbrun, K. F. *Polymer News* 1994, 4, 55-66.
7. Mendelson, R. A.; Finger, F. L. *J Polym Sci* 1975, 19, 1061-1078.
8. Vlachopoulos, J. *Transactions Society Rheol* 1981, 16, 219-685.
9. Duveau, H. Amélioration d'un processus de fabrication de filets en matière thermoplastique; Thèse de l'Université de Lille, 1991.
10. Seriai, M. Préviation du gonflement de divers polymères à partir de leur comportement viscoélastique dans des conditions d'extrusion capillaire variées; Thèse de l'Université de Saint-Etienne, 1991.
11. Swan, P. L.; Dealy, J. M.; Garcia-Rejon, A.; Derdouri, A. *Polym Engineer Sci* 1991, 31, 705-710.
12. Koopmans, R. J. *J Polym Sci, Part A : Polymer Chemistry* 1988, 26, 1157-1164.
13. Koopmans, R. J. *Polym Engineer Sci* 1992, 32, 1741-1764.
14. Hamielec, P.; Vlachopoulos, J. *J Appl Polym Sci* 1983, 28, 2389-2392.
15. Mijangos-Santiago, F.; Dealy, J. M. *Polym Engineer Sci* 1991, 31, 1176-1181.
16. Yazici, R.; Kalyon, D. M.; Han, S. B. ANTEC '94, p. 1172-1174.
17. Eggen, S.; Hinrichsen, E. L. *Polym Engineer Sci* 1996, 36, 410-424.
18. Utracki, L. A.; Backerdjian, Z.; Kamal, M. R. *J Appl Polym Sci* 1975, 19, 481-501.
19. Wilson, N. R.; Bentley, M. E.; Morgan, B. T. *SPE Journal* 1970, 26, 34-40.
20. Swan, P. L.; Dealy, J. M.; Garcia-Rejon, A.; Derdouri, A. *Polym Eng Sci* 1991, 31, 705-710.
21. Henze, E.; Wu, W. *Polym Engineer Sci* 1973, 13, 153-159.
22. Yang, B.; Lee, L. J. *Polym Engineer Sci* 1987, 27, 1079-1094.
23. Huneault, M. A.; Lafleur, P. G.; Carreau, P. J. *Polym Engineer Sci* 1990, 30, 1544-1550.
24. Agarwal, P. K.; Bagley, E. B.; Hill, C. T. *Polym Engineer Sci* 1978, 18, 282-287.
25. Pecora, L.; DiRaddo, R. W. An experimental study on the effect of die geometry on swell and sag in the parison extrusion stage, CNRC, Canada, 1993.
26. Orbey, N.; Dealy, J. M. *Polym Engineer Sci* 1984, 24, 511-518.
27. Ghijssels, A.; De Clippeleir, J. *Internat Polym Processing IX* 1994, 3, 252-257.
28. Benoît, H.; Berlot, R. Initiation à la chimie et à la physico-chimie macromoléculaires. Propriétés phy-

- siques des polymères. Mise en oeuvre, Groupe français d'études et d'applications des polymères, 1970.
29. Huang, D.; White, J. L. *Polym Engineer Sci* 1980, 20, 182–189.
  30. Hinrichsen, E. L.; Eggen, S. Abstracts of the Polymer Processing Society Tenth Annual Meeting Akron USA, April 5–8, 1994, p. 14–15.
  31. The TPU Comittee, Comparative property testing of polyether-based thermoplastic for use in wet food contact applications, *Polyurethane* 1995, September 26–29.
  32. Gogolewski, S. Molecular stability of biomedical polyurethanes, Genève, Suisse, 1989, p. 14.1–14.22.
  33. Song, M. S.; Shen, Y. D.; Chen, H.; Hu, C. J. *J Elastomers Plastics* 1995, 27, 368–383.
  34. Kutty, S. K. N.; De, P. P.; Nando, G. B. *Plastics, Rubber and Composites Processing and Applications* 1991, 15, 23–29.
  35. Shonaike, G. O.; Sugimoto, R.; Matsuo, T. *SPE Journal* 1996, 171–190.
  36. Ozaki, H.; Hayashi, S. ANTEC '94, 2661–2665.
  37. Hewitt, L. E. Moldability and thermal behavior of estane thermoplastic polyurethanes; BFGoodrich Company-Chemical Group, Avon Lake Technical Center, Ohio 44012, USA, 1997.
  38. Dufrancatel-Veiller, L. Etude du gonflement des polymères et de son incidence sur la précision dimensionnelle des profilés extrudés. Application aux polyuréthanes thermoplastiques; Thèse de Doctorat; Université des Sciences et Technologies de Lille-Ecole des Mines de Douai; France; 1998.
  39. Walker, L. M.; Wagner, N. J. The microstructure of shearing liquid crystal polymers; In *Theoretical and Applied Rheology*; Moldenaers, P.; Keunings, R., Eds.; Proc. Xith Int. Congr. on Rheology, Brussels, Belgium, August 17–21, 1992.
  40. Amsden, C. S. *Caoutchoucs et Plastiques* 1985, 12, 654, 101–105.
  41. Wang, C. S.; Kenney, D. J. *J Elastomers Plastics* 1995, 27, 182–199.
  42. Gibson, A. G. Converging dies; In *Rheological measurement (Chap. 3)*; Collyer, A. A.; Clegg, D. W., Eds.; Elsevier Applied Science, London, 1988.