Rheograms for engineering thermoplastics from melt flow index *)

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Abstract: A method proposed earlier has been extended to estimate complete flow curves or rheograms of engineering plastics. Master curves that are independent of the grade and temperature have been generated and presented for acrylics, polyacetal, nylons, polyethylene terephthalate, polycarbonate and polysulfone. The influence of the various molecular parameters on the viscosity behaviour of polymer melts have been explained rationally. More specifically, the effects of chain branching and of chain rigidity on the master curve of a resin type have been elucidated with reference to polyacetal and polysulfone, respectively. The method presented here can be used effectively by processors of engineering plastics.

Key words: Rheogram, engineering thermoplastics, melt flow index

Notation

F	force due to the weight of piston and load (dynes)
l	length of nozzle (cm)
L	load (kg)
M_e	molecular weight between entanglement points along a polymer molecule
MFI	melt flow index (gm/10 min)
n	slope of the shear stress versus shear rate curve on log-log scale
Q	flow rate (cm^3)
R_N	radius of nozzle (cm)
R_P	radius of piston (cm)
T_1	temperature at condition 1 (K)
T_2	temperature at condition 2 (K)
T_g	glass transition temperature given in table 2 (K)
T_s	standard reference temperature ($= T_g + 50$ K)
$\dot{\gamma}$	shear rate (sec^{-1})
η	apparent viscosity (poise)
ρ	density of the polymer (gm/cm^3)
τ	shear stress (dynes/cm^2)

1. Introduction

Engineering thermoplastics are high performance materials that are increasingly replacing conventional materials such as metals, glass and wood in a number of applications, where a combination of high ratings for mechanical, thermal, electrical and chemical properties is desired. The applications are in various automotive, structural, industrial markets. Typical applications include electrical switches, gears, bearings, cams, auto ignition etc. The following polymers are generally categorized as engineering materials: acrylics, polyacetals, nylons, thermoplastic polyesters, polycarbonate, polysulfone, polyphenylene sulfide, polyphenylene oxide/polystyrene blends, polyimides, polyamide-imides, polyethers, fluoropolymers etc.

There are a number of advantages offered by polymers over the conventional materials. These include high strength-to-weight ratio, corrosion resistance, versatility of part design and ease of fabrication. In a number of large volume applications such as automotive parts, the cost effectiveness of a material is governed not merely by the material cost but also by the improved processability and design flexibility offered by the material. Use of polymers allows production of parts with complex shapes in a single molding operation reducing the number of parts in design of a product and eliminating several assembly steps compared to a product made of metal components. In saving of installation cost, there are numerous examples of snap fits, molded-in hinges and self-tapping screws. A specific example is the use of polycarbonate for a railway signal light made of nine molded components, replacing an assembly of forty metal and glass parts, besides reducing the weight from 7 kg to 1 kg [1]. Thus the processibility of engineering thermoplastics is an important consideration in materials engineering.

A variety of processing techniques are employed in converting the engineering plastics into finished products. Besides injection molding, extrusion and blow molding are the other two major processes. Acrylic and polycarbonate sheets replacing glass windows in building and buses are produced by extrusion. The bottles of polyethylene terephthalate produced by blow molding are increasingly being used as beverage containers. In all these processing techniques, the polymer melt is subjected to shearing flows over a wide range of temperature and shear rates. A knowledge of the complete flow curve or rheogram depicting the variation of melt viscosity with shear rate at various temperatures is therefore essential for an assessment of the material processibility, process design/optimization and trouble-shooting.

2. Background

The data on melt flow characteristics are acquired by the use of rheometers such as the Weissenberg Rheogoniometer, Instron Capillary Rheometer, Rheometrics Mechanical Spectrometer, etc. However, these sophisticated instruments are quite expensive and require trained operators. Generation of the necessary flow data could therefore be beyond the financial and technical means available to most plastics processors. Moreover, since the polymer melt viscosity depends both on the temperature and shear rate, a family of curves needs to be generated for each of the variety of grades available for every engineering thermoplastic. A procedure which could unify a number of these variables and yet provide an adequate estimate of the flow behaviour during processing, is undoubtedly desirable. Shenoy et al. [2] have successfully demonstrated a method to estimate the rheograms of polyolefins and styrenics at temperatures relevant to the processing conditions with the use of master curves, knowing the melt flow index and glass transition temperature of the resins.

In the present paper, the unifying approach [2] is extended to a number of engineering thermoplastics, namely, acrylics, polyacetals, nylons, polyethylene terephthalate, polycarbonate and polysulfones. Master curves have been generated for these plastics which can be used by the processor to estimate the rheograms for a resin, once the MFI and glass transition temperature of the resin are known. The MFI value is either supplied by the resin manufacturer or can be readily measured on a relatively inexpensive melt flow indexer.

3. Data collection

Data on the viscosity versus shear rate curves at different temperatures were compiled from the literature for various grades of acrylics, acetals, nylons, polyethylene terephthalate, polycarbonate and polysulfone. A summary of the polymers analysed in the present study is given in table 1. These data were then used to generate master curves independent of the polymer grade and temperature of measurement for estimating the rheograms of the engineering thermoplastics investigated.

4. Data analysis

The melt flow index (MFI) is defined as the weight of polymer in grams extruded in ten minutes through a capillary of specific diameter and length by pressure applied through dead weight as per ASTM 1238-73 [2]. The specific test conditions for the most common engineering thermoplastics are given in Appendix I.

The apparatus for determining MFI is basically an extrusion rheometer. The MFI therefore represents a point at specific shear rate and shear stress values on the viscosity versus shear rate curve. The expressions for shear stress τ and shear rate $\dot{\gamma}$ in the melt flow apparatus are given by the well known conventional forms as follows:

$$\tau = \frac{R_N F}{2 \pi R_p^2 l}, \tag{1}$$

$$\dot{\gamma} = \frac{4Q}{\pi R_N^3} \tag{2}$$

where piston radius $R_p = 0.4737$ cm, nozzle radius $R_N = 0.105$ cm, nozzle length $l = 0.8$ cm, force $F = $ test load L(kg) $\times 9.807 \times 10^5$ dynes, flow rate $Q = \dfrac{\text{MFI}}{600 \rho}$ cm^3/sec.

Since the geometry of a melt flow indexer is fixed as given above, eqs. (1) and (2) reduce to give

$$\tau = 9.13 \times 10^4 L, \tag{3}$$

$$\dot{\gamma} = 1.83 \frac{\text{MFI}}{\rho}. \tag{4}$$

As the MFI value is generated at a fixed temperature and a fixed load, a single point on the shear stress

Table 1. Polymers analysed in the present study

Polymers	Grade	M_w	M_n	MFI (Temperature, °C/ Load condition, kg)	Temperature at which data were obtained, °C	Number of data points (Shear rate range, sec^{-1})	Source
1	2	3	4	5	6	7	8
Acrylics	Lucite 40	–	–	1.12[c] (220/3.8)	220	4(1 – 1000)	Ref. [6]
	– do –	–	–	4.9[c] (240/3.8)	240	4(1 – 1000)	– do –
	– do –	–	–	19.6[c] (260/3.8)	260	4(1 – 1000)	– do –
	Lucite 129	–	–	0.9[c] (200/3.8)	200	5(1 – 10000)	Ref. [7]
	– do –	–	–	27[c] (250/3.8)	250	5(1 – 10000)	– do –
	Lucite 130	–	–	0.002[c] (150/3.8)	150	3(1 – 100)	– do –
	– do –	–	–	1.28[c] (200/3.8)	200	4(10 – 10000)	– do –
	– do –	–	–	38[c] (250/3.8)	250	4(100 – 10000)	– do –
	Lucite 140	–	–	5.0[b] (230/3.8)	230	5(1 – 10000)	– do –
	– do –	–	–	25.2[a] (260/3.8)	260	5(1 – 10000)	– do –
	– do –	–	–	58.8[a] (280/3.8)	280	4(1 – 10000)	– do –
	Plexiglas V-100	–	–	0.03[a] (170/3.8)	170	3(3 – 30)	– do –
	– do –	–	–	0.3[a] (190/3.8)	190	4(3 – 60)	– do –
	– do –	–	–	1.8[a] (210/3.8)	210	4(3 – 60)	– do –
	– do –	–	–	7.9[b] (230/3.8)	230	4(3 – 60)	– do –
	Plexiglas VM 100	–	–	0.003[c] (150/3.8)	150	4(3 – 60)	Ref. [7]
	– do –	–	–	0.08[c] (170/3.8)	170	4(3 – 60)	– do –
	– do –	–	–	0.9[c] (190/3.8)	190	4(3 – 60)	– do –
	– do –	–	–	4.7[c] (210/3.8)	210	4(3 – 60)	– do –
	Plexiglas VS 100	–	–	0.007[c] (150/3.8)	150	4(3 – 60)	– do –
	– do –	–	–	0.2[c] (170/3.8)	170	4(3 – 60)	– do –
	– do –	–	–	2.2[c] (190/3.8)	190	4(3 – 60)	– do –
	– do –	–	–	11.2[c] (210/3.8)	210	4(3 – 60)	– do –
	Implex A	–	–	0.007[c] (190/3.8)	190	3(3 – 20)	– do –
	– do –	–	–	0.036[c] (210/3.8)	210	3(3 – 20)	– do –
	– do –	–	–	0.16[c] (230/3.8)	230	3(3 – 20)	– do –
Polyacetals	Type 1	–	–	1.1[b] (180/2.16)	180	4(30 – 3000)	Ref. [8]
	– do –	–	–	5.1[b] (200/2.16)	200	4(30 – 3000)	– do –
	Type 2	–	–	4[b] (180/2.16)	180	4(30 – 3000)	– do –
	SV-249	–	–	2.8[c] (190/2.16)	190	4(6 – 200)	Ref. [9]
	SV-284	–	–	0.5[c] (190/2.16)	190	4(6 – 200)	– do –
	SV-310	–	–	1.1[c] (190/2.16)	190	4(6 – 200)	– do –
Nylons	Plaskon 8201	37000	20000	5.0[c] (231/2.16)	231	4(10 – 4000)	Ref. [7]
	– do –	– do –	– do –	13.7[c] (260/2.16)	260	4(10 – 10000)	– do –
	– do –	– do –	– do –	29.5[c] (288/2.16)	288	4(10 – 10000)	– do –
	Plaskon 8205	75000	37500	1.9[c] (260/2.16)	260	4(10 – 2000)	– do –
	– do –	– do –	– do –	2.5[c] (268/2.16)	268	4(10 – 2000)	– do –
	– do –	– do –	– do –	4.0[c] (288/2.16)	288	4(10 – 2000)	– do –
	Nylon 6	– do –	– do –	8.2[c] (230/2.16)	230	3(1 – 100)	Ref. [10]
	– do –	– do –	– do –	16.7[c] (250/2.16)	250	2(10 – 100)	– do –
	– do –	– do –	– do –	30.6[c] (270/2.16)	270	2(10 – 100)	– do –
	– do –	– do –	19100	33[c] (230/2.16)	230	4(10 – 4000)	Ref. [11]
	Zytel 42NC10	–	34000	4[c] (280/2.16)	280	5(1 – 10000)	Ref. [7]
	– do –	–	– do –	6.3[c] (295/2.16)	295	5(1 – 10000)	– do –
	Zytel 101NC10	39000	18000	49[c] (280/2.16)	280	4(10 – 10000)	– do –
	– do –	– do –	– do –	63[c] (290/2.16)	290	4(10 – 10000)	– do –
	– do –	– do –	– do –	80[c] (300/2.16)	300	4(10 – 10000)	– do –
	Nylon 66	–	–	45[c] (288/2.16)	288	4(10 – 10000)	Ref. [11]
	– do –	–	–	49[c] (291/2.16)	291	4(10 – 10000)	– do –
	Maranyl A-100	–	–	113[c] (280/2.16)	280	5(10 – 10000)	Ref. [12]
	Nylon 610	–	–	235[c] (280/2.16)	280	4(10 – 10000)	Ref. [11]
	Nylon Copolymer	–	–	79[c] (280/2.16)	280	4(10 – 10000)	– do –
PET	Fiber Grade IV = 0.57	–	–	54[c] (275/2.16)	275	9(1 – 5000)	Ref. [13]
	– do –	–	–	64[c] (285/2.16)	285	9(1 – 5000)	– do –

Table 1 (continued)

Polymers	Grade	M_w	M_n	MFI (Temperature, °C/ Load condition, kg)	Temperature at which data were obtained, °C	Number of data points (Shear rate range, sec^{-1})	Source
1	2	3	4	5	6	7	8
	– do –	–	–	86°) (295/2.16)	295	9(1 – 5000)	– do –
	– do –	–	–	103°) (305/2.16)	305	9(1 – 5000)	– do –
	Molding Grade IV = 0.722	–	–	15.7°) (275/2.16)	275	9(1 – 5000)	– do –
	– do –	–	–	19.6°) (285/2.16)	285	9(1 – 5000)	– do –
	– do –	–	–	24.5°) (295/2.16)	295	9(1 – 5000)	– do –
	– do –	–	–	28.5°) (305/2.16)	305	9(1 – 5000)	– do –
	Tire Cord Grade IV = 0.887	–	–	4.7°) (275/2.16)	275	8(8 – 1000)	– do –
	– do –	–	–	5.6°) (285/2.16)	285	8(1 – 1000)	– do –
	– do –	–	–	6.6°) (295/2.16)	295	8(1 – 1000)	– do –
	– do –	–	–	7.4°) (305/2.16)	305	8(1 – 1000)	– do –
	Bottle Grade I IV = 1.044	–	–	1.5°) (275/2.16)	275	8(1 – 1000)	– do –
	– do –	–	–	1.6°) (285/2.16)	285	8(1 – 1000)	– do –
	– do –	–	–	1.77°) (295/2.16)	295	8(1 – 1000)	– do –
	– do –	–	–	1.96 (305/2.16)	305	8(1 – 1000)	– do –
	Bottle Grade II IV = 1.102	–	–	0.88°) (275/2.16)	275	7(1 – 500)	– do –
	– do –	–	–	1.0°) (285/2.16)	285	8(1 – 1000)	– do –
	– do –	–	–	1.1°) (295/2.16)	295	8(1 – 1000)	– do –
	– do –	–	–	1.13°) (305/2.16)	305	8(1 – 1000)	– do –
	Unknown	–	–	4.9°) (275/2.16)	275	4(10 – 5000)	Ref. [14]
PC	Makrolon 2805	293000	12000	6.13°) (290/1.2)	290	3(10 – 1000)	Ref. [10]
	Lexan 121	–	–	7.36°) (288/1.2)	288	3(20 – 2000)	Ref. [16]
	Lexan 141	–	–	1.3°) (250/1.2)	250	4(20 – 300)	Ref. [17]
	– do –	–	–	3.5°) (270/1.2)	270	4(20 – 300)	– do –
	– do –	–	–	6.1°) (290/1.2)	290	4(20 – 300)	– do –
	Lexan 151	–	–	0.86°) (288/1.2)	288	3(20 – 2000)	Ref. [16]
	– do –	–	–	1.0°) (290/1.2)	290	3(20 – 2000)	– do –
PSF	RV = 0.95	–	80000	0.04°) (275/2.16)	275	3(1 – 30)	Ref. [18]
	RV = 0.82	–	61000	0.07°) (275/2.16)	275	3(1 – 30)	– do –
	RV = 0.75	–	52000	0.15°) (275/2.16)	275	3(1 – 30)	– do –
	RV = 0.6	–	35000	0.44°) (275/2.16)	275	3(1 – 30)	– do –
	RV = 0.5	–	25000	2.7°) (275/2.16)	275	3(1 – 30)	– do –
	RV = 0.5	–	25000	9.72°) (375/2.16)	375	3(1 – 30)	– do –
	RV = 0.4	–	17000	9.32°) (275/2.16)	275	3(1 – 30)	– do –
	UDEL P1700	–	–	4.4°) (350/2.16)	350	3(10 – 1000)	Ref. [19]
	UDEL P3500	–	–	1.57°) (350/2.16)	350	3(10 – 1000)	– do –

a) MFI value calculated from eq. (5) knowing the MFI as per b and T_g from table 2.
b) MFI value given by manufacturer under ASTM testing conditions.
c) MFI value read out from τ versus $\dot{\gamma}$ curve using eq. (3) and (4).

versus shear rate curve at that specific temperature can be obtained using eqs. (3) and (4). This fact can then be used to determine the value of MFI from a known shear stress versus shear rate curve for a specific polymeric system when the MFI is not reported. The different test load conditions and the corresponding shear stress values as per eq. (3) are summarized in Appendix I for the engineering thermo-plastics investigated. Knowing the shear stress, the shear rate at the MFI conditions can be determined so that the value of MFI can be calculated using eq. (4). The method has been checked for propriety by calculating the MFI values for resins with reported MFI. These have been found to be in good agreement.

Shenoy et al. [2] have shown that a master curve can be obtained by plotting MFI × η versus $\dot{\gamma}$/MFI

on a log-log scale. They have also provided the mechanistic rationale for such a unification. The master curve obtained would be temperature independent, if the value of MFI used is determined at the temperature to which the viscosity versus shear rate curve pertains. Since this is not readily possible and the ASTM test conditions have to be conferred to, the use of a modified WLF-type equation has been suggested [2] to determine the MFI value at the required temperature, knowing the MFI at the ASTM temperature and glass transition temperature of the polymer

$$\log \frac{\text{MFI}(T_2)}{\text{MFI}(T_1)} = \frac{8.86 \, (T_2 - T_s)}{101.6 + (T_2 - T_s)}$$

$$- \frac{8.86 \, (T_1 - T_s)}{101.6 + (T_1 - T_s)} \qquad (5)$$

where T_1 – ASTM recommended test temperature (K),

T_2 – temperature at which MFI is to be known (K),

T_s – (= T_g + 50) standard reference temperature (K),

T_g – glass transition temperature of the engineering polymers as tested in table 2.

Table 2. Glass transition temperatures for different engineering thermoplastics

Engineering thermoplastics	Glass transition temperature	Source
Acrylics	378 K	Ref. [20]
Acetals	350 K	Ref. [21]
Nylons	323 K	Ref. [20]
Poly(ethylene terephthalate)	343 K	Ref. [21]
Polycarbonates	414 K	Ref. [20]
Polysulfones	460 K	Ref. [21]

Glass transition temperature is sensitive to molecular parameters such as molecular weight, its distribution, branching, crosslinking, etc. Thus, for different grades of polymers of same generic type they are likely to be slightly different. However, in the present context of engineering approximations, a single value has been used for each generic polymer. It is, nevertheless, important to use the appropriate T_g in each individual case in order to get reliable estimates of the rheograms as already indicated in [2].

In cases when the MFI value is required at a load condition different from the determined one, the following equation can be used as suggested by Shenoy et al. [2]:

$$\frac{\text{MFI} \, (L_2)}{\text{MFI} \, (L_1)} = \left(\frac{L_2}{L_1}\right)^{1/n} \qquad (6)$$

where L_1, L_2 are different load conditions and n is the slope of the linear portion of shear stress versus shear rate curve on a log-log scale.

5. Results and discussion

Figures 1 – 6 show the plots of η. MFI versus $\dot{\gamma}/$MFI on logarithmic scales, for acrylics, polyacetals, nylons, polyethylene terephthalate, polycarbonate and polysulfones. With the exception of polyacetals and polysulfones, a single master curve has been obtained for each of the other polymers, which is independent of the polymer grade and the temperature of flow measurement. In the case of polyacetals, data for the linear polymer grades fall on a single curve, whereas the data for the branched polymer grades fall on another unique curve. For the various grades of polysulfones, two separate curves were obtained representing the high and low molecular weight grades. Before elucidating the influence of the molecular parameters such as the degrees of branching (as in polyacetals) and chain length (as in polysulfone) on the master curve, a phenomenological discussion of the flow mechanism in polymer melts is in order.

The method of unifying the viscosity data of various grades of a particular polymer in terms of a modified viscosity parameter, η. MFI, and a modified shear rate parameter, $\dot{\gamma}/$MFI, was found to be applicable to addition polymers such as polyethylenes, polypropylene and styrenics [2]. Its applicability to flexible condensation polymers such as polyacetals, aliphatic nylons and polyethylene terephthalate, and to rigid condensation polymers such as polycarbonate and polysulfone (table 3) has been demonstrated in the present work. In view of the demonstrated usefulness of the unifying approach, it is important to review the various molecular parameters that would influence the viscous flow behaviour of polymer melts.

The viscosity of a polymer melt represents resistance to flow offered by the material. The extent of this resistance would be governed by molecular mobility which is influenced by the amount of free volume available for motion of the individual molecules, the level of physical entanglement of the flexible molecules, and the intermolecular forces between adjacent molecules. These factors are not
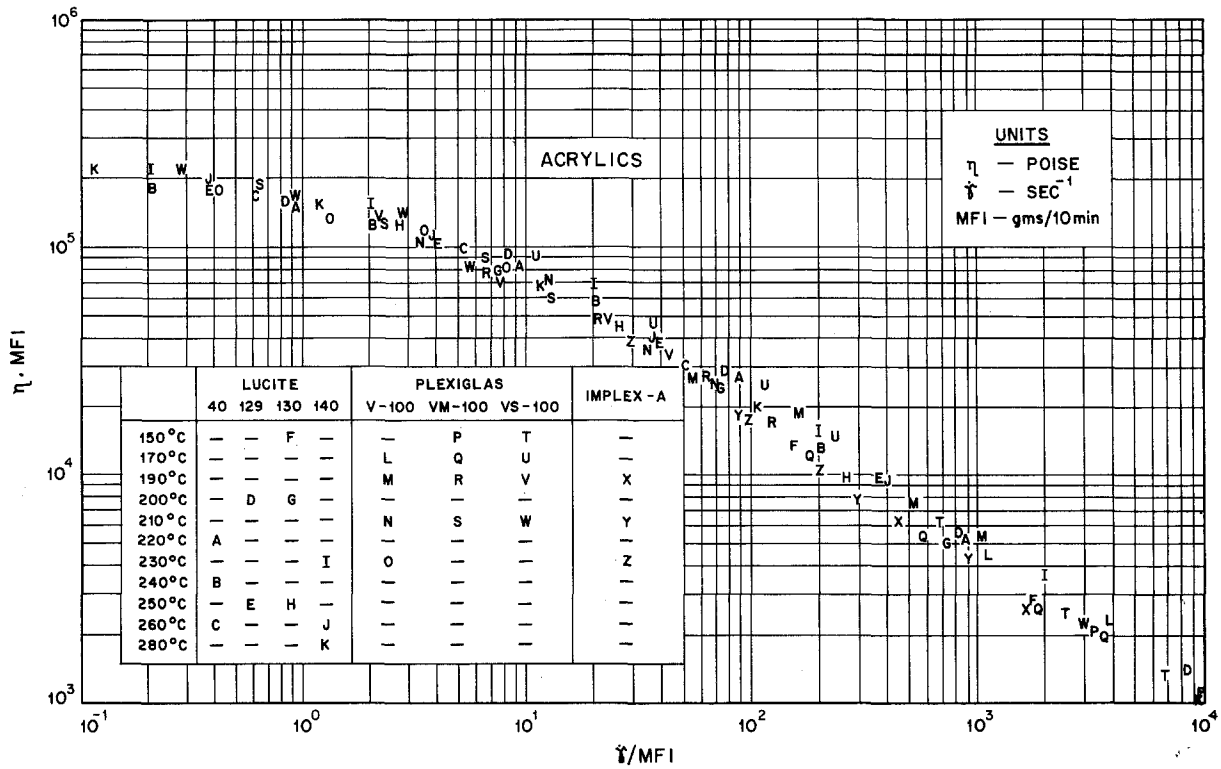
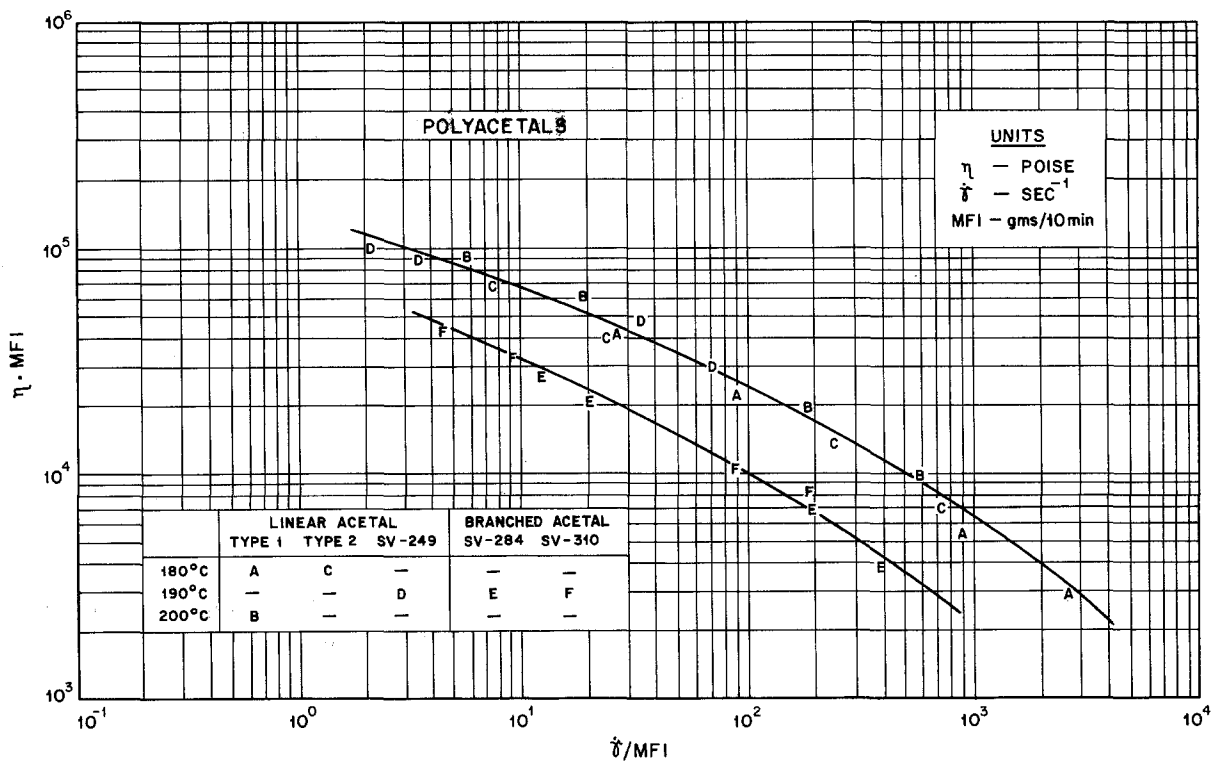Fig. 1. Master curve for acrylics at 3.8 kg test load condition

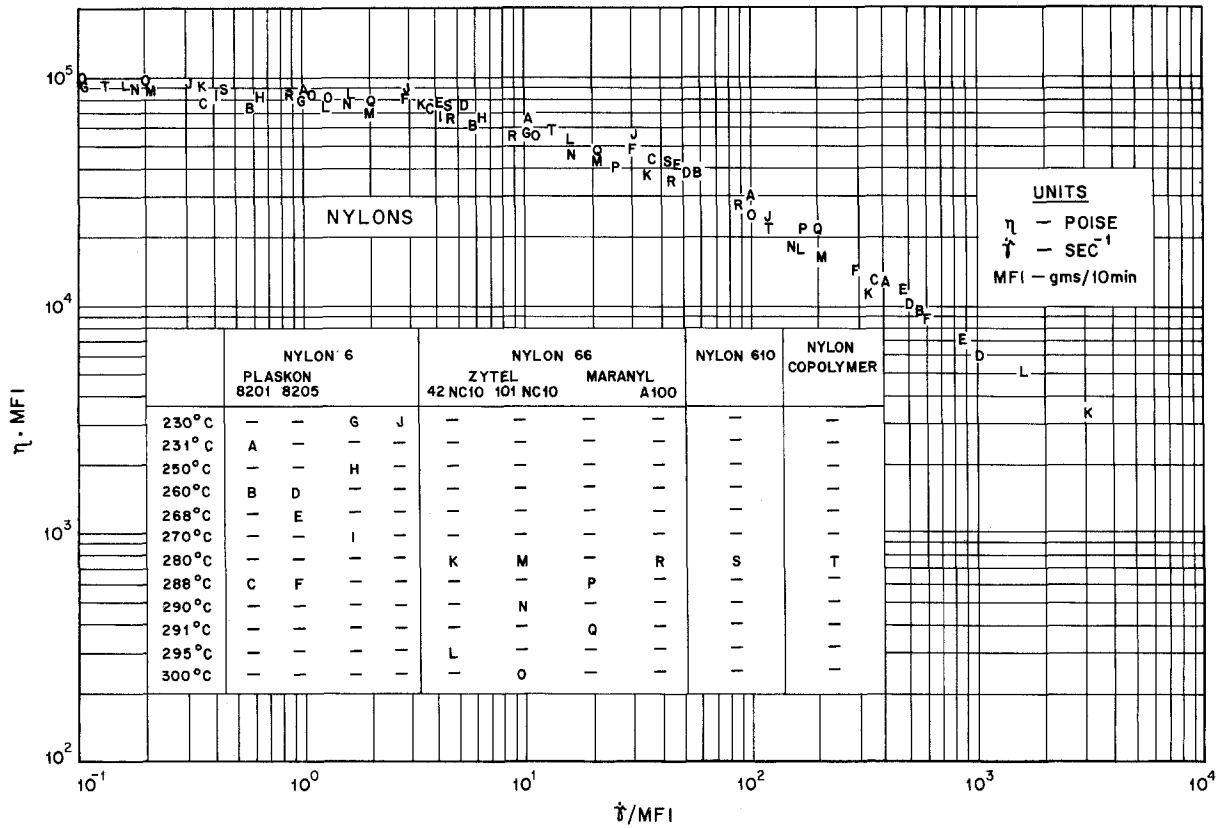Fig. 2. Master curve for polyacetals at 2.16 kg test load condition

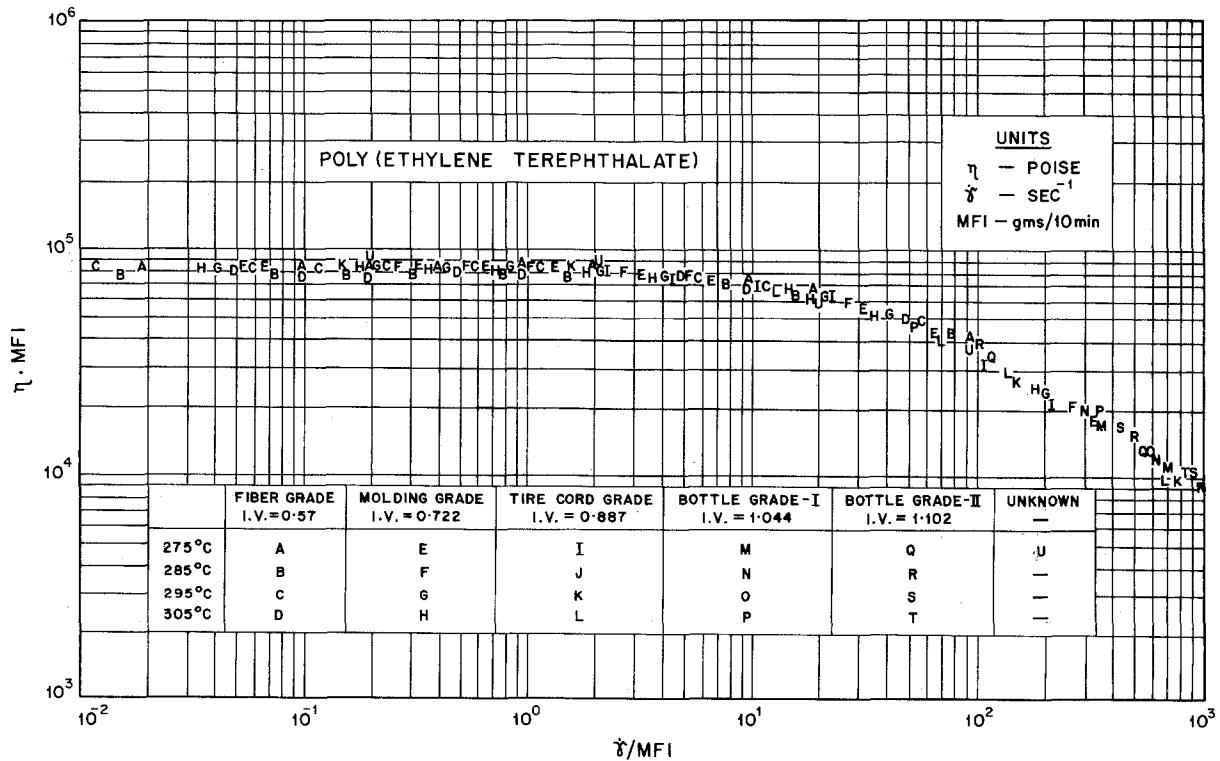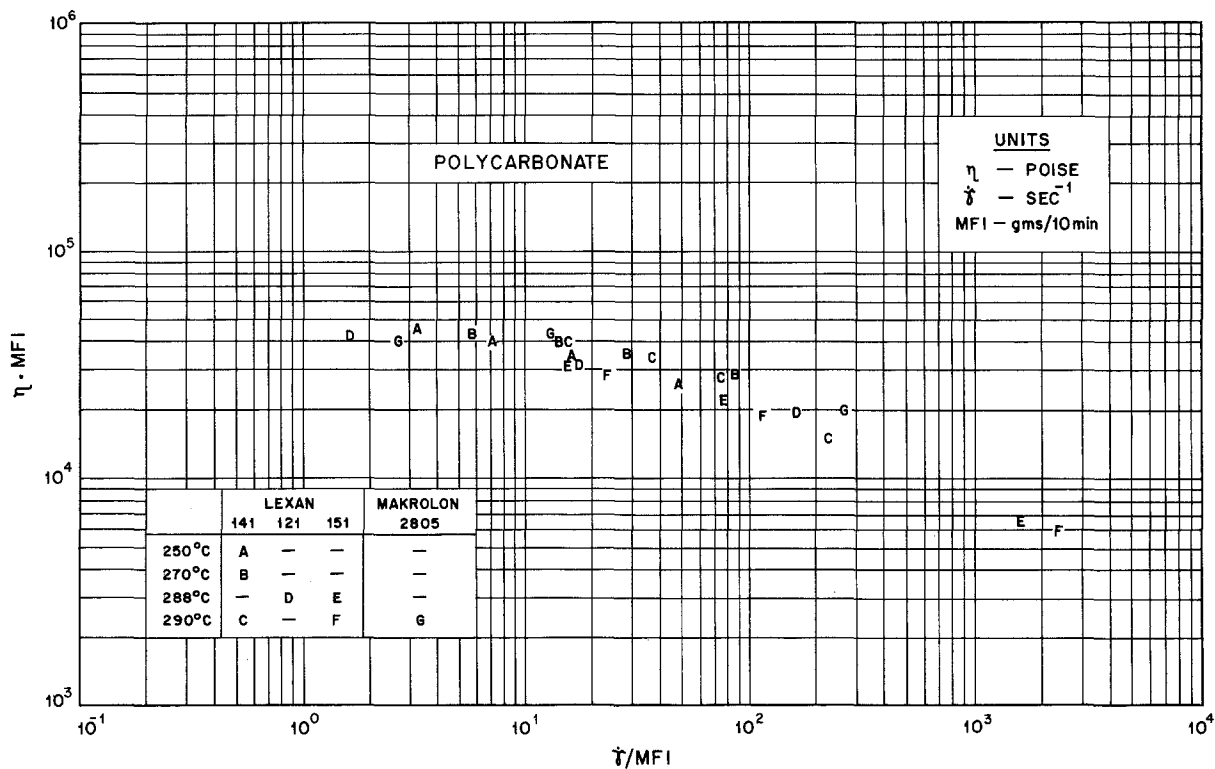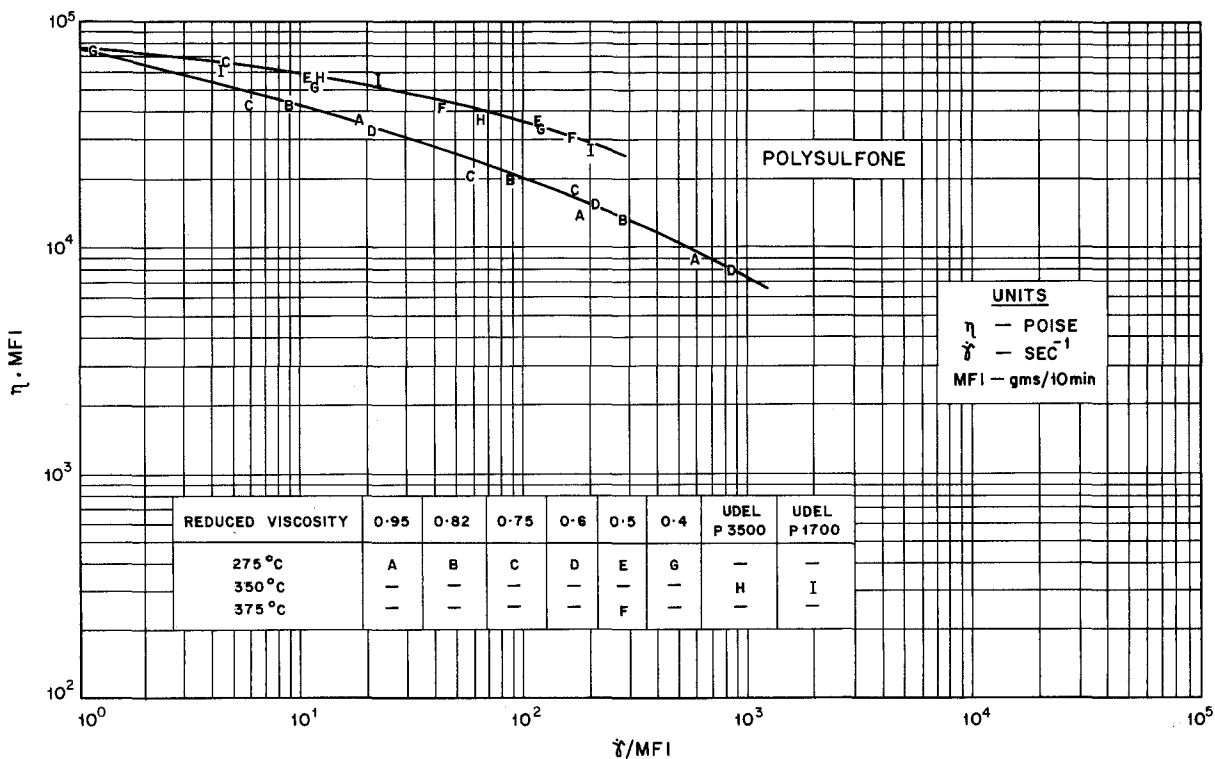Fig. 3. Master curve for nylons at 2.16 kg test load condition

	FIBER GRADE I.V.=0·57	MOLDING GRADE I.V. = 0·722	TIRE CORD GRADE I.V. = 0·887	BOTTLE GRADE-I I.V. = 1·044	BOTTLE GRADE-II I.V. = 1·102	UNKNOWN —
275°C	A	E	I	M	Q	·U
285°C	B	F	J	N	R	—
295°C	C	G	K	O	S	—
305°C	D	H	L	P	T	—

Fig. 4. Master curve for polyesters at 2.16 kg test load condition

Fig. 5. Master curve for polycarbonates at 1.2 kg test load condition

Fig. 6. Master curve for polysulfones at 2.16 kg test load condition

Table 3. Chemical structures of polymers investigated

Acrylics	Addition polymers	Flexible	$-\!\!\left[CH_2-\underset{\underset{COOCH_3}{\overset{\overset{CH_3}{\mid}}{\mid}}}{C}\right]\!\!-$
Acetals	Condensation polymers	Flexible	$-\!\!\left[CH_2-O\right]\!\!-$
Nylon 6	Condensation polymer	Flexible	$-\!\!\left[NH(CH_2)_5CO\right]\!\!-$
Nylon 66	Condensation polymer	Flexible	$-\!\!\left[NH(CH_2)_6NH-CO(CH_2)_4CO\right]\!\!-$
Nylon 610	Condensation polymer	Flexible	$-\!\!\left[NH(CH_2)_6NH-CO(CH_2)_8CO\right]\!\!-$
Poly(ethylene terephthalates)	Condensation polymers	Flexible	$-\!\!\left[OCH_2CH_2O\underset{O}{\overset{\parallel}{C}}-\!\!\bigcirc\!\!-\underset{O}{\overset{\parallel}{C}}\right]\!\!-$
Polycarbonates	Condensation polymers	Rigid	$-\!\!\left[O-\!\!\bigcirc\!\!-\underset{\underset{CH_3}{\mid}}{\overset{\overset{CH_3}{\mid}}{C}}-\!\!\bigcirc\!\!-O-\underset{}{\overset{\overset{O}{\parallel}}{C}}\right]\!\!-$
Polysulfones	Condensation polymers	Rigid	$-\!\!\left[\bigcirc-\underset{\underset{CH_3}{\mid}}{\overset{\overset{CH_3}{\mid}}{C}}-\!\!\bigcirc\!\!-O-\!\!\bigcirc\!\!-\underset{\underset{O}{\parallel}}{\overset{\overset{O}{\parallel}}{S}}-\!\!\bigcirc\!\!-O\right]\!\!-$

Table 4. Molecular parameters influencing viscosity

Influencing variable	Relevant molecular parameters	
	Primary effective parameter	Contributory parameters
1. Free volume	Chain ends per unit volume	a) Degree of polymerization as signified by the number average molecular weight b) Molecular weight distribution c) Degree of branching
	Packing ability	a) Chain length b) Chain flexibility c) Size of pendant groups d) Intermolecular interactions
2. Entanglement density	Chain length relative to the critical chain length between entanglements	a) External length of a repeat unit b) Number average molecular weight c) Chain flexibility
3. Intermolecular interactions	Secondary bonding ability	Presence of groups with hydrogen bonding ability
	Level of secondary forces	Polarity of the chain units
	Packing ability	a) Chain flexibility/rigidity b) Chain size c) Size of pendant groups

totally independent. For example, the intermolecular interactions would influence packing and hence free volume. In general, the flow resistance would be reduced with increasing free volume, decreasing entanglement density, and weaker intermolecular interactions. Let us now briefly review the molecular and environmental (physical) parameters affecting the influence and relative contribution of the three factors to the flow resistance, that is, the viscosity. The pertinent molecular parameters are summarized in table 4.

The free volume available for motion of the individual molecules in a polymer melt would be governed by the number of chain ends and the packing ability of the molecules. The greater the number of chain ends present per unit volume, the higher is the free volume. This is because a polymer segment near a chain end will, on the average, have a higher jump frequency than the usual polymer segment [6]. The phenomenon results from the fact that the chain end loosens the local liquid structure and thereby facilitates motion. Any segment, whether or not it is in the particular chain that supplies the chain end, will move more freely as a result of the chain end being near by. The number of chain ends per unit volume increase with decreasing number average molecular weight. For a given number average molecular weight, more the chain end density, higher is the degree of chain branching and broader the molecular weight distribution. Close packing of the polymer molecules would have a negative effect on the free volume. The packing ability is governed by chain flexibility (or rigidity), chain length (average molecular weight), and size of the pendant groups, the most important parameter being the chain flexibility. Chain flexibility would determine whether the preferred configuration of the polymer is random coil or rodlike. Rigid chain linear polymer molecules are expected to pack closer than their flexible counterparts. The melt densities of the rigid chain polymers are therefore relatively high. (The adverse effect of bulky side groups on packing is quite obvious). In summary, the free volume is primarily affected by the number of chain ends per unit volume and secondarily by molecular packing.

Because of their long flexible chain structure, polymer molecules in the melt are physically entangled with each other. As a result of the entanglements, the thermal motion of a polymer chain is constrained. The molecular weight between entanglement points along a molecule, M_e, would increase as the mass of the polymer in unit volume, ρ, decreases [3]. This relation is quite obvious when one considers that, if a highly entangled group of polymer chains is diluted with diluent, the value of ρ can be decreased to a point where the molecules no longer overlap and no entanglements will be present. The parameter of physical significance is the chain length between entanglement points.

This critical entanglement chain length can be computed from the value of M_e, which is related to the point on the log-log plot of viscosity versus molecular weight, at which there is a change in slope of the curve. The values of M_e reported by Bueche [3] and the corresponding critical entanglement lengths for a number of polymers are summarized in table 5. From the data, it is apparent that the critical chain length is the shortest for polyethylene which represents the most linear, unsubstituted, flexible polymer chain. Thus the chain in a polymer with a short critical chain length has more possible places along its length where entanglements could occur, as compared to the polymer with a long chain length between entanglements. For a given polymer, a higher molecular weight grade resin, would exhibit a greater entanglement density. The probability of entanglement of molecules is expected to be low in the case of rigid chain polymers, and therefore the contribution of entanglements to viscosity in these polymers would be low relative to the flexible polymers.

Table 5. Degree of polymerization at critical entanglement length

Polymer	M_e	Molecular weight	DP at M_e
Polyethylene	1000	28	35
Polymethyl- methacrylate	5000	100	50
Polyvinylacetate	11000	86	127
Polyisobutylene	8500	58	146
Polypropylene	7000	42	166
Polystyrene	20000	104	192

The third factor influencing viscosity is the level of intermolecular interaction. If the primary molecular motion for causing flow is assumed to be the sliding movement of adjacent molecules, then it is necessary to overcome the secondary bonding forces between the molecules for the flow to occur. Polymers with polar groups in the main chain, side chain or as pendant groups would offer greater resistance to the sliding motion. Since the binding effect of the secondary bond forces of attraction extends to a distance of about $5-10$ Å from a molecule, any molecular parameters that disrupt packing of adjacent molecules and increase the separation distance between them would reduce this resistance. The molecular parameters of chain flexibility/rigidity, chain length and the size of the pendant group are relevant in this context.

On the basis of the above physical considerations certain qualitative generalizations can be made:

(i) In the case of linear flexible polymers, the viscosity behaviour would be governed primarily by the entanglement density and secondarily by the free volume considerations.

(ii) For rigid chain polymers, the most important factor influencing viscosity would be the high level of intermolecular forces arising from a close molecular packing. The viscosity of these polymers would therefore be more temperature dependent than the flexible polymers [4]. Free volume effects are also relevant. However, the influence of entanglements would be marginal (fig. 7).

(iii) Most addition polymers like polyethylene, polypropylene, polystyrene with high molecular weights
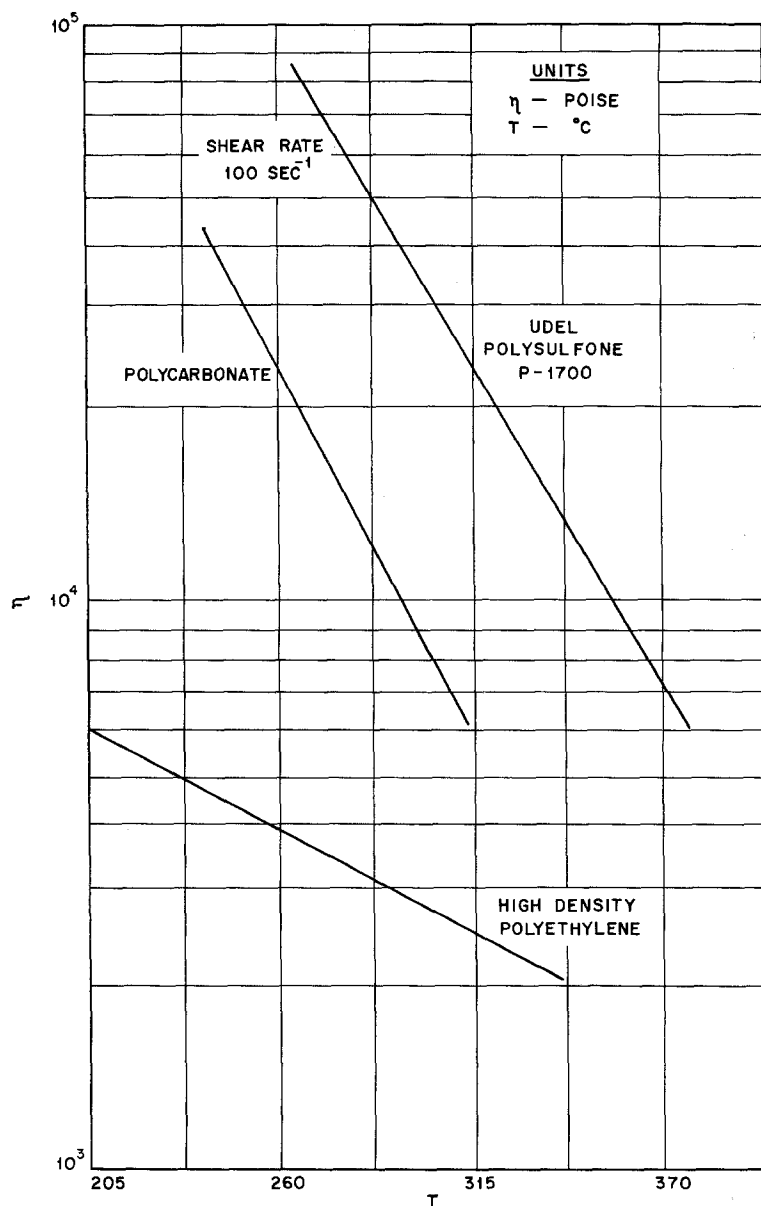
Fig. 7. Viscosity versus temperature for different polymers from [19]

(50000 to 1000000) have relatively long extended chain lengths in excess of 5000 Å, whereas the condensation polymers represent short polymer chains extending to a length of about 1000 Å (number average molecular weight: 10000 to 30000). The polyolefins would therefore have a high entanglement density as compared to the nylons and thermoplastic polyesters.

(iv) The shear thinning behaviour of thermoplastics is due to the orienting influence of the imposed velocity gradient which results in disentanglement [4]. Therefore, the shear rate dependence of melt viscosity is more pronounced in the case of the flexible long chain polyolefins, as compared to the rigid chain polycarbonate and polysulfone (fig. 8).

On the basis of the above considerations, the dependence of the master curve on chain branching in polyacetals, and on the chain length in polysulfone can also be readily elucidated.

In arriving at the master curves, the viscosity and shear rate are normalized via the melt flow index. As melt flow index is itself insensitive to subtle changes in molecular parameters such as molecular weight distribution, this limitation would be expected to be present even in the master curves. The melt flow index of a resin is varied primarily by varying the number
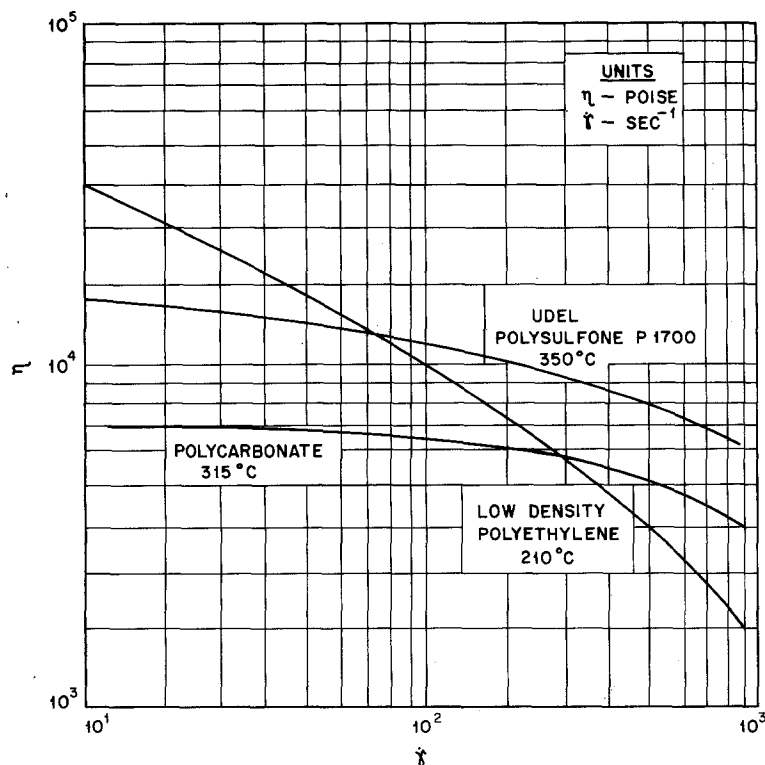
Fig. 8. Flow curves for different polymers from [19]

average molecular weight, M_n. However, the relationship between MFI and M_n would be different for linear and branched polymers. At a given number average molecular weight, the branched polymer melt would have a greater chain end density than the linear polymer. The resulting increase in free volume would mean a lower viscosity for the branched polymer grade relative to the linear grade, at a given shear rate, as observed in the case of polyacetals (fig. 2). This is valid as long as the chain length in the branch is shorter than the critical chain length between entanglements. In the case of long chain branching, the branches can contribute to an increase in the entanglement density thereby nullifying the free volume effect.

In the case of polysulfone, the higher molecular weight grades (RV > 0.6 as given in table 6) exhibit lower viscosity than the low molecular weight grades (fig. 6). This behaviour is contradictory to the one generally observed with linear flexible polymers, and can be explained in terms of the rigid chain character of polysulfone. Most rigid chain polymers form anisotropic melts. There are various arrangements of molecular packing that are feasible. Two of the most common ordering arrangements are those corresponding to the smectic and nematic phases of liquid crystals. These are illustrated in figure 9 [5]. The

Table 6. Properties of the experimental polysulfone resin as given in [14]

Reduced viscosity (RV)	Number average molecular weight (M_n)
0.4	17000
0.5	25000
0.6	35000
0.75	52000
0.82	61000
0.95	80000

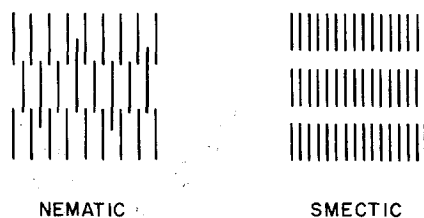

NEMATIC   SMECTIC

Fig. 9. Molecular arrangements in rigid chain polymer melts

smectic phase is represented by a parallel arrangements of molecules arranged in layers. The arrangement within the layers may be either random or ordered. In either case the long axes of the molecules in a given layer are parallel to one another and per-

pendicular to the plane of the layer. In the nematic phase, the molecules are still oriented in a parallel fashion, however, the layer arrangement no longer exists. The resulting one-dimensional order is, therefore, less than that in the smectic phase. It is obvious that the intermolecular interactions are stronger in the smectic phase with a domain structure as compared to the nematic phase. Therefore the nematic phase is less viscous than the smectic phase [5]. With increasing length of the rigid polymer chain, the "kinetic" probability of the molecules ordering into a nematic arrangement rather than into a smectic state increases. It could thus be postulated that beyond a certain critical length of the rigid chain, the packing of the molecules in the molten phase is less efficient leading to lower viscosity. The behaviour observed with polysulfones seems to follow this physically appealing logical argument.

Figures 1 to 6 represent the master curves, for estimating the rheograms of the engineering thermoplastics studied from knowledge of the MFI and the glass transition temperature of the resin. The steps involved in generating such rheograms are summarized below:

– Obtain MFI value under standard specified temperature and loading conditions either from the manufacturer or via measurement on a standard melt flow indexer.

– Check whether the loading condition of the obtained MFI value is the same as that specified in the master curve. If it is different, then calculate a new value of MFI using eq. (6) for the loading condition given in the master curve.

– When the specified temperature condition is different from the condition at which the rheogram is desired, use eq. (5) to get the value of the effective MFI at the required temperature.

– Obtain the rheogram simply by substituting the correct value of the effective MFI in the master curve.

6. Conclusion

The viscosity versus shear rate flow curves at relevant processing temperatures can be generated for engineering thermoplastics from a knowledge of the melt flow index and glass transition temperature of the resin, with the use of a master curve. Master curves have been reported for acrylics, polyacetals, nylons, polyethylene terephthalate, polycarbonates and polysulfones. The rheograms generated by using the technique proposed, would give an approximate magnitude of viscosity, adequate for most exercises in process design, optimization, trouble-shooting and for assessing processibility of the resin. As melt flow index is itself insensitive to subtle changes in parameters such as molecular weight distribution, this limitation would be expected to be present even in the master curves. Physical considerations have been proposed for elucidating the influence of parameters such as chain branching and chain length on the viscosity behaviour. The relative influence of the various molecular parameters varies depending on whether the polymer represents a flexible long chain (e.g. polyolefins), a flexible short chain (e.g. thermoplastic polyesters) or a rigid short chain (e.g. polysulfone). Differences in molecular-weight distribution, branching etc. would be seen more in the very low and very high shear rate regions and not within the working ranges of most polymer processing operations. Hence the method would still retain its effectiveness as a handy tool for the polymer processor.

Appendix I

Table 1a. Standard testing conditions of temperature

Engineering resins	Temperature °C	Load (Piston + weight) kgs	Shear stress dynes/cm^2	Approximate Pressure kg/cm^2
Acrylics	230	1.200	$1.10 \cdot 10^5$	1.69
	230	3.800	$3.46 \cdot 10^5$	5.34
Acetals	190	2.160	$1.97 \cdot 10^5$	3.04
	190	1.050	$9.59 \cdot 10^4$	1.48
Nylons	275	0.325	$2.97 \cdot 10^4$	0.46
	235	1.000	$9.13 \cdot 10^4$	1.41
	235	2.160	$1.97 \cdot 10^5$	3.04
	235	5.000	$4.56 \cdot 10^5$	7.03
Poly(ethylene terephthalate)	275	2.160	$1.97 \cdot 10^5$	3.04
Polycarbonates	300	1.200	$1.10 \cdot 10^5$	1.69
Polysulfone	190	2.160	$1.97 \cdot 10^5$	3.04

Table 1b. ASTM specifications for piston and die dimensions

Piston	Die
Diameter (0.3730 ± 0.0003 in = 9.474 ± 0.007 mm)	(0.0825 ± 0.0002 in = 2.095 ± 0.005 mm)
Length (0.250 ± 0.005 in = 6.35 ± 0.13 mm)	(0.315 ± 0.0008 in = 8.00 ± 0.02 mm)

References

1. Plastics Design Forum, p. 70, May-June 1979.
2. Shenoy, A. V., S. Chattopadhyay, V. M. Nadkarni, Rheol. Acta 22, 90 (1983).
3. Bueche, F., Physical Properties of Polymers, pp. 61 – 84, Interscience Publishers (New York 1962).
4. Metzner, A. B., in: E. C. Bernhardt (ed.), Processing of Thermoplastic Materials, pp. 6 – 71, Van Nostrand (New York 1959).
5. Brochure JJ-14, Eastman Liquid Crystal Products, Eastman Kodak Company, Rochester, USA (1973).
6. Lupton, J. M., Chemical Engg. Progr. Symp. Series No. 49, 60, 17 (1964).
7. Westover, R. F., in: E. C. Bernhardt (ed.), Processing of Thermoplastic Materials, pp. 547 – 679, Van Nostrand (New York 1959).
8. Barker, S. J., M. B. Price, Polyacetals, p. 115, Iliffe Books (London 1970).
9. Pritchard, J. H., K. F. Wissbrun, J. Appl. Polym. Sci. 13, 233 (1969).
10. Bankar, V. G., J. E. Spruiell, J. L. White, J. Appl. Polym. Sci. 21, 2135 (1977).
11. Kohan, M. I., Nylon Plastics, Ch. 4, John Wiley and Sons (New York 1973).
12. Crowson, R. J., M. J. Folkes, Polym. Engg. Sci. 20, 934 (1980).
13. Private Communication by E. I. duPont de Nemours and Co. (1977).
14. Wu, S., Polym. Engg. Sci. 19, 638 (1979).
15. Knutsson, B. A., J. L. White, K. A. Abbas, J. Appl. Polym. Sci. 26, 2347 (1981).
16. Anon, Lexan Products Dept., General Electric Co., Tech. Bulletin, Lexan for Extrusion (1980).
17. Yamada, M., R. S. Porter, J. Appl. Polym. Sci. 18, 1711 (1974).
18. Shaw, M. T., J. C. Miller, Polym. Engg. Sci. 18, 372 (1978).
19. Injection Moulding of UDEL Polysulfone, Technical Brochure, Union Carbide Company, U.S.A. (1975).
20. Ganesh Kumar, N., J. Polymer Sci.: Macromolecular Reviews 15, 255 (1980).
21. Brandrup, J., E. H. Immergut, Polymer Handbook 2nd ed., Wiley (New York 1975).

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