Estimation of the melt rheology of polymer waste from melt flow index

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The need for recycling of polymeric waste has been well recogmized as a result of the escalating prices of the petrochemical feedstocks and the growing awareness to curtail solid waste that causes environmental pollution. During processing, the molecular weight of the polymer is reduced due to thermal and shear degradation. Since the melt rheology of the processed material is sensitive to the changes in molecular structure, knowledge of the complete flow curve depicting the variation of melt viscosity with shear rate at processing temperatures is a useful tool for assessing the reprocessibility of waste material and for specifying the conditions of reprocessing. In the present paper, an effective method is proposed to generate the melt flow curves of polymer waste from knowledge of its melt flow index. The method makes use of a master curve that can be obtained by plotting the available viscosity data in terms of modified functions based on the melt flow index. The master curves characteristic of the particular generic resin type are presented for low-density polyethylene, polypropylene and polystyrene.

Keywords Melt flow index; rheograms; recycling; polymer waste

INTRODUCTION

Polymers have been increasingly replacing conventional materials like glass, wood and metals in a number of applications due to the property advantages offered by them such as high strength-to-weight ratio, corrosion resistance, versatility of part design and ease of fabrication. However, polymers are derived from petroleum feedstocks, which are limited and are becoming expensive. The escalating prices of the raw materials, the necessity of conserving natural resources and the growing awareness to reduce solid waste for minimizing environmental pollution have resulted in the realization of the need to recycle plastic scrap and waste.

During processing of polymers in extrusion, injection moulding, blow moulding and other conversion processes, the polymeric material is exposed to thermal, oxidative as well as shear induced degradation, causing molecular scission. The physical characteristics of the waste polymer such as the flow behaviour, tensile strength, elongation and impact are different from and generally inferior to those of the virgin polymer. It is therefore necessary to provide guidelines to the processors for determining the maximum concentration of polymer waste that can be added to the virgin material during processing, without drastic loss in product properties. Also the processing conditions for the virgin and recycled material would be different in accordance with the changes in the melt rheology. Because of the sensitivity of melt rheology to small differences in molecular structure, knowledge of the complete flow curve depicting the variation of melt viscosity with shear rate and temperature is a useful tool for assessment of material processibility, process optimization and troubleshooting.

Here it is shown that the melt flow index can be used to estimate the viscosity behaviour of the polymer waste at temperatures relevant to processing.

BACKGROUND

It is important to be able to predict the extent of degradation occurring during specific processing steps so as to correlate it quantitatively to measurable processing parameters. This can be done by studying the molecular changes that occur in repetitive extrusion through a capillary rheometer or a laboratory extruder[1-14]. Molecular weight reduction which occurs during degradation in processing can be characterized in terms of parameters like normal stress difference[5], die swell ratio[8] and shear viscosity[5,9,13-15] as a function of temperature and shear rate. Schott and Kaghan[16] found that six passes through a commercial screw extruder at 260°C decreased the weight-average molecular weight of a polypropylene sample from 270000 to approximately 80000, with a corresponding decrease in the melt viscosity.

The melt flow data are generally obtained on sophisticated instruments like the Weissenberg rheogoniometer, Instron capillary rheometer, Rheometrics mechanical spectrometer, etc., which are expensive and require trained operators for data generation. These are, therefore, generally beyond the technical capabilities and financial means of most plastics processors. The flow parameter easily available to a processor is the melt flow indes (*MFI*), which can be measured using a simple, inexpensive apparatus. However, the *MFI* is a single point measurement and its utility for process optimization is limited unless it is correlated to the rheograms.

The change in *MFI* has been used by researchers to study the extent of thermal and shear degradation of

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Table 1

Polymer	Grade	Shearing history	*MFI* (temperature, °C/ load condition, kg)	Data temp. (°C)	No.of data points (shear rate range, s^{-1})	Source ref.
LDPE	–	Virgin	0.8[a] (190/2.16)	190	7 (0.03–6)	5
	–	Brabender worked sample for 60 mm	1.3[a] (190/2.16)	190	7 (0.03–6)	5
PP	Daplon	1 cycle thro' an injection moulding machine	1.3[b] (190/2.16)	190	4 (10–300)	13
		3 cycles ···	1.6[b] (190/2.16)	190	4 (10–300)	13
		6 cycles ···	2.2[b] (190/2.16)	190	4 (10–300)	13
		9 cycles ···	3.2[b] (190/2.16)	190	4 (10–300)	13
		12 cycles ···	4.7[b] (190/2.16)	190	4 (10–300)	13
		15 cycles ···	6.7[b] (190/2.16)	190	4 (10–300)	13
	Profax	1 cycle ···	1.6[b] (190/2.16)	190	5 (20–500)	13
		3 cycles ···	2.2[b] (190/2.16)	190	5 (20–500)	13
		6 cycles ···	3.6[b] (190/2.16)	190	5 (20–500)	13
		9 cycles ···	5.1[b] (190/2.16)	190	5 (20–500)	13
		12 cycles ···	6.5[b] (190/2.16)	190	5 (20–500)	13
		15 cycles ···	9.2[b] (190/2.16)	190	5 (20–500)	13
PS	Styron 686	1 pass thro' 2½ in extruder at 50 rpm	17.1[a] (220/5)	220	3 (20–700)	14
		2 passes ···	18.1[a] (220/5)	220	3 (20–700)	14
		3 passes ···	21.5[a] (220/5)	220	3 (20–700)	14
		4 passes ···	31.8[a] (220/5)	220	3 (20–700)	14
		5 passes ···	41.7[a] (220/5)	220	3 (20–700)	14
	Styron 686	1 pass thro' 2½ in extruder at 100 rpm screw speed	24.5[a] (220/5)	220	3 (20–500)	14
		2 passes ···	26.4[a] (220/5)	220	3 (20–500)	14
		3 passes ···	32.3[a] (220/5)	220	3 (20–500)	14
		4 passes ···	39.2[a] (220/5)	220	3 (20–500)	14
		5 passes ···	44.1[a] (220/5)	220	3 (20–500)	14

[a] *MFI* value read out from τ versus γ curve using equations (3) and (4)
[b] *MFI* value given under ASTM testing conditions

polymer materials[4,6,12,13] in processing as effected by temperature and addition of heat stabilizers and antioxidants. Though *MFI* may be a good indicator of the effect of processing history on the polymer, it cannot correlate directly with processing behaviour, since the values of temperature and shear rate employed in the *MFI* test differ substantially from those encountered in actual processing. However, it would be desirable if a method for estimating the flow curves from the melt flow index could be established. A procedure has been successfully developed by Shenoy *et al.* for polyolefins and styrenics[17], cellulosics[18] and a number of other engineering thermoplastics[19] to estimate the rheograms from knowledge of the melt flow index and the glass transition temperature of the polymer.

The purpose of the present paper is to extend the approach proposed earlier by the authors to polymer waste for estimating the viscosity versus shear rate variation at any required temperature. The rheograms would then be useful to judge whether a particular polymeric waste can be reprocessed under a certain set of processing conditions and to set new processing conditions if required. As very little data are available on the viscosity behaviour of recycled material, the analysis developed in the present paper is based on only three polymers, namely low-density polyethylene, polypropylene and polystyrene. Details of the systems used are given in *Table 1*.

DATA ANALYSIS

The melt flow index (*MFI*) is defined as the weight of polymer in grams extruded in 10 min under the application of a dead weight through a melt flow apparatus as per ASTM 1238-73 (see Appendix). Thus *MFI* is basically a flow parameter generated through an extrusion rheometer. Hence expressions for shear stress τ and shear rate $\dot{\gamma}$ given by the well known conventional forms can be written 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 R_P = piston radius, R_N = nozzle radius, l = nozzle length, F = test load $(L) \times 9.807 \times 10^5$, and Q = flow rate $(= MFI/600\rho$ by definition of *MFI*). The geometrical parameters are all fixed as per ASTM 1238-73 given in the Appendix.

Using the geometric parameters of the melt flow apparatus, equations (1) and (2) can be simplified to give

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

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

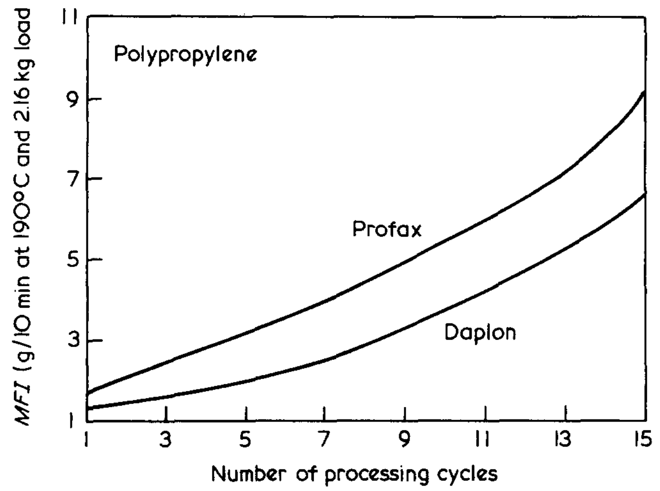

Figure 1 Variation of *MFI* with number of reprocessing cycles taken from ref.13

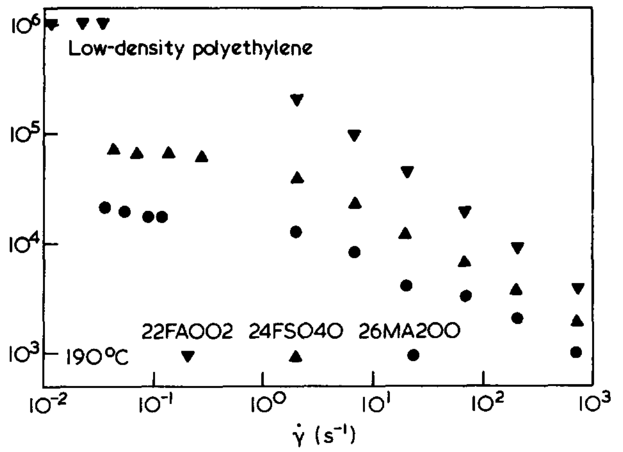

Figure 2 Viscosity *versus* shear rate curve for three different grades of LDPE with different *MFI* at 190°c

Since the test load for a particular polymer is fixed, as per equations (3) and (4), the *MFI* of the polymer essentially represents a single point on the shear stress versus shear rate curve. Conversely, this fact can be used for estimating the *MFI* from a known shear stress versus shear rate curve when the *MFI* is not given. This method has been successfully employed by Shenoy *et al.*[18,19] and Rideal and Padget[12]. Rideal and Padget actually measured viscosity on a Weissenberg rheogoniometer at shear stress equivalent to that in the *MFI* apparatus and used it to estimate the *MFI* of the polymers, since these were too low to be measured accurately on the melt flow indexer.

The apparent viscosity is related to the shear stress and shear rate by the equation:

$$\eta = \tau/\dot{\gamma} \qquad (5)$$

Equations (3) and (4) can then be modified to give:

$$MFI \times \eta = 4.98 \times 10^4 \rho L \qquad (6)$$

$$\dot{\gamma}/MFI = 1.83/\rho \qquad (7)$$

For a given polymer, as the density and *MFI* load condition are fixed, the right-hand sides of equations (6) and (7) are both constant. A master curve could thus be obtained by plotting $MFI \times \eta$ versus $\dot{\gamma}/MFI$ on a log–log scale at the temperature of *MFI* measurement. For estimating an effective *MFI* at temperatures other than the ASTM test temperature, the modified WLF type equation suggested by Shenoy *et al.*[17] can be used:

$$\log\left(\frac{MFI(T_2)}{MFI(T_1)}\right) = \frac{8.86(T_2 - T_S)}{101.6 + (T_2 - T_S)} - \frac{8.86(T_1 - T_S)}{101.6 + (T_1 - T_S)} \qquad (8)$$

where T_1 = temperature (K) of *MFI* measurement, T_2 = temperature (K) at which *MFI* is desired, T_S = standard reference temperature (K) taken as $T_g + 50$, and T_g = glass transition temperature (K) of the polymer.

In cases where the *MFI* value is required at a load condition different from the determined one, the following equation can be used:

$$\frac{MFI(L_2)}{MFI(L_1)} = \left(\frac{L_2}{L_1}\right)^{1/n} \qquad (9)$$

RESULTS AND DISCUSSION

The viscosity of a polymer melt represents resistance to flow offered by the material. The flow resistance would be reduced with increasing free volume, decreasing entanglement density and weaker intermolecular interactions. These factors are dependent on molecular parameters like molecular weight, molecular weight distribution, branching, etc. The viscosity of the melt would therefore decrease with repeated processing, since the molecular weight of the polymer is progressively reduced due to thermal and shear degradation in each processing cycle. The melt flow index of the reprocessed material would accordingly be higher than the virgin polymer. *Figure 1* shows the increase in *MFI* with processing cycle based on data from *Table 1*.

Shenoy *et al.*[17] have shown how different grades of a polymer of the same generic type can be coalesced to give a master curve. *Figure 2* taken from ref. 17 shows a plot of viscosity versus shear rate for three grades of LDPE with *MFI*'s of 0.2, 4 and 10 at a temperature of 190°C. The curves were generated from data taken on the Weissenberg rheogoniometer and Instron capillary rheometer. Using a plot of $\eta \times MFI$ versus $\dot{\gamma}/MFI$, the

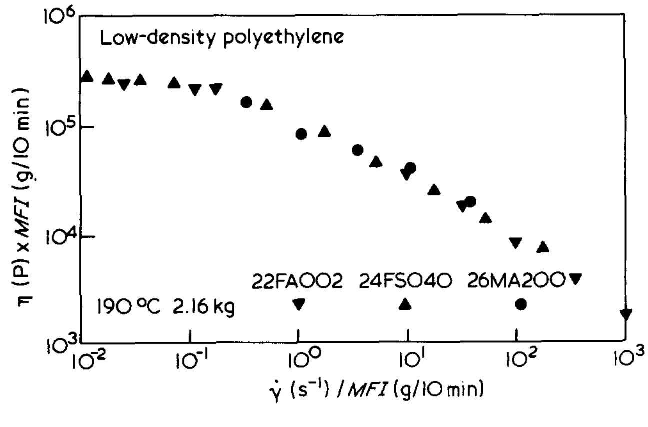

Figure 3 Viscosity master curve for three different grades of LDPE with different *MFI* at 190°C

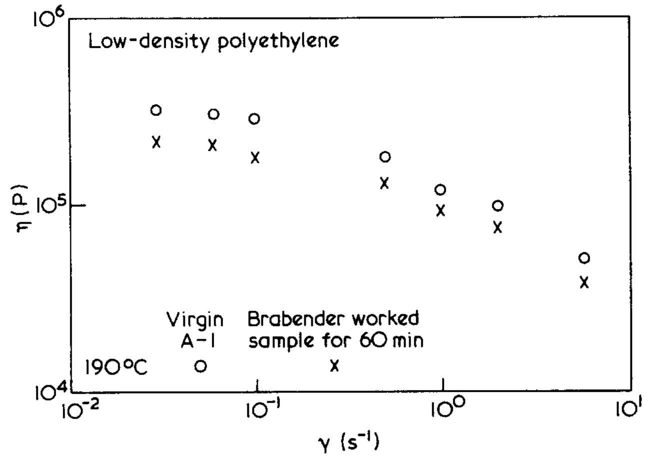

Figure 4 Viscosity *versus* shear rate curve for virgin and reprocessed low-density polyethylene taken from ref.5

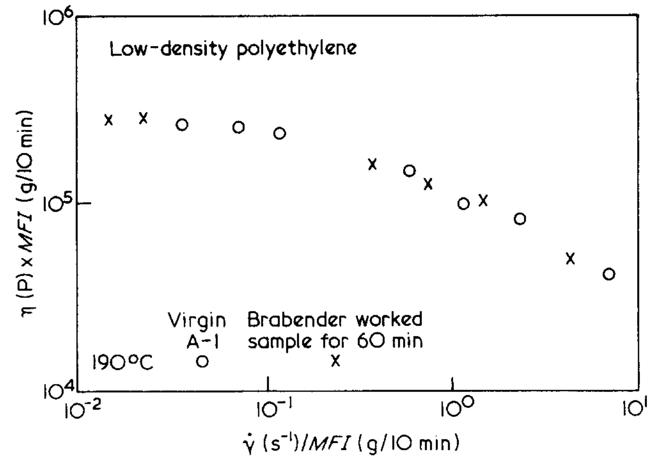

Figure 5 Viscosity master curve for reprocessed low-density polyethylene at 2.16 kg test load condition

three curves were unified to give a single curve as shown in *Figure 3* taken from ref. 17.

The polymer samples with different processing histories essentially represent polymer grades with different melt flow indexes. The unifying approach that coalesced the grade dependence for virgin polymers[17] should therefore be applicable to the reprocessed polymers. *Figure 4* depicts the viscosity versus shear rate data for virgin and reprocessed low-density polyethylene. The recycled sample was processed in a Brabender mixer for 60 min at 190°C which increased the melt flow index of the polymer by about 60%. These data when plotted in the form of a modified viscosity function ($\eta \times MFI$) versus a modified shear rate function ($\dot{\gamma}/MFI$) on a log–log scale coalesce into a single curve. This is illustrated in *Figure 5*. The general validity of the unifying approach is further confirmed by the fact that *Figure 5* can be neatly superimposed on the master curve for virgin low-density polyethylene reported by Shenoy *et al.*[17] This is illustrated in *Figure 6*. The data used for generating *Figure 6* summarized in *Table 2*.

The master curve for reprocessed polypropylene is shown in *Figure 7*. The reprocessed materials were obtained from two grades of virgin polypropylene by subjecting them to repetitive processing in an injection moulding machine[13]. Csupor and Toth[13] have provided a series of rheograms of the reprocessed materials representing 1, 3, 6, 9, 12 and 15 injection moulding cycles, and they have also reported the melt flow index values of the reprocessed resin samples. It is interesting to note that all the curves of Csupor and Toth coalesce into a single curve when plotted in terms of the modified viscosity and shear rate functions.

In *Figure 8* the unifying approach has been successfully demonstrated for reprocessed polystyrene. Springer *et al.*[14] used repetitive extrusion to impart varying shear history to the material. The virgin polymer, general purpose polystyrene, was extruded at two different screw speeds of 50 and 100 rpm with 1–5 passes in each case. Again, all the viscosity data of Springer *et al.* at 220°C fall on a single curve.

Though the present work includes only three different types of polymer, it can be seen conclusively that the master curves generated hold good for virgin as well as reprocessed material. Thus, the master curves reported for virgin polymers by Shenoy *et al.* for olefins and styrenics[17], cellulosics[18] and engineering thermoplastics[19] could be reliably used for generating rheograms of reprocessed materials.

It is a common practice to determine the utility of polymer waste by determining the critical *MFI* in a plot of end-use property versus *MFI* beyond which a significant adverse effect on the property is observed. *MFI* then becomes a convenient method for indicating the value of the reprocessed material and whether it is viable for further reprocessing. Once it is ascertained that the reprocessed material still has potential for use, it is necessary to obtain the rheogram for the material in order to make the proper choice of processing conditions. This can be done with the help of the master curves by using the following procedure.

(i) The *MFI* of the reprocessed material is first to be obtained under ASTM specified temperature and loading conditions.

(ii) In cases when the loading condition is different from that specified in the master curve, a new value of *MFI* is to be obtained using equation (9) at the loading condition of the master curve.

(iii) When the specified temperature condition is different from the condition at which the rheogram is desired, equation (8) is to be used for calculating the effective *MFI* value at the desired temperature.

(iv) The correct value of the effective *MFI* is then to be used in the master curve, and the viscosity versus shear rate curve can easily be generated by mere substitution.

CONCLUSION

The unifying approach has been successfully demonstrated to coalesce rheograms of resin grades with different shearing history, in terms of a modified viscosity function ($\eta \times MFI$) and a modified shear rate ($\dot{\gamma}/MFI$). The master curve so generated can be used for estimating the rheograms of the polymer waste at any required temperature merely from knowledge of *MFI* and the glass transition temperature of the polymer. This method would then be a very handy aid for plastics processors, especially for assessing the potential and processing conditions for reprocessing plastic scraps and in-plant waste. Though limited data have been analysed herein, the

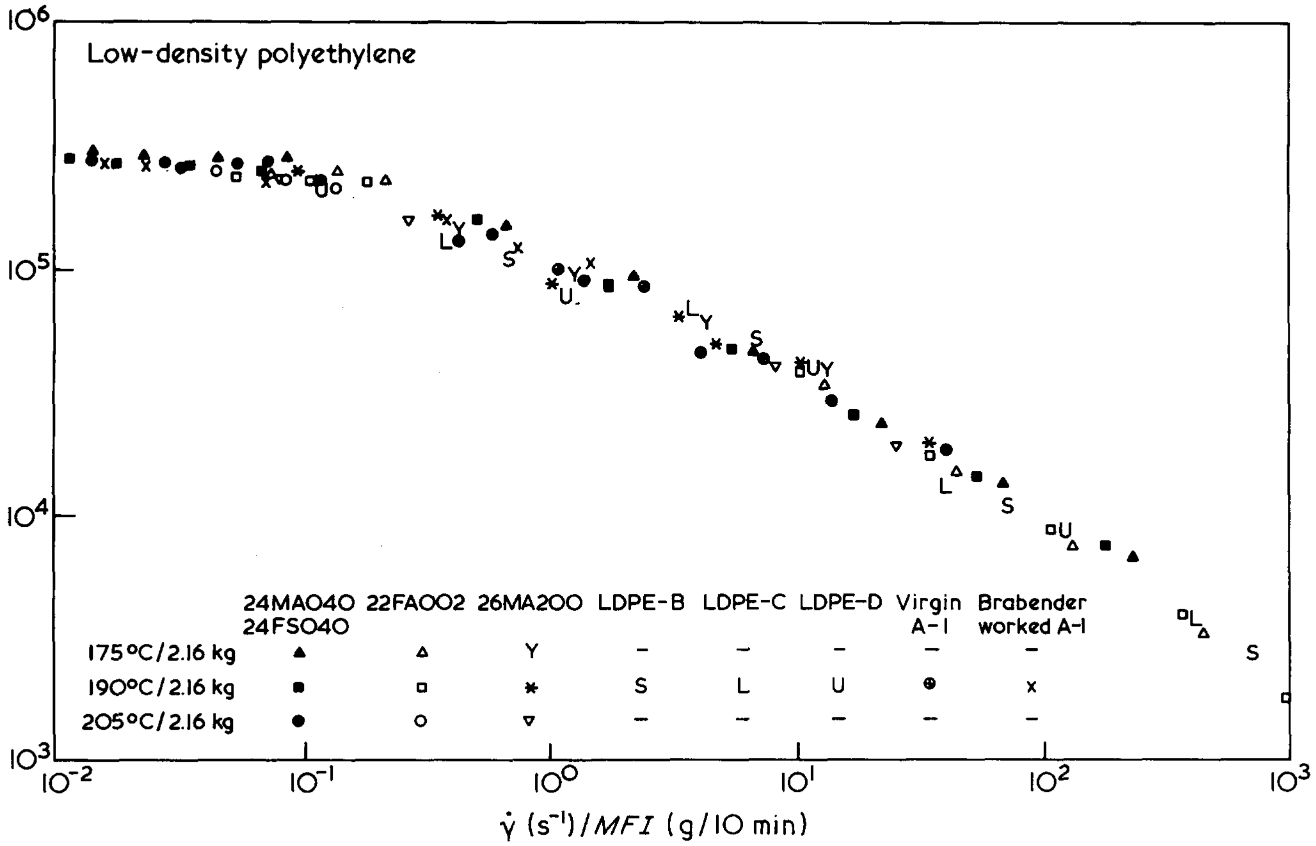

Figure 6 Viscosity master curve for low-density polyethylene at 2.16 kg test load condition taken from ref.17

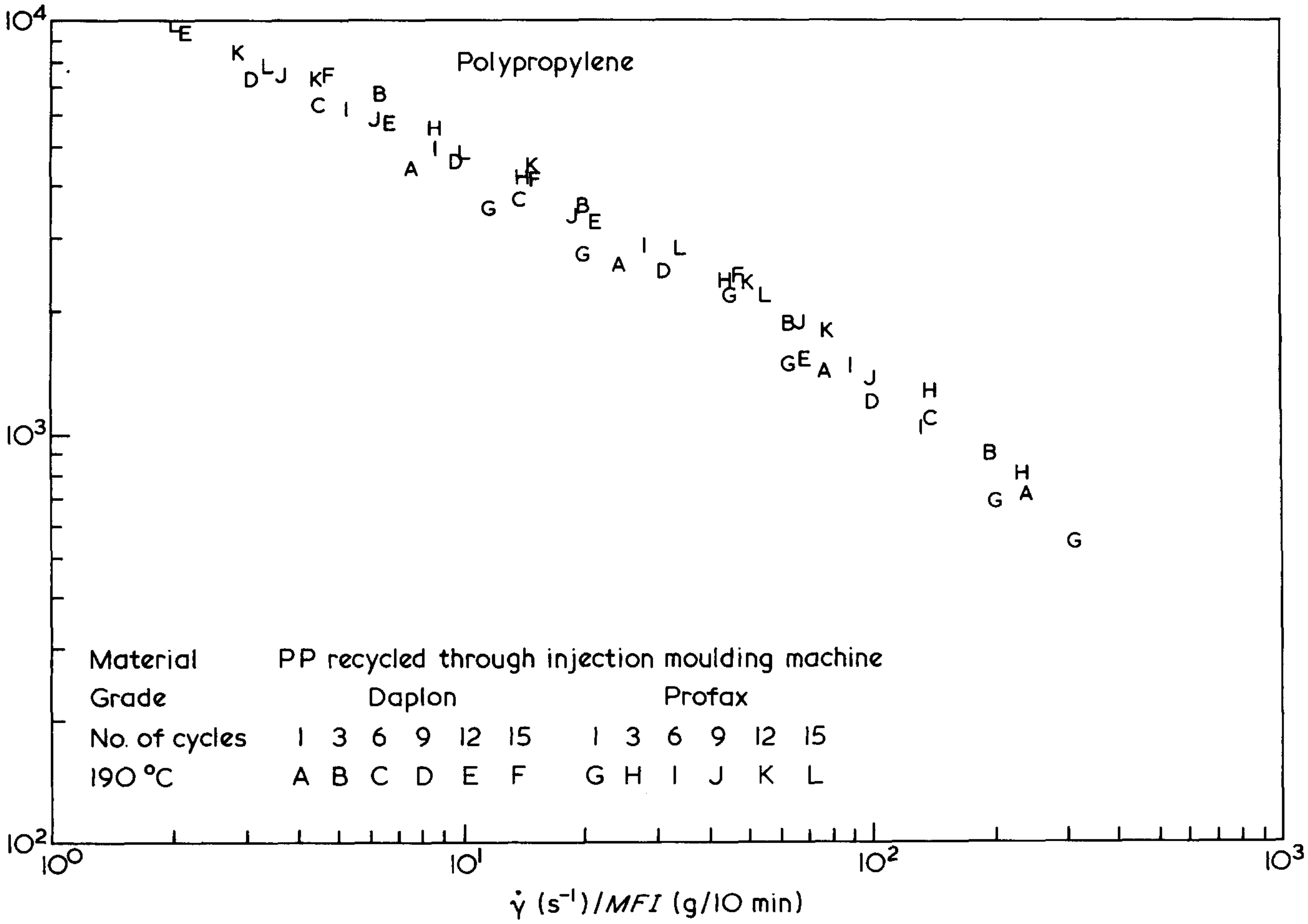

Figure 7 Viscosity master curve for reprocessed polypropylene at 2.16 kg test load condition

Table 2 Details of the LDPE grades used in *Figure 6*

Polymer	Grade	*MFI* (temperature, °C/ load condition, kg)	Data temp. (°C)	No.of data points (shear rate range, s^{-1})	Source ref.
LDPE	Indothene 22FA002	0.16[a] (175/2.16)	175	9 (0.01–1000)	17
		0.2[b] (190/2.16)	190	9 (0.01–1000)	17
		0.25[a] (205/2.16)	205	9 (0.01–1000)	17
	Indothene 24MA040	3.0[a] (175/2.16)	175	10 (0.01–1000)	17
		4.0[b] (190/2.16)	190	10 (0.01–1000)	17
		5.0[a] (205/2.16)	205	10 (0.01–1000)	17
	Indothene 24FS040	3.0[a] (175/2.16)	175	10 (0.01–1000)	17
		4.0[b] (190/2.16)	190	10 (0.01–1000)	17
		5.0[a] (205/2.16)	205	10 (0.01–1000)	17
	Indothene 26MA200	16[a] (175/2.16)	175	10 (0.01–1000)	17
		20[b] (190/2.16)	190	10 (0.01–1000)	17
		25[a] (205/2.16)	205	10 (0.01–1000)	17
	LDPE B	1.2[b] (190/2.16)	190	4 (0.01–1000)	20
	LDPE C	2.1[b] (190/2.16)	190	4 (0.01–1000)	20
	LDPE D	6.9[b] (190/2.16)	190	4 (0.01–1000)	20
	LDPE A-1	0.8[c] (190/2.16)	190	7 (0.03–6)	5
	LDPE A1 (Brabender worked sample for 60 min)	1.3[c] (190/2.16)	190	7 (0.03–6)	5

[a] *MFI* value calculated from equation (7) knowing the *MFI* as per *b* and T_g of the polymer
[b] *MFI* value given by manufacturer under ASTM testing conditions
[c] *MFI* value read out from τ versus $\dot{\gamma}$ curve using equations (3) and (4)

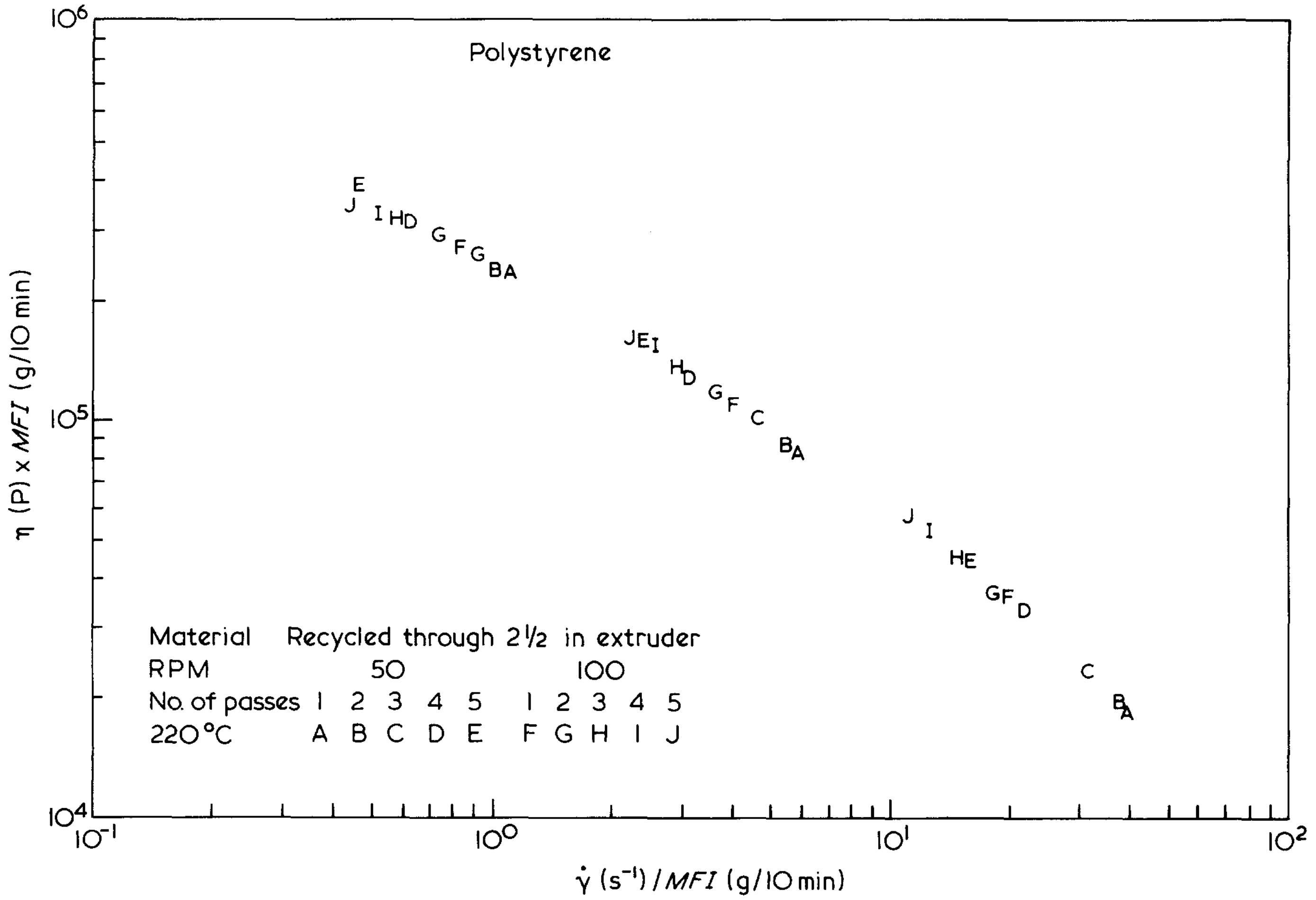

Figure 8 Viscosity master curve for reprocessed polystyrene at 5.0 kg test ,oad condition

technique is applicable for all polymers and the master curves generated earlier by the authors for virgin polymers of different types could all be used for generating rheograms of polymer waste from knowledge of the melt flow index of the waste material.

NOMENCLATURE

F	force due to the weight of piston and load
l	length of nozzle
L	weight of piston and load (in kg)
n	pseudoplasticity index given by the slope of the shear stress versus shear rate curve on log–log scale
Q	flow rate
R_N	radius of nozzle
R_P	radius of piston
T_1	temperature (K) at condition 1
T_2	temperature (K) at condition 2
T_g	glass transition temperature (K)
T_S	standard reference temperature (K) equal to T_g+50
$\dot{\gamma}$	shear rate
ρ	density of the polymer
η	apparent viscosity
τ	shear stress

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APPENDIX

Table A1 Standard testing conditions of temperature and load as per ASTM 1238 for the polymers studied in the test

Polymer	Temperature (°C)	Load (Piston + weight) (kg)	Approximate pressure (kg cm^{-2})	(psi)
Polyethylene	125	0.325	0.46	6.50
	125	2.160	3.04	43.25
	190	0.325	0.46	6.50
	190	2.160	3.04	43.25
	190	10.000	14.06	200.00
	190	21.600	30.40	432.50
Polypropylene	230	2.160	3.04	43.25
Polystyrene	190	5.000	7.03	100.00
	200	5.000	7.03	100.00
	230	1.200	1.69	24.00
	230	3.800	5.34	76.00

Table A2 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