

Dependence of Bulk Viscosities (Mooney and Wallace) on Molecular Parameters of Natural Rubber

S. NAIR

The dependence of bulk viscosities (Mooney viscosity and Wallace plasticity) on molecular parameters of natural rubber was studied by comparing the characteristics of rubbers from twelve clones. For total solids films, Mooney viscosity and Wallace plasticity showed a linear relationship; they were also related (linearly, in most cases) to the molecular parameters of intrinsic viscosity, number-average and weight-average molecular weights, for normal as well as viscosity-stabilised rubbers. The relationships between bulk viscosities and molecular parameters were not so well defined for crepe rubbers prepared from the same source materials, probably due to the variations in the rates of chain scission and cross-linking during processing.

The bulk viscosity of rubber is an important property usually ascertained with the Wallace and Mooney instruments in quality control tests. The Wallace plastimeter is used for measuring the plasticity retention index (PRI) and its importance is described by BATEMAN AND SEKHAR (1966), while the Mooney viscometer is used mainly for measuring and checking the extent of viscosity stabilisation in CV (stabilised or controlled viscosity) rubbers. The two viscosities are related in a linear relation (Figure 1) and this relationship has been verified by O'CONNELL (1966) in the case of some 120 clones.

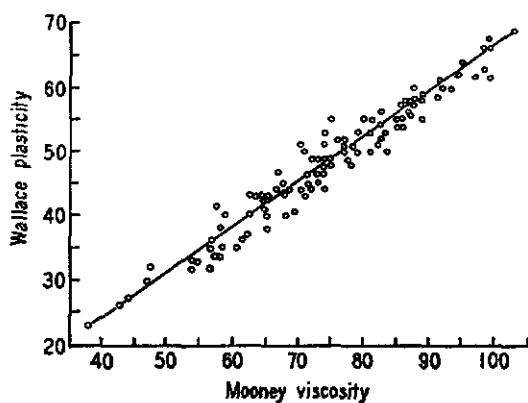


Figure 1. Wallace Plasticity vs Mooney viscosity for different clonal rubbers.

The correlation coefficient is 0.97 and the relationship is in accordance with the equation

$$P_0 = -3.19 + 0.691 V_R$$

where P_0 is the initial Wallace plasticity reading and V_R is the Mooney viscosity.

The study was undertaken to examine the reason for the variation in bulk viscosities of rubbers from different clones.

This variation in the bulk viscosities of rubbers from different clones causes serious problems in the preparation of viscosity-stabilised (CV) rubbers. Narrow ranges (55-65 Mooney) in the viscosity of the final rubber are only obtained by a judicious blending of the latices. Rubbers with Mooney viscosities much above 65 units require pre-mastication and hence have no advantage in processing over ordinary unstabilised rubbers. The correlations between bulk viscosities and molecular parameters have been examined in the study to determine if the variations in bulk viscosities are dependent on the size of the rubber molecule itself. If this is so, any attempt to change the bulk viscosity of a given batch of rubber would necessarily require an alteration in the size of the rubber molecule. Other methods of altering the viscosity by addition of oil (e.g., low viscosity (LV) rubbers) and use of other additives exist but are not relevant to this discussion.

The bulk viscosities relate to the properties of an entangled mass of polymer molecules as

a whole, while the molecular parameters apply only to the properties of an individual molecule.

The molecular parameters chosen for investigation were: (a) intrinsic viscosity ($[\eta]$); (b) number average molecular weight (M_n); (c) weight average molecular weight (M_w); (d) radius of gyration (ρ_z); and (e) mean square distance of separation between chain ends of the molecule (\bar{r}^2).

Intrinsic viscosity is a measure of the extended configuration of a single molecule in a dilute solution (FLORY, 1963). The degree of expansion of the molecule and its distance of separation from its neighbours depend on the solvent and the concentration of the solution. M_n is obtained by extrapolating the data from osmotic pressure measurements while M_w , ρ_z and \bar{r}^2 are obtained by a Zimm plot (ZIMM, 1948) with data obtained from a light-scattering photometer (NAIR, 1968). Previous studies had shown that a close relationship existed between Mooney viscosity and intrinsic viscosity for masticated rubbers (STERN, 1950), while no such relationship was found in the case of unmasticated rubbers (BLOOMFIELD, 1960).

EXPERIMENTAL

Rubbers from twelve clones were obtained from the Experiment Station of the Rubber

Research Institute of Malaya, the collections being made over a two-week period.

The viscosity-stabilised (CV) rubbers were obtained by adding 0.15% w/w hydroxylamine hydrochloride based on the rubber content in latex. The natural latices were filmed directly on to glass plates and left to dry, while those mixed with hydroxylamine hydrochloride were left standing for a few hours prior to crepeing.

All values of intrinsic viscosity were obtained by extra-polation according to the method of SCHULZ AND BLASCHKE (1941).

The number average molecular weights (M_n) were measured on a Mechrolab model 501 membrane osmometer. The osmotic measurements were done within the concentration range of 0.001–0.007 g/ml, since at lower concentrations the A_2 values obtained were almost zero, resulting in anomalous values for M_n being obtained. A typical M_n determination is set out in Table 1.

The osmotic pressure readings were repeated until two consecutive readings within 0.02 cm were obtained. The graph of $(\pi/c)^{1/2}$ vs. c (Figure 2) shows that the experimental points do not deviate very much from being on a straight line (correlation coefficient: 0.999). The intercept and gradient for calculating M_n and A_2 were obtained by the method of least squares.

TABLE 1. OSMOTIC MEASUREMENTS AND RESULTING M_n AND A_2 OF RRIM 501

Concentration (g/ml)	Osmotic pressure				π (P-P ₀)	π/c	$(\pi/c)^{1/2}$
	P ₀ (solvent)	P ₁	P ₂	P (average)			
0.001482	18.34	18.55	18.56	18.555	0.215	145.1	12.04
0.002963	18.34	18.85	18.85	18.85	0.51	172.1	13.11
0.004445	18.34	19.27	19.29	19.28	0.94	211.5	14.55
0.005926	18.34	19.82	19.83	19.825	1.485	250.6	15.83

(π/c) at $c=0$

114

from graph

M_n

255 000

of $(\pi/c)^{1/2}$ vs c .

A_2

6.66×10^{-4}

(See Figure 2)

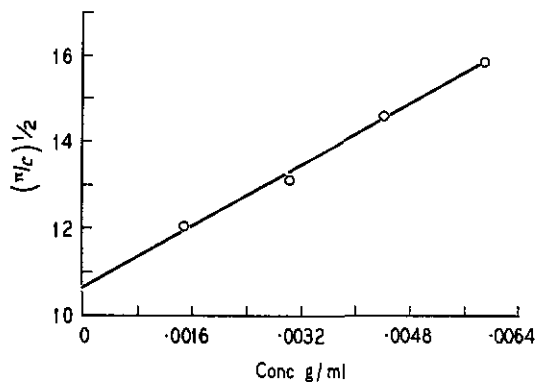


Figure 2. Graph of $(\pi/c)^{1/2}$ vs. c for RRIM 501 in toluene.

The light scattering measurements were carried out with a Brice Phoenix light scattering instrument. The solvent used was tetrahydrofuran and the solution was clarified by ultracentrifugation, followed by filtering through

sintered glass filters of various porosities. Figure 3 gives a typical Zimm plot from which the various molecular parameters are calculated. The intercept of the Zimm plot from which M_w is calculated decreases as the molecular weight increases.

Correlation coefficients were calculated for the various graphs and the regression lines were also drawn in cases where the linear relationships were satisfactory.

RESULTS AND DISCUSSION

Three sets of experimental data were obtained from the following:

- (i) total solids films of rubbers from the twelve clones (collected in November 1967);
- (ii) total solids films of normal and CV rubbers of the twelve clones (collected in March 1968); and
- (iii) normal and CV crepes of rubbers of the twelve clones (collected in May 1968).

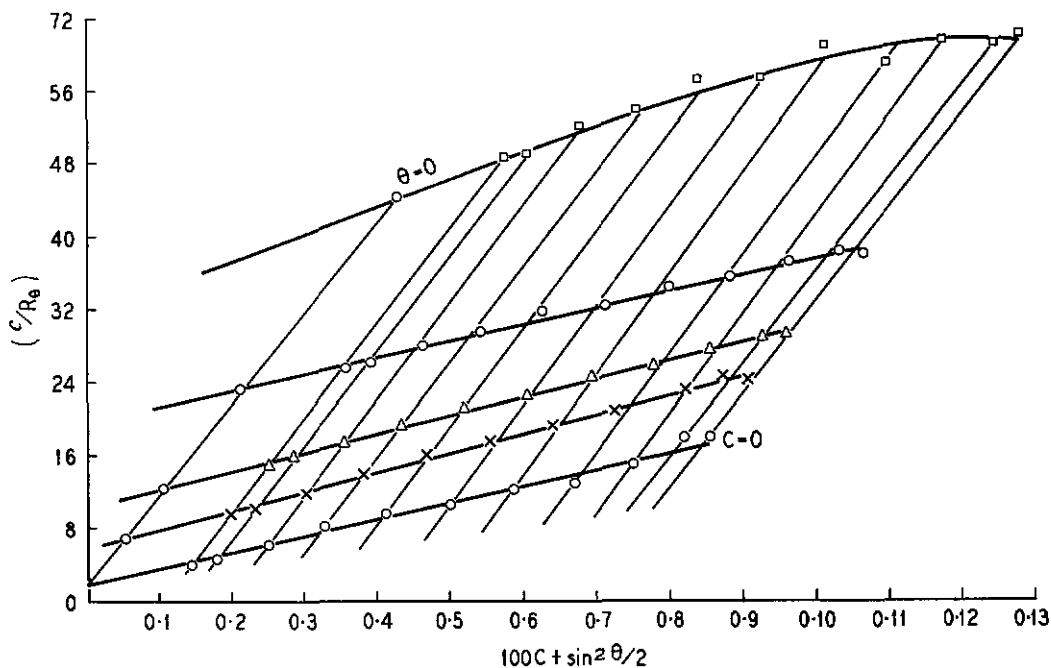


Figure 3. Zimm plot of RRIM 605.

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TABLE 2. INTRINSIC AND BULK VISCOSITIES OF TWELVE CLONAL RUBBERS

Clone	Total solids film				Cuplump crepe		
	Intrinsic viscosity $[\eta]$	Mooney viscosity (V_R)	Unaged Wallace (P_0)	Aged Wallace (P_{30})	V_R	P_0	P_{30}
RRIM 501	6.34	39	28	29	69.5	47	35
RRIM 513	6.96	59.5	40	40	76.5	49	42
RRIM 519	7.01	53	36	41.5	89	59	53
RRIM 605	7.20	56.5	41	38	85	62	46
RRIM 607	7.65	78	55	50	101	73	57
GT 1	7.71	68.5	55	46	86.5	65	61
RRIM 623	8.27	67	54	50	77	55.5	52
PB 5/63	8.39	82.5	57	53.5	97	71	58
RRIM 628	8.57	96.5	66	56	108	74	62
PB 86	8.62	81	54	53	97.5	72	57
Tjir 1	8.73	73	55	54	87	68	59
PB 5/51	9.30	86.5	60	52.5	87.5	73	58

The collection made in March 1968 is significant because of wintering then in vogue.

The bulk and intrinsic viscosities of the twelve clonal rubbers from the first collection are listed in Table 2.

A plot of intrinsic $[\eta]$ and Mooney viscosities (Figure 4) shows that a relationship does

exist between them. The correlation coefficient is 0.87, but there is some scatter of the points probably arising from the differences in molecular weight distribution, the presence of non-rubbers in the latex and its gel content. The influence of these factors on the Mooney viscosities is not yet known. Figure 5 shows a

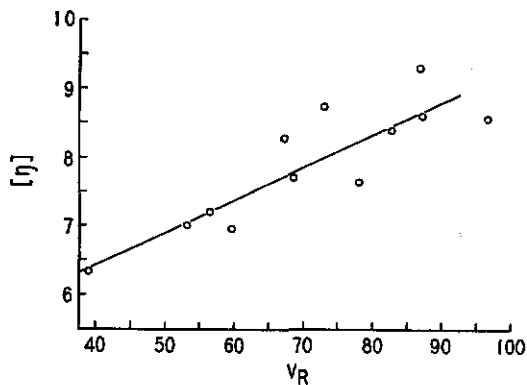


Figure 4. $[\eta]$ vs. V_R (T.S. films).

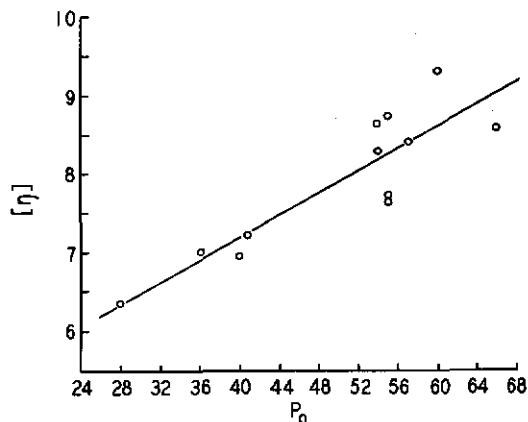


Figure 5. $[\eta]$ vs. P_0 (T.S. films).

similar relationship between initial Wallace plasticity (P_0) and intrinsic viscosity $[\eta]$, the correlation coefficient being 0.89 in this case. The relationship between $[\eta]$ and P_0 is only to be expected once a relationship between $[\eta]$ and V_R has been established, since V_R and P_0 are themselves linearly related as shown earlier (Figure 1). An attempt to plot $[\eta]$ of the total solids film against either the aged Wallace plasticity of the film or any of the cuplump crepe viscosities did not result in any good correlation. The unknown amount of scission, cross-linking and hardening effects are believed to be responsible here in altering the relationship. The PRI (ratio of unaged to aged Wallace plasticities expressed as a percentage) of the total solids films is higher than that of the cuplump crepes, as is generally known. This high PRI of total solids films is due to simultaneous chain reformation and chain scission, giving relatively high values for P_{30} (aged plasticity). On the other hand, some hardening has already occurred in the cuplump rubbers so that, during ageing, chain scission takes place without much compensation through hardening. This results in the final low plasticity readings.

The dependence of the number-average molecular weight on the bulk viscosities is next examined (Table 3).

TABLE 3. OSMOTIC PARAMETERS OF TWELVE CLONES

Clones	$M_n \times 10^{-5}$	Second virial coefficient $A_2 \times 10^{-4}$	$\frac{1}{A_2} \times 10^4$
RRIM 501	3.37	5.37	0.186
RRIM 513	4.34	5.70	0.175
RRIM 519	4.79	5.62	0.178
RRIM 605	5.25	5.28	0.189
RRIM 607	7.23	4.27	0.234
GT 1	10.00	4.03	0.248
RRIM 623	6.18	5.31	0.188
PB 5/63	12.39	3.77	0.265
RRIM 628	9.30	3.90	0.256
PB 86	11.21	3.85	0.259
Tjir 1	6.04	4.81	0.208
PB 5/51	10.00	4.03	0.248

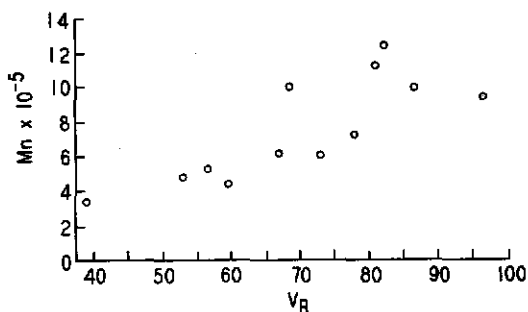


Figure 6. M_n vs. V_R (T.S. films).

The relationship between M_n and V_R is depicted in Figure 6 and this is different from that between $[\eta]$ and V_R because these molecular indices— M_n and $[\eta]$ are quite different for wide distributions (NAIR AND SEKHAR, 1967). The correlation coefficient here is 0.8 and a curvilinear relationship is indicated. The intrinsic viscosity $[\eta]$ corresponds to an average molecular weight greater than the number-average molecular weight but lower than the weight-average molecular weight. The plot of M_n vs $1/A_2$ (Figure 7) shows an inverse dependence of these two parameters—similar to such relationships found for other polymers (FLORY, 1953). The correlation coefficient of the two variables in Figure 7 is 0.95.

The drawing of Zimm plots and the extrapolation to obtain the intercepts for calculation

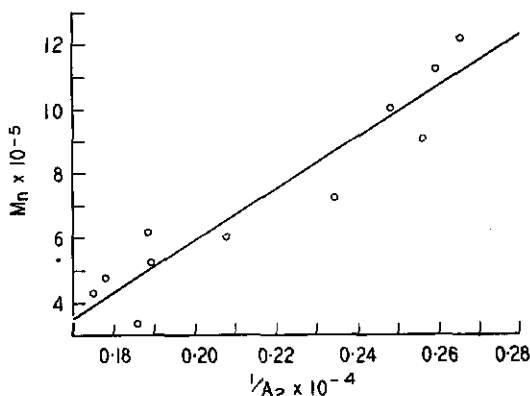


Figure 7. M_n vs. $1/A_2$ (T.S. films).

TABLE 4. LIGHT-SCATTERING DATA FOR TWELVE CLONES

Clone	M_w $\times 10^{-6}$	A_2 $\times 10^4$	ρ_z ($^\circ$)	$(\bar{r}^2/M_w)^{\frac{1}{2}}$ $\times 10^8$
RRIM 501	3.46	0.06	924.8	1.218
RRIM 513	2.71	4.10	1473	2.191
RRIM 519	3.01	3.81	1555	2.194
RRIM 605	4.52	6.10	1746	2.011
RRIM 607	4.28	2.80	1744	2.064
GT 1	3.39	5.63	1611	2.143
RRIM 623	3.39	5.63	1585	2.108
PB 5/63	8.14	5.51	2017	1.732
RRIM 628	10.17	3.03	1932	1.484
PB 86	4.07	2.58	1438	1.746
Tjir 1	3.87	3.16	1589	1.977
PB 5/51	6.78	5.24	1830	1.721

of molecular weights are subject to large errors in the very high molecular weight range. From Table 4 it is apparent that there is no definite trend in the M_w values, but the radius of gyration (ρ_z) shows some relationship with V_R for the different clones. The Zimm plot for RRIM 501 is slightly different from the others and the A_2 value obtained seems somewhat suspect. From the ratios in the last column, it is also apparent that RRIM 501 has a very low value—indicating some anomaly in the Zimm plot for this clone.

TABLE 5. MOLECULAR PARAMETERS AND WALLACE PLASTICITIES (TOTAL SOLIDS FILMS) COLLECTION OF MARCH 1968

Clone	$[\eta]$	M_n $\times 10^{-5}$	A_2 $\times 10^4$	P_0
RRIM 501	5.63	2.55	6.66	32
RRIM 513	5.53	27.09	4.58	43
RRIM 519	5.99	3.91	6.28	41
RRIM 605	6.30	5.05	5.82	46
RRIM 607	7.63	9.13	4.33	64
GT 1	6.91	11.66	4.82	51.5
RRIM 623	6.68	7.12	5.09	50
PB 5/63	8.40	20.18	3.48	65
RRIM 628	7.60	12.14	3.84	63
PB 86	8.51	8.10	4.70	75
Tjir 1	8.63	13.77	3.52	70.5
PB 5/51	7.18	10.78	4.45	67.5

It can, however, be concluded from this experiment that Mooney viscosities of clonal rubbers are related to their molecular sizes. RRIM 501 seems to have very low Mooney viscosity levels consistently and also comparatively very small molecular parameters. No wonder it has always been known in the industry as a 'soft' rubber!

In another experiment, the correlation was extended to include CV rubbers of the same twelve clones, though the collections were all made during the wintering season. In this experiment no light-scattering measurement was made to save time and labour and also because of the large errors involved in the measurements. Table 5 lists the molecular parameters of the normal latices of the twelve clones; in Table 6, the values given are for latices of the same clones after the addition of hydroxylamine hydrochloride to obtain viscosity stabilisation (CV).

Table 5 listing the molecular parameters of the twelve clones shows that wintering has changed the relative order of the clones in regard to their intrinsic viscosity. It is also seen that M_n and P_0 values seem to agree except for the very high value of M_n for RRIM 513. The A_2 values, however, have the same inverse relationship with M_n as in the previous experiment. A curvilinear relationship between $[\eta]$ and P_0 is also noticed.

It is noticed from Table 6 that $[\eta]$, M_n and P_0 readings are spread over a lower and smaller

TABLE 6. MOLECULAR PARAMETERS AND WALLACE PLASTICITIES OF CV RUBBERS (TOTAL SOLIDS FILMS)

Clones	$[\eta]$	M_n $\times 10^{-5}$	A_2 $\times 10^4$	P_0
RRIM 501	5.16	1.75	7.09	20
RRIM 513	5.51	8.66	5.32	37
RRIM 519	5.88	5.62	5.95	37
RRIM 605	5.70	4.50	7.64	31
RRIM 607	6.82	10.38	6.71	42
GT 1	6.18	5.62	6.96	33
RRIM 623	6.70	9.64	5.26	37
PB 5/63	7.29	14.39	4.95	51
RRIM 628	7.52	8.10	4.80	47
PB 86	6.85	11.21	5.34	42
Tjir 1	7.56	9.64	2.63	53
PB 5/51	6.89	4.33	5.44	57

range than the films without the addition of hydroxylamine. The relation between $[\eta]$ and P_o (unaged Wallace) can be represented by a straight line (Figure 8) with a correlation coefficient of 0.85, while the relation between M_n and P_o is less definite and the point for PB 5/51 is too far out. Since the Mooney viscosities of this set of samples were mixed up, a fresh lot of samples in crepe form (instead of total solids films as in the previous two experiments) was prepared.

From Table 7 it is seen that the correlation between $[\eta]$ and V_R and P_o is not as good as in the previous cases (Figures 3, 5 and 8). RRIM 513 has the lowest intrinsic viscosity but not the lowest V_R and P_o values. The rubber from another clone with anomalous values is PB 86 which has the highest intrinsic viscosity but not correspondingly highest V_R . RRIM 501, which in all previous collections had the lowest value for all three parameters, has an intrinsic viscosity higher than that of two other clones. The only factor that could have any effect during the preparation of the crepes is crepeing itself, which is not unlike mastication. The differences in behaviour between total solids films and crepes could be accounted for by the processing effect which affects different clones differently. For some clones it is possible that any free radicals produced on the chains by rupture during processing recombine to give branched molecules, while in others the scavenging effect of oxygen

TABLE 7. INTRINSIC AND BULK VISCOSITIES OF CLONAL CREPES

Clone	Ordinary crepe			CV crepe		
	$[\eta]$	V_R	P_o	$[\eta]$	V_R	P_o
RRIM 501	6.65	41.8	32	6.34	35.5	26
RRIM 513	5.95	74	44	5.78	67.5	38
RRIM 519	6.51	66	41.5	6.24	54.3	33.5
RRIM 605	6.36	61	38.5	6.12	51	32.5
RRIM 607	7.72	74.5	51	7.65	70	44
GT 1	7.59	70.5	45	7.26	65.8	41
RRIM 623	6.51	63	43	7.44	56.5	39
PB 5/63	7.17	78	52.5	7.06	76.3	47
RRIM 628	8.35	79	57	8.25	77.5	52
PB 86	9.35	77	55	8.37	66	44
Tjr 1	7.28	86	57	7.41	78.8	54
PB 5/51	8.50	85.5	56.5	8.01	80.0	53

is more predominant. It is also possible that the non-rubbers have some contributory effect on such scavenging efficiency of oxygen.

CONCLUSIONS

The intrinsic viscosity and number-average molecular weight have fair correlation with Mooney viscosity and Wallace plasticity for clonal rubber as evident from the results obtained for the twelve clones examined. The radius of gyration obtained from light-scattering measurements shows reasonable agreement with the bulk viscosities although there is not as good an agreement between weight-average molecular weight and bulk viscosities for the rubbers from the twelve clones. These correlations also hold for viscosity-stabilised (CV) rubbers. For crepes of both normal and CV rubbers prepared from latices of these twelve clones, however, the correlation between molecular size and bulk viscosities is not as good.

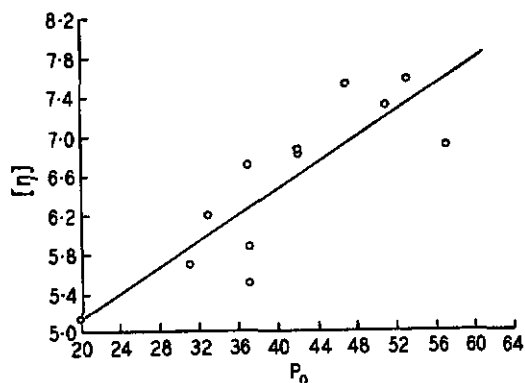


Figure 8. $[\eta]$ vs. P_o (C.V. T.S. films).

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Chemistry Division
Rubber Research Institute of Malaya
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