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WORKING PARTY ON STRUCTURE AND PROPERTIES
OF COMMERCIAL POLYMERS*

A Collaborative Study of the RHEOLOGICAL PROPERTIES AND UNSTABLE MELT SPINNING CHARACTERISTICS OF LINEAR AND BRANCHED POLYETHYLENE TEREPHTHALATES

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A collaborative study of the rheological properties and unstable melt spinning characteristics of linear and branched polyethylene terephthalates

Abstract - A comparative study by several industrial and academic laboratories of the rheological properties and melt spinning behavior of a series of molecularly characterized linear and a branched polyethylene terephthalate is reported. Steady shear viscosity, normal stresses, dynamic sinusoidal behavior, and capillary entrance elongational flow behavior are reported. The branched melt has a lower shear and dynamic viscosity (at the same molecular weight), a higher steady state compliance and principal normal stress difference (at the same shear stress). The elongational viscosity of the branched sample seems to be increasing with tensile stress. The branched sample exhibits much greater spinline stability than the linear polyester. The results of different laboratories are compared.

INTRODUCTION, PARTICIPATING LABORATORIES

Instabilities are the plague of the film and fiber fabrication. Their occurrence is generally quite sensitive to detailed process conditions and molecular structure. The most extensive investigations have related to instabilities in melt spinning of fibers (ref. 1-12) and film coasting (ref. 3,13,14) which are called "draw resonance." At low drawdown ratios, there is generally a stable spinline exhibiting only minor diameter fluctuations due to system noise. At a critical draw ratio (take-up velocity/extrusion velocity) a periodically varying disturbance is observed and fibers with high amplitude periodic diameter fluctuation are obtained.

There have been relatively few basic studies of the influence of polymer structure on the draw resonance instability. Four studies relating to polypropylene have appeared (ref. 10-12, 14). A generation ago Bergonzoni and DiCresce (ref. 14) in one of the basic studies of draw resonance found that stability was decreased by increasing molecular weight. In more recent investigations, Ghijsels and Ente (ref. 10) found a molecular weight distribution as well as a molecular weight effect with narrowing of the molecular weight distribution being stabilizing. Minoshima et al (ref. 11) in a simultaneous independent study found a distribution breadth effect of the same type observed by Shijsels and Ente (ref. 10). Yamane and White (ref. 12) have considered the thermal viscracking of polypropylene and noted that viscracked samples which have lower molecular weights and narrower molecular weight distributions exhibit greater spinline stability. There are no studies of the influence of long chain branching on stability, though it has been noted that long chain branched polyethylenes generally show greater spinline stability than linear polyethylenes (ref. 7). While there have been some studies of draw resonance of polyethylene terephthalates (ref. 3,5) none have been concerned with the influence of polymer structure.

In the present manuscript we describe a study of the rheological and melt spinning characteristics of a series of well characterized linear and branched polyethylene terephthalates (PET). Special attention is given to the onset of instabilites and to their variation with polymer structure.

This report describes the contributions of several laboratories and investigators. The names of the laboratories will be abbreviated in the text. These are summarized below:

BASF AG Ludwigshafen, West Germany (BASF) H.M. Laun

Celanese Research Company, Summit, New Jersy U.S.A. (CEL) K.F. Wissbrun

E.I. Dupont de Nemours Wilmington, Delaware U.S.A. (Dupont) G. Vassilatos

Eidgenossische Technische Hochschule, Institut fur Polymere Zurich, Switzerland (ETH) J. Meissner

ICI Plastics Division, Welwyn Garden City, England (ICI) D. Groves

Rheometrics, Piscataway, New Jersey, U.S.A. and Frankfurt am Main West Germany (RHEO) A. Franck/J. Starita

Rhone Poulenc, Paris, France (RP) A.J. de Vries/D. Millaud

University of Stuttgart, Institut fur Kunststofftechnologie, Stuttgart, West Germany (IKT) H.G. Fritz

University of Tennessee, Polymer Engineering, Knoxville, Tennessee, U.S.A. (UT) J.L. White/H. Yamane

The latter address (UT) is that of the Principal Author and H. Yamane during the course of the experimental studies reported in this paper. Both are at the time of this writing at The University of Akron.

MATERIALS

Four samples were supplied by Rhone Poulenc. These samples are designed A, B, C and D. Sample B is distinguished from the other samples by the incorporation of long chain branching.

The samples were characterized by RP, using several different procedures. The results of the measurements are summarized in Table 1.

TABLE 1. Characterization of polyester samples (RP).

METHOD		A	B	C	D
	M_n	19,000	15,000	20,000	21,000
	M_w	51,000	61,000	41,000	57,000
	M_z	82,000	152,000	62,000	89,000
	M_w/M_n	2.68	4.07	2.5	2.71
	M_z/M_w	1.61	2.49	1.51	1.56
Light Scattering	M_w	44,000	64,000	---	---
End Group	M_n	23,000	18,500	18,500	28,000
Specific Viscosity	M_w	43,000	---	44,000	60,000

GPC

The four samples were analyzed by GPC using N-methyl pyrollidone at 190°C on three Shodex ABO columns. Under these conditions no degradation appears to occur. Molecular concentration is measured by a Shodex refractometer at room temperature. No precipitation was observed. The column was calibrated with anionic polystyrenes with molecular weights between 22,000 and 2,000,000. The correction factor between PET and polystyrene has been found to be about 1.

End group analysis

The number average molecular weight was estimated from the concentration of end groups of the PET. Carboxylic end groups were determined by infra red spectroscopy and methylester end groups were determined by gas chromatography by the Ziesel method.

Light scattering

Weight average molecular weights were determined on a FICA 50 goniometer at 25°C. Dichloracetic acid was used as a solvent.

Specific viscosity

The weight average molecular weight was estimated from specfic viscosity. Measurements were made on one weight percent solutions in a 50/50 phenol/orthochlorophenol solvent at 25°C. An empirical equation

$$M_w = 5.69 \times 10^4 \ \eta_{sp}^{1.18} \qquad (1)$$

was used to determine the weight average molecular weight. The weight average molecular weights seem to vary as

$$B > D > A > C$$

The molecular weight distributions as determined by M_w/M_n order as

$$B > D \sim A > C$$

but M_w/M_n for B is only about 4.0 and for A and D is about 2.7. It is 2.0 for C.

Drying conditions

Varying drying conditions in vacuum ovens were used by the different research teams. The humidity contents of four PET samples as delivered and dried were measured by BASF using a Mitsubishi moisture meter CA-02 at 200°C. These results are summarized in Table 2 and 3, respectively.

TABLE 2. Drying conditions of polyester samples.

Laboratory	Temperature	Time
BASF	160°C	8.hours
Cel	150°C	16 hours
DuPont	150°C	16 hours
ICI	80°C	100 hours
	80°C	4 months
	160°C	6 hours
IKT	25°C 180°C	5 hours
	180°C	6 hours
RP	160°C	4 hours
Rheo	130°C	24 hours
UT	130°C	12 hours

TABLE 3. Humidity of polyester samples (BASF)

Sample	Humidity (%) as delivered	dried
A	0.35	0.01
B	0.35	0.01
C	0.15	0.034
D	0.11	0.033

RHEOLOGICAL PROPERTIES

Experimental

A number of different methods were applied to obtain rheological responses of the polymer melts.

Cone-plate measurements of steady shear viscosity were carried out by Rheo, RP and UT. RP and UT's measurements were at 285°C. Rheo made studies at 270°, 280° and 290°C. RP also made studies at 240°C (after 10 minutes at 285°C).

Parallel disc measurements of the steady shear viscosity were made by Cel at 285°C.

Capillary measurements of steady shear viscoisty, were reported by BASF, Cel, ETH, ICI, IKT, RP and UT. All teams reported studies at 285°C. ICI also presented results at 270°C.

Sinusoidal oscillation cone-plate measurements of dynamic storage modulus G' and dynamic viscosity η' were carried out by Rheo at 270°, 280° and 290°C. BASF measured the dynamic rheological properties at 285°C using a bicone geometry in a Weissenberg rheogoniometer, Cel measured η' and η^* in the parallel disc geometry.

Creep recovery measurements were made by Rheo in a Rheometrics Stress Rheometer at 285°C.

Principal normal stress difference N_1 were measured by Rheo, RP and UT using a Rheometrics Mechanical Spectrometer in a cone-plate mode. Cel measured N_1-N_2 in a parallel disc mode in a Rheometrics Mechanical Spectrometer.

ICI determined elongational viscosities from capillary die entrance pressure drop measurements.

The rheological background of cone plate η and N_1 measurements, capillary η and sinusoidal oscillation η' and G' are described in the monograph by Walters (ref. 15). The calculation of the capillary die entrance elongational viscosity measurements is based on the theory of Cogswell (ref. 16).

Results

Shear viscosities η as a function of shear rate for resins B,C, and D at 285°C are shown in Fig. 1. Generally all of the resins are Newtonian at low shear rates. At higher shear rates, the viscosity decreases. The data generally order with D the highest viscosity, B the lowest and C intermediate. The shear viscosity of melts A and B at 285°C are shown in Fig. 2.

The behavior of C is very close to melt A, i.e.,

$$D > A \sim C > B$$

There is some discrepancy of data from different laboratories in this plot. For system D, the Cel, ICI and UT data are the highest and the BASF data are the lowest. The ETH, IKT and RF data are intermediate. The data from the different laboratories would range ±30% about an intermediate curve. For system C, the Cel data is the highest and BASF the lowest. The scatter is less here with the band about an intermediate curve being ±12%. For system B, Cel and RP tend to have the highest viscosity measurements and BASF the lowest. The scatter is similar to melt C.

There is also scatter in data in individual laboratories between rotational cone-plane and capillary instruement measurements. This was especially noted by BASF.

The principal normal stress difference N_1 is plotted as a function of shear stress σ_{12} for resins A, B, C and D. in Fig. 3. The RP and UT data is quite similar. These generally show that the B data are the highest followed by a grouping of A, C and D. The D results are the highest of the group and A and C are similar in magnitude, i.e.,

$$B > D > A \sim C$$

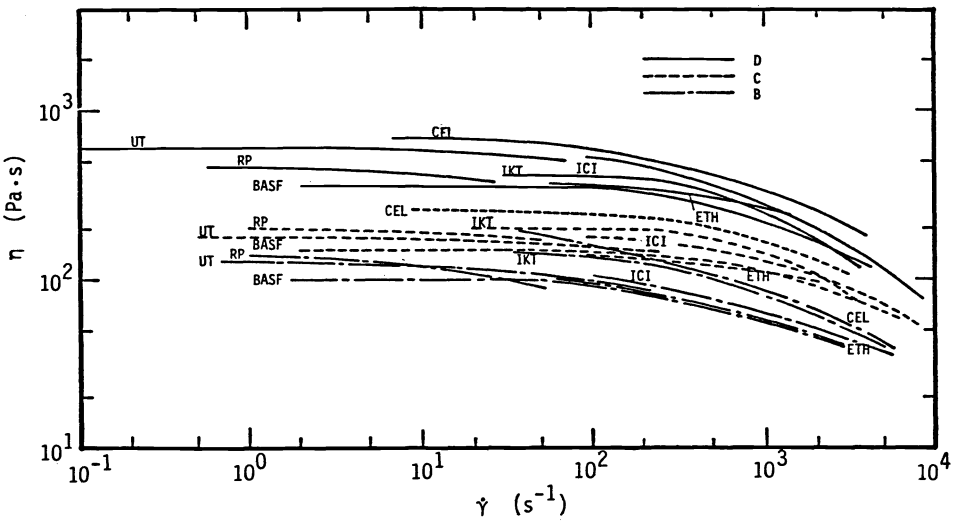


Fig. 1. Shear viscosities of polyesters B, C, and D versus shear rate at 285°C.

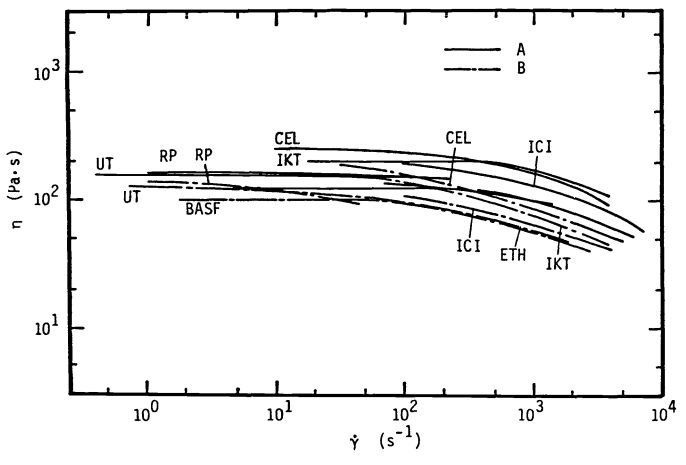


Fig. 2. Shear viscosities of polyesters A and B versus shear at 285°C.

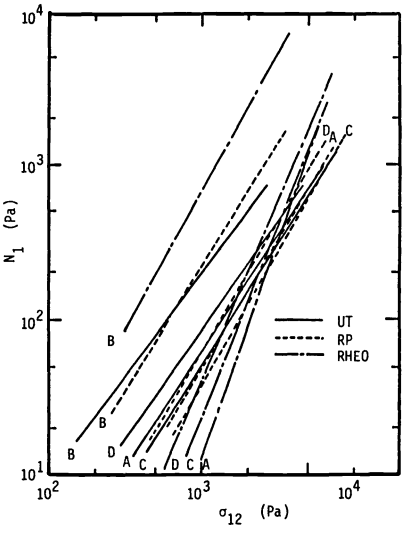


Fig. 3. Principal normal stress differences as a function of shear stress (Rheo, RP, UT) at 285°C.

Normal stress differences N_1-N_2 determined by Cel are plotted as a function of shear stress σ_{12} in Fig. 4. Again B is the highest and A and C the lowest.

Low frequency dynamic viscosities $\eta'(\omega)$ were obtained by BASF at 285°C and by Rheo at 270°C, 280°C and 290°C. These are plotted in Fig. 5. These order

$$D > C > A > B$$

which is similar to the shear viscosity.

Storage modulus $G'(\omega)$ is plotted as a function of frequency in Fig. 6.

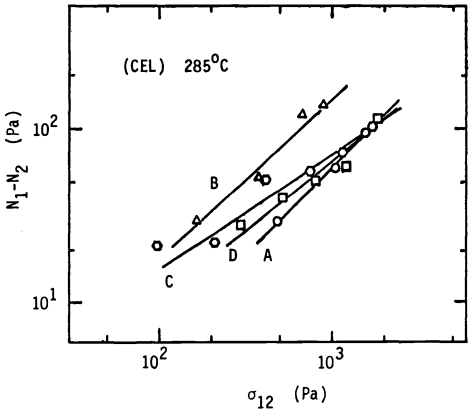


Fig. 4. Normal stress differences N_1-N_2 as a function of shear stress (Cel) at 285°C.

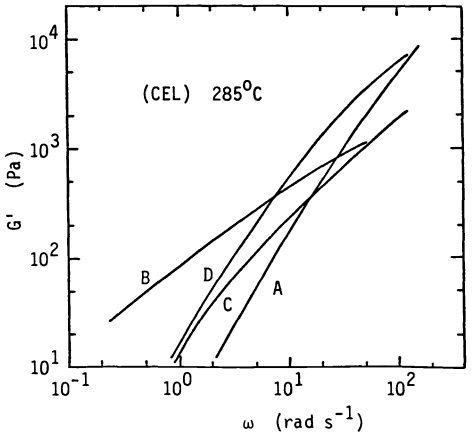
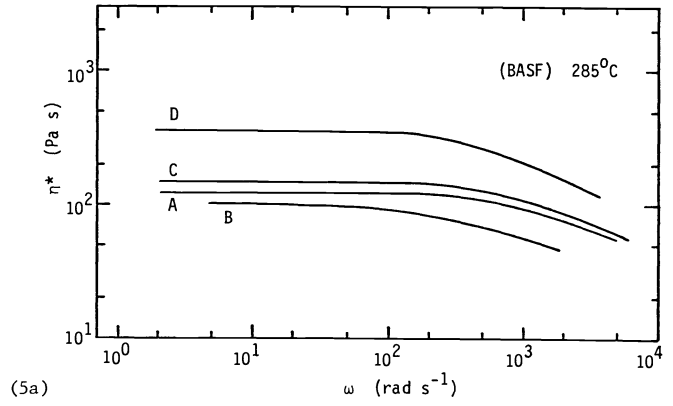
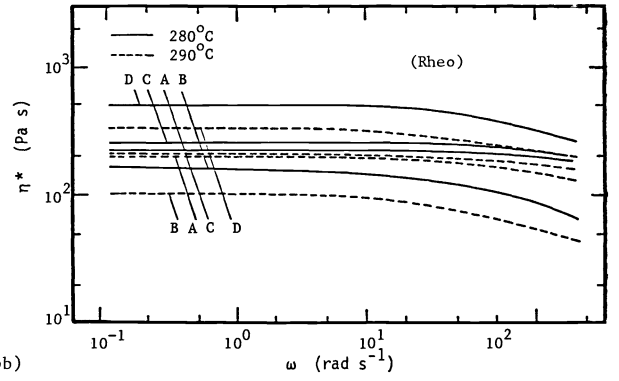


Fig. 6. Storage modulus G' (ω) as a function of frequency (ω) (Cel) at 285°C.



(5a)



(5b)

Fig. 5. Complex viscosities $\eta^*(\omega)$ as a function of frequency
(a) (BASF at 285°C)
(b) (Rheo at 280°C and 290°C)

DISCUSSION

Shear and dynamic viscosity

Experimentally it has been found for many systems that the dynamic viscosity $\eta(\dot{\gamma})$ through the empirical Cox-Merz relation (ref. 17)

$$\eta(\dot{\gamma}) = \eta^*(\omega)$$

where

$$\eta^* = \sqrt{(\eta')^2 + (G'/\omega)^2}$$

At zero frequency η^* and η' equal $\eta(0)$ or η_o. We have tested this in Fig. 7 using Cel's data.

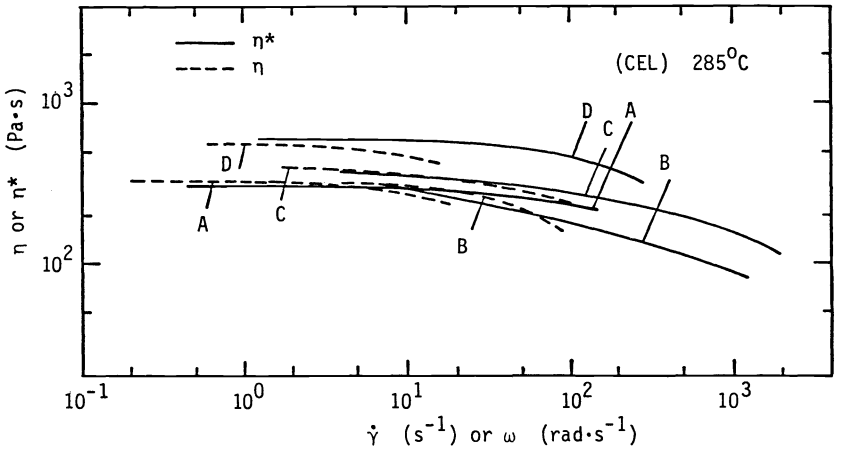


Fig. 7. Comparison of $\eta^*(\omega)$ and $\eta(\dot{\gamma})$ based on the data of Cel at 285°C.

In Fig. 8 we plot η_o versus M_w using UT's data. The different ordering of the molecular weight and viscosity for sample B, whose viscosity is much lower, is striking. It is however to be expected based on investigations by different laboratories involving branched polycondensates (ref. 18), polybutadienes (ref. 19) and polystyrenes (ref. 20). Long chain branching lowers viscosity at constant molecular weight in this range of chain lengths.

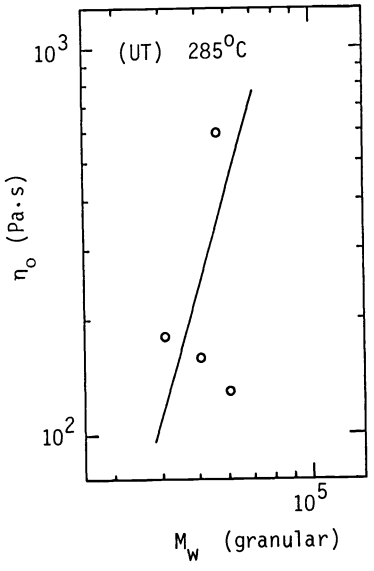


Fig. 8. Zero shear viscosities as a function of molecular weight (UT).

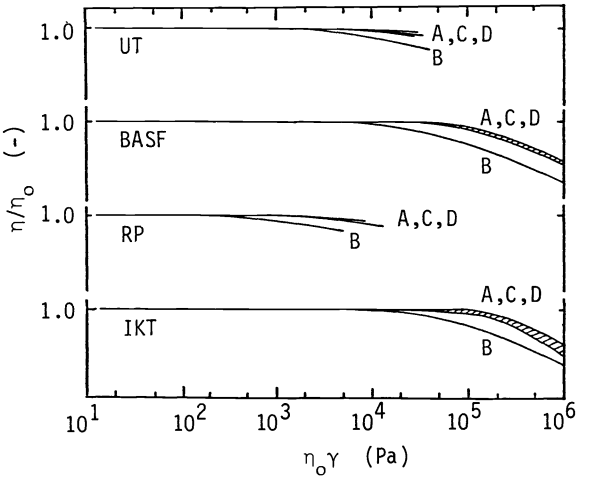


Fig. 9. η/η_o as a function of $\eta_o\dot{\gamma}$ (BASF, IKT, RP, UT).

BASF, RP, IKT and UT determined plots of reduced viscosity η/η_o as a function for $\eta_o\gamma$. Plots of this type are known for Vinogradov and Malkin (ref. 21). They have been found to be molecular weight distribution sensitive (ref. 22), falling off more rapidly with broad distribution samples. It was found that η/η_o falls off more rapidly for the B polymer (see Fig. 9).

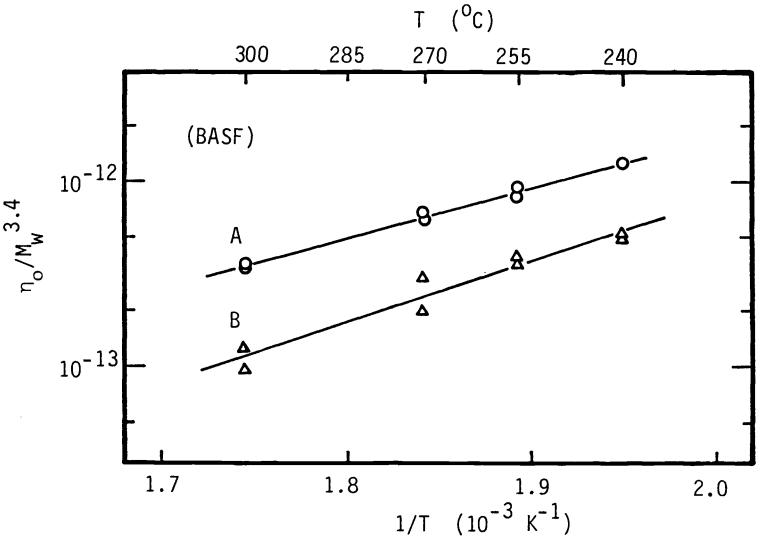


Fig. 10. $\eta_o/Mw^{3.4}$ as a function of 1/T (BASF).

The activation energy of viscous flow defined by

$$\eta_o = Ae^{E/RT} \tag{3}$$

is of order 50.6 KJ/mole for the linear samples and 63 KJ/mole for the branched sample. The higher value for the branched sample is perhaps not unexpected as it is well know that low density (long chain branched) polyethylenes have higher activation energies of viscous flow than linear polyethylenes.

Normal stresses and steady state compliance

The ordering of the normal stresses at constant shear stress is also striking. Plots of this type (ref. 22,23) reflect the steady state compliance J_e.

$$J_e = \lim_{\sigma_{12}\to 0} \frac{\gamma}{\sigma_{12}} \tag{4}$$

through the relation (ref. 24)

$$\lim_{\sigma_{12}\to 0} N_1 = 2 J_e \sigma_{12}^2$$

Our normal stress data suggest that the long chain branched B sample has a much larger value of J_e than A, C, or D which have similar values of J_e. Values of J_e computed by BASF and

TABLE 4. Steady state compliance and mean relaxation times of polyesters (Rheo)

Material	Sinusoidal Oscillation (280°C)	Creep Recovery (285°C)	η_o(pascal-sec) (280°C)x10^{-2}	$\bar{\tau}$ (sec)(280°)
A	1.9	---	2.2	0.0042
B	8.9	7.5	1.6	0.0142
C	1.5	2.5	2.6	0.0039
D	2.7	---	5.0	0.0135

from dynamic data and creep recovery are in accord with this ordering. The results are summarized in Table 4. Generally the value of J_e for B is much larger than for samples A, C and D. It is lowest for samples A and C.

Masuda et al (ref. 20) have determined J_e for long chain branched polystyrenes and found them larger than for linear polymers of similar molecular weight.

We may define a characteristic relaxation time $\bar{\tau}$ by (ref. 24).

$$\bar{\tau} = J_e \eta_o \tag{6}$$

We calculated $\bar{\tau}$ from Rheo's J_e and η_o data at 280°C. The results are summarized in Table 4. The values of $\bar{\tau}$ are the largest for samples B and D which are about the same, and lowest for A and C whose magnitudes are roughly 1/3 of B and D.

Discrepances in data

The discrepancy in rheological data from the different laboratories would appear to be due in some part to variations in drying conditions. The ester group concentration and molecular weight of molten PET will adjust itself to equilibriate with the moisture content.

The thermal stability of different PET sample has been investigated by BASF by measuring the viscosity. Comparing the change of zero shear viscosity at 285°C, sample D appears to be the most thermally unstable and the other three PET (A, B and C) are rather stable.

Comparison of the thermal stability of linear PET (A) and branched PET (B) has been further studies by BASF. These PET's were kept at 285°C for periods up to 15 minutes. The specific viscosities and the molecular weight of these samples were measured by RP. In the first 10 minutes, the molecular weight of these samples decreased about 12% for PET A and 30% for PET B. From 10 minutes to 15 minutes both A and B stayed fairly stable.

ELONGATIONAL FLOW

Elongational viscosity has been determined by ICI using Cogswell's entrance flow technique. It is plotted as a function of tensile stress σ_{11} for the four PET samples in Fig. 11. Samples A, C and D show similar elongational flow behavior decreasing with increasing with σ_{11}. However sample B exhibits different behavior in elongational flow with elongational viscosity increasing with σ_{11}.

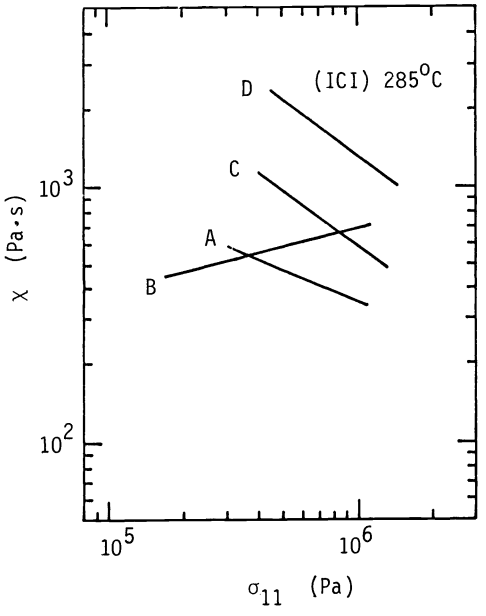


Fig. 11. Elongational viscosities χ as a function of normal stress σ_{11} (ICI).

The differences observed seem remarkable when it is considered that the stretch rate hardening sample B exhibits more shear thinning than A, C or D.

MELT SPINNING INSTABILITIES

Experimental

Investigations of the onset of large magnitude disturbances in melt spinning were carried out by Dupont, RP and UT. The studies involved different types of apparatus.

RP and UT carried out melt spinning with similar ram extruders (Instron capillary rheometer). In each case capillaries of diameter of order 0.6 mm were used. The UT die had and L/D ratio of 50. An air gap of 2 to 4.5 cm was placed between the die exit and a water quench bath. RP used 2.1, 2.5, 3.3 and 4.5 cm length threadline and UT's were 3 or 4 cm. UT also introduced in some experiments an isothermal chamber into the region between the die exit and the bath. In this case the air gap was 2.5 cm.

Dupont made melt spinning studies using a twin screw extruder with a capillary die of diameter 1.6 mm and L/D ratio of 6. The extrudate traveled through an air gap of length L before entering a water bath. Values of L of 3.0, 7.0, 10.2 and 14.6 cm were used.

RP also made studies using a slit die and cast film. Two distances were used between the die exit and the quench bath. These were 1.1 cm and 2.1 cm.

A range of methods were used to detect the onset of the instability. UT used the readings on a Rothschild Tensiometer plus microscopic inspections of filaments. RP's melt spinning experiments detected spinline diameter directly using an optical instrument. Dupont used a mechanical instrument similar to UT.

Results

Generally diameter fluctuations are observed under all conditions at low drawdown ratios. These are of small amplitude and incoherent. We observe that at a critical drawdown ratio, the amplitude suddenly grows and the oscillations become periodic. This is shown in Fig. 12.

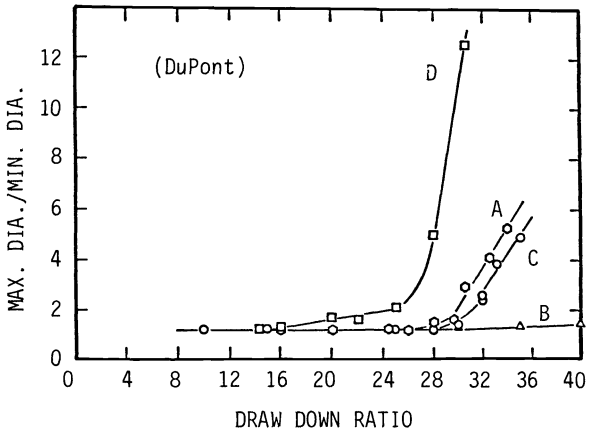


Fig. 12. Diameter fluctuation magnitude as a function of draw ratio (Dupont).

The critical drawdown ratios V_L/V_0 obtained by the different groups are summarized in Table 5. Data for isothermal and non-isothermal runs are shown. Generaly agreement in the results for different laboratories seems clear. First the non-isothermal runs for each laboratory are more stable than the isothermal runs. Secondly, resin B, the branched polymer is far more stable than resins A, C and D. Indeed in the non-isothermal runs, it was not possible to induce draw resonance in resin B. The situation with resins A, C and D is not clear. Dupont finds resin D more unstable than A or C. RP and UT find it more stable. Most likely they are rather similar and we are observing experimental scatter.

The influence of gpa distance between the face of the die and the surface of the die was investigated for sample A. It was found that increasing this distance stabilized the spinline. (Table 6)

Draw ratios to break were reported by Dupont. The non-isothermal draw ratios V_L/V_0 at air gaps of 14.6 cm were over 800 and similar in magnitude. For an air gap of 3 cm, the value for B dropped to 98. The isothermal values for an L of 14.6 cm were 219 for B, 193 for C and 98 for D.

TABLE 5. Critical draw ratios for various polyesters obtained by different laboratories at air gap.

Polymer	Dupont		RP		UT	
	Non-Isothermal L_w = 14.6cm	Isothermal L_w = 14.6cm	Non-Isothermal Fiber L=2.5cm	Film	Non-Isothermal L_w= 3.4cm	Isothermal L_w = 2.5cm
A	80	29.6	18.7	20	>80	19.1
B	200	40	breaks at 55	40	>80	48.9
C	90	30.0	19.2	20	>80	22.9
D	67	27.2	50	--	>80	25.1

TABLE 6. Influence of air gap length on non-isothermal spinline stability of polyester A.

	Air gap length (cm)	Critical draw down ratio
Dupont	3.0	19
	7.0	24
	10.2	26
	14.6	80
RP	2.1	18.6
	2.5	18.65
	3.3	18.9
	4.5	28

Discussion

The general experimental results of this report are very similar to those reported previously on various melts and are consistent with the extensive theoretical literature on this topic (ref. 13, 25-32). The isothermal melt of a Newtonian fluid has a critical drawdown of 20.2 (ref. 13, 25) which is close to the values of Table 5 for isothermal spinning. Non-isothermal spinlines are more stable (ref. 25, 30). Increasing spinpath length prior to the quench bath gives greater opportunity for the spinline to cool and thus stabilize. RP notes that increasing length increases the Stanton number, defined by Shah and Pearson as (ref. 26)

$$N_{St} = K\frac{V_o^{1/6}}{C_P Q^{1/2}} L \tag{7}$$

where K is a constant related to the relationship between local Nusselt number (heat transfer coefficient) and spinline velocity, L is spinline length, V_o is linear fiber velocity at the spinneret, Q is flow rate, C_p heat capacity. Shah and Pearson's Fig. 3 defines the increase in stability for a Newtonian fluid as a function of Stanton number.

The enhanced stability of the B polyester sample would seem most certainly associated with the greater melt elasticity indicated by the normal stresses in Figs. 3 and 4. This at first seems in qualitative agreement with the predictions of Zeichner (ref. 27) and Fisher and Denn (ref. 29). The stabilization according to these authors is through the Weissenberg number $\tau V_o/L$ with shear rate thinning playing a destabilizing role. However $\bar{\tau}$ as defined by Eq. (6) is about the same for samples B and D and larger than A and C by factors of three. η/η_o falls off more rapidly with $\eta_o\dot{\gamma}$ for samples B than A, C or D. Unlike the predictions of Fisher and Denn or the observations of Minoshima et al (ref. 11) and Yamane and White (ref.12) on linear polyolefins the draw resonance instability is not more serious with B than D but rather the reverse. Levels of fall-off of η/η_o are though small as compared to polyolefins. The level of stability enhancement for sample B is in any case much greater than would be predicted.

A different view develops if one contrasts ICI's elongational flow results with the instability data. White and coworkers (ref. 7,11,12) have long argued that the occurrence of draw resonance is closely associated with experimental simple elongational flow response and that stretch rate hardening is stabilizing. Sample B exhibits a strain rate hardening here as it apparently does in the spinline when subjected to disturbances. All of the above

suggests long chain branching plays additional roles in elongational flow deformation rate hardening beyond that usually noted in constitutive equations.

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