

# Viscosity Measurements on Concentrated Natural Rubber Solutions after Mastication and Sunlight Degradation

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*The relationship between viscosity and speed of rotation of spindle of a Brookfield viscometer was found to be curvilinear for concentrated natural rubber solutions in toluene. Three exponential relations between viscosity,  $\nu$  and speed of rotation of spindle,  $x$  were examined and the one found to give the best fit for both masticated and sunlight degraded rubbers is  $\nu = a_1 - b_1 \log x$ . The constants,  $a_1$  and  $b_1$  were found to be related to concentration  $c$  by the relations  $a_1 = a_1 c^{\beta_1}$  and  $b_1 = a_2 c^{\beta_2}$ . Both  $\beta_1$  and  $\beta_2$  appeared to have constant values while  $a_1$  and  $a_2$  varied with amount of degradation.*

Rubber through the medium of concentrated solutions is used in a variety of applications ranging from adhesives and paints to textile coatings and this study was undertaken to examine their flow behaviour.

The viscosity as measured by the Brookfield viscometer indicates the bulk behaviour of many entangled molecules in solution while the intrinsic viscosity measurement virtually gives the behaviour of an individual molecule in solution. This is shown by the fact that in a good solvent the individual polymer molecule has an expanded configuration and hence, a high intrinsic viscosity while in a poor solvent the intrinsic viscosity is small due to the compacting of the molecules. The viscosity as given by the Brookfield viscometer on the other hand has a high value for poor solvents and a low value for good solvents.

Mastication and sunlight degradation have been chosen because of (i) their different mechanisms and (ii) their importance. Mastication degrades polymer molecules by shear action and is specific to the molecules of longer chain lengths while sunlight degrades the molecules randomly irrespective of chain length. A three-peaked distribution is reduced to a unimodal one by mastication while in sunlight degradation the three-peaked distribution is retained (NAIR, 1966). Mastication is a process employ-

ed throughout the rubber industry and its importance needs no elaboration. Sunlight is a very potent degradative agent for natural rubber in its raw state and the consequences of this effect are carried over into the vulcanised product as manifested by inferior physical properties and tyre failure (O'CONNELL, 1966).

Some workers have studied the use of the Brookfield viscometer with concentrated solutions. REYNOLDS AND GEBHART (1960) have studied the effect of solvent properties on the viscosity of concentrated solutions. LEAMAN (1951) has made an exhaustive literature survey and has given some plots of log viscosity against log rate of shear but did not derive any relationship. BACK (1959) has suggested the general relation  $\nu = b x^a$  for a number of polymers and for a series of forty readings, the calculated viscosities agree within  $\pm 6\%$  of the observed values.

## EXPERIMENTAL

Samples of natural rubber masticated and sunlight degraded to different extents together with control samples were dissolved in toluene to give concentrated solutions, varying from 4 to 10% concentration. Mastication was carried out on a cold mill for 4, 8, 12, 16, 20 and 30 passes while time of exposure to sunlight varied for 5, 10, 20 and 40 hours. The solutions were

then thermostated at  $25 \pm 0.1^\circ\text{C}$  by immersing the containers with the solutions in a thermostat bath and the Brookfield viscosities at each concentration measured at 6, 12, 30 and 60 revolutions per minute. Spindles 1, 2, 3 and 4 were used to obtain accurate readings at any given concentration. The guard ring was used during the measurements and great care was taken to ensure that no bubbles were trapped beneath the spindles. No special precautions were taken to exclude oxygen since the non-rubbers present would minimise any oxidation. All readings with the Brookfield synchro-electric viscometer were repeated to avoid any inconsistent results.

The relationship between viscosity ( $v$ ) and speed of rotation of spindle ( $x$ ) is curvilinear for both masticated and sunlight degraded rubbers (Figure 1). Three curvilinear equations of the exponential type were fitted to the experimental points to compare the fits obtained.

$$v = a_1 - b_1 \log x \quad \dots\dots(1)$$

$$\log v = a_2 - b_2 \log x \quad \dots\dots(2)$$

$$\log v = a_3 - b_3 x \quad \dots\dots(3)$$

Equation (2) is similar to the one used by BACK (1959). To compare the goodness of fit obtaining of the three equations, departures of the observed and expected viscosities were calculated. The statistical calculations confirm the visual observation (Figure 1) that equation (1) gives the best fit and it was found that the constants  $a_1$  and  $b_1$  varied with concentration. The nature of their relationships was examined by fitting a linear law to the double logarithmic plot of the constants and concentrations [Figures 2(a)-(d)]. It was found that the general law relating viscosity ( $v$ ) to speed of rotation ( $x$ ) and concentration ( $c$ ) is of the form

$$v = a_1 c^{\beta_1} - a_2 c^{\beta_2} \log x \quad \dots\dots(4)$$

### RESULTS AND DISCUSSIONS

It has been observed that on an average an error of  $\pm 10\%$  is likely to result for masticated rubbers and an error of  $\pm 15\%$  for sunlight degraded rubbers when the general equation (4) is used to estimate viscosities for given values of speed of rotation of spindles and concentrations within the range of observed data.

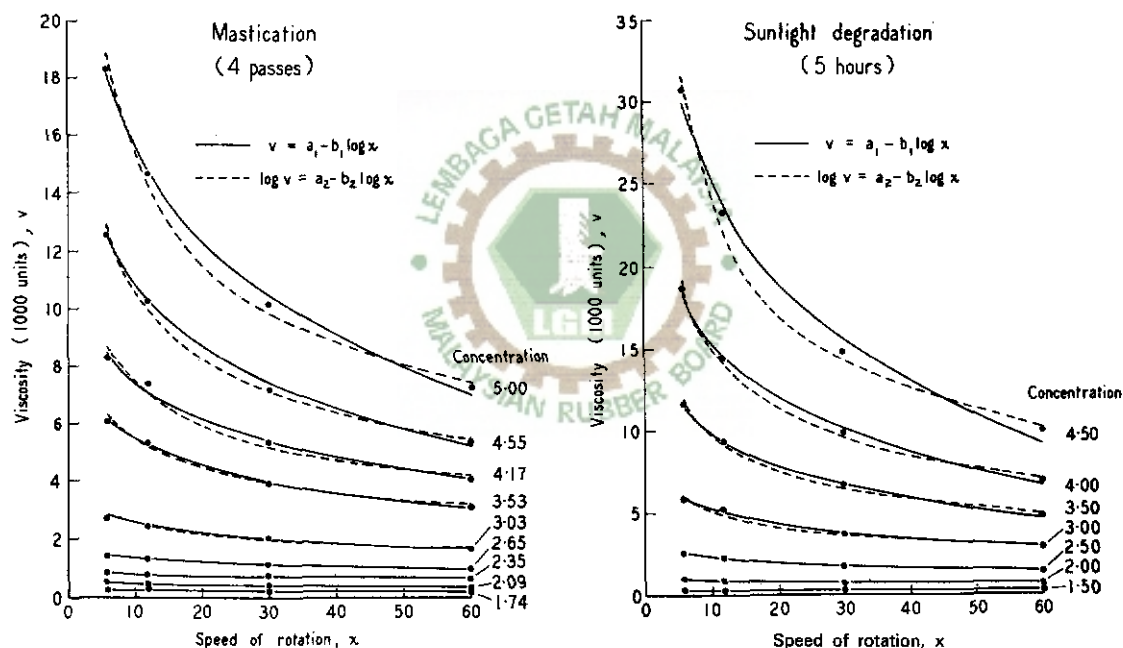
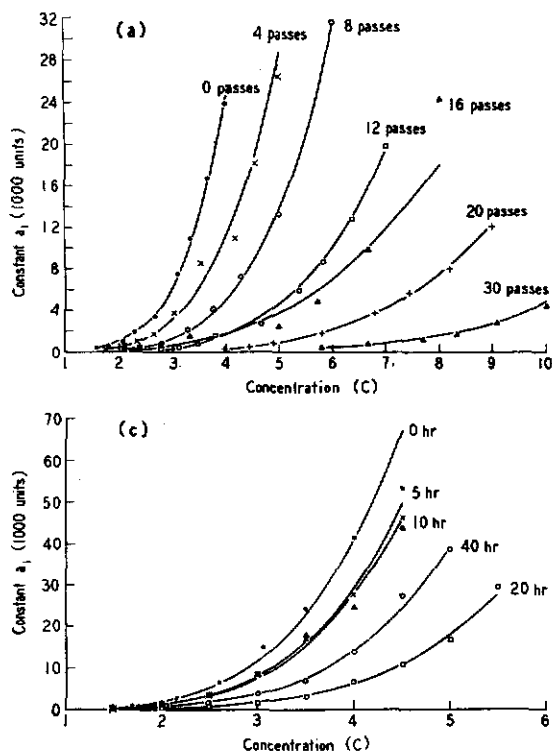
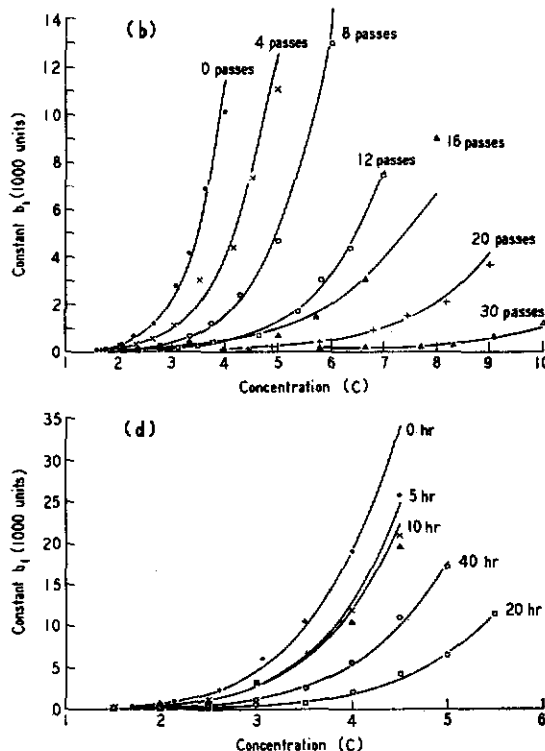


Figure 1. Relationship between viscosity ( $v$ ) and speed of rotation of spindle ( $x$ ) for different concentrations for masticated and sunlight degraded rubbers.



Figures 2(a) and 2(b). Relationships between the constants ' $a_1$ ' and ' $b_1$ ' of the equation  $v = a_1 - b_1 \log x$  and concentration ' $c$ ' for different passes for masticated rubbers.

An examination of Tables 1(a) and 1(b) shows that  $\beta_1$  and  $\beta_2$  to be constant for both masticated and sunlight samples. The average values for masticated rubbers are  $\beta_1 = 4.47$  and



Figures 2(c) and 2(d). Relationships between the constants ' $a_1$ ' and ' $b_1$ ' of the equation  $v = a_1 - b_1 \log x$  and concentration ' $c$ ' for different no. of hours in sunlight for degraded rubbers.

$\beta_2 = 5.59$  (16 passes omitted) while for sunlight they are  $\beta_1 = 4.60$  and  $\beta_2 = 5.48$  [Tables 1(a) and 1(b)]. Since these values are very near to each other in both the cases in spite of the

TABLE 1(a) RELATIONSHIPS OF THE CONSTANTS ' $a_1$ ' AND ' $b_1$ ' OF  $v = a_1 - b_1 \log x$  WITH CONCENTRATION ' $c$ ' FOR DIFFERENT NO. OF PASSES (FOR MASTICATED RUBBERS)

| Passes | $a_1 = a_1 c^{\beta_1}$ | $b_1 = a_2 c^{\beta_2}$ | Using common values of $\beta_1$ and $\beta_2$ |        | ( $\eta$ ) |
|--------|-------------------------|-------------------------|------------------------------------------------|--------|------------|
|        |                         |                         | $a_1$                                          | $a_2$  |            |
| 0      | $38.50 c^{4.68}$        | $4.42 c^{5.67}$         | 46.51                                          | 4.76   | 7.65       |
| 4      | $26.80 c^{4.84}$        | $3.19 c^{5.15}$         | 23.32                                          | 1.95   | 6.50       |
| 8      | $9.19 c^{4.55}$         | $0.619 c^{5.61}$        | 10.20                                          | 0.636  | 5.52       |
| 12     | $3.76 c^{4.89}$         | $0.150 c^{5.57}$        | 3.34                                           | 0.145  | 5.30       |
| 16     | $21.46 c^{3.24}$        | $1.42 c^{4.08}$         | —                                              | —      | —          |
| 20     | $0.865 c^{4.85}$        | $0.0083 c^{5.98}$       | 0.704                                          | 0.0168 | 3.50       |
| 30     | $0.105 c^{4.61}$        | $0.0004 c^{6.89}$       | 0.141                                          | 0.0021 | 2.80       |

Note: common values of  $\beta_1$  and  $\beta_2$  (excluding 16 passes) are respectively 4.47 and 5.59.

TABLE 1(b). RELATIONSHIPS OF THE CONSTANTS ' $a_1$ ' AND ' $b_1$ ' OF  $v = a_1 - b_1 \log x$  WITH CONCENTRATION ' $c$ ' FOR DIFFERENT NO. OF HOURS IN SUNLIGHT FOR DEGRADED RUBBERS

| Hours in sunlight | $a_1 = a_1 c^{\beta_1}$ | $b_1 = a_2 c^{\beta_2}$ | Using common values of $\beta_1$ and $\beta_2$ |       |
|-------------------|-------------------------|-------------------------|------------------------------------------------|-------|
|                   |                         |                         | $a_1$                                          | $a_2$ |
| 0                 | 93.37 $c^{4.88}$        | 16.95 $c^{5.06}$        | 73.57                                          | 10.72 |
| 5                 | 48.48 $c^{4.61}$        | 6.24 $c^{5.51}$         | 49.27                                          | 6.42  |
| 10                | 55.72 $c^{4.47}$        | 7.99 $c^{5.27}$         | 48.88                                          | 6.42  |
| 20                | 7.50 $c^{4.82}$         | 0.464 $c^{5.83}$        | 9.92                                           | 0.816 |
| 40                | 21.67 $c^{4.66}$        | 2.27 $c^{5.56}$         | 23.19                                          | 2.48  |

Note: common values of  $\beta_1$  and  $\beta_2$  are respectively 4.60 and 5.48.

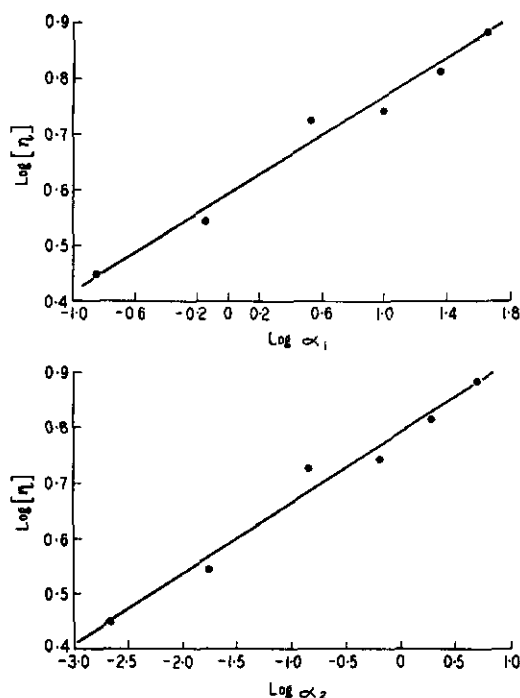


Figure 3. Relationship between the constants ' $a_1$ ' and ' $a_2$ ' (using common values of  $\beta_1$  and  $\beta_2$ ) with intrinsic viscosity ( $\eta$ ) for masticated rubbers.

different mechanisms involved and the different molecular weight distributions produced, average values of  $\beta_1$  and  $\beta_2$  of both the methods were obtained i.e.  $\beta_1 = 4.54$  and  $\beta_2 = 5.54$ . It

is possible that these constant values for  $\beta_1$  and  $\beta_2$  are only dependent on the polymer solvent systems and not on any other factors.

Intrinsic viscosity ( $\eta$ ) is a measure of the molecular weight of a polymer and it decreases with increasing number of passes on the mill. The relationships between  $\log a_1$  and  $\log a_2$  with  $\log (\eta)$  are fairly well represented by a straight line in Figure 3 for masticated rubbers. The relationship for sunlight degraded rubbers is not marked possibly because of the inversion for 20 and 40 hours. The final relationship deduced is of the form:

$$v = f_1(\eta) c^{4.54} - f_2(\eta) c^{5.54} \log x \quad \dots (5)$$

In equation (5) where the viscosity is given by two terms, the term  $f_2(\eta) c^{5.54} \log x$  represents the non-Newtonian contribution to the viscosity.

#### CONCLUSIONS

It has been found that the equation  $v = a_1 - b_1 \log x$  gives the best representation of experimental data for the natural rubber/toluene system unlike that found by BACK (1959). In this expression the term involving  $\log x$  represents the non-Newtonian contribution. The final expression deduced is

$$v = a_1 c^{4.54} - a_2 c^{5.54} \log x$$

For masticated rubbers,  $\log a_1$  and  $\log a_2$  are linearly related to the logarithm of the intrinsic viscosity of the samples while for sunlight degraded rubbers this relationship is not very evident. It is possible that this may be due to the differences in the rate and amount of branching

in the two cases. More work has to be done to determine any precise relationship existing between branching and flow behaviour.

#### ACKNOWLEDGEMENT

The authors wish to acknowledge the assistance of Mr Yee Shin Yew for some experimental data and Mrs Lucy Yong and Mrs Pearly Lim for the statistical computations.

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*Kuala Lumpur* June 1968

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