

Effect of Physical Degradative Agencies on Some Molecular Parameters of Natural Rubber

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The activation energy of heat degradation of a natural rubber sample as determined by osmotic measurements is 25.7 kcal/mole. This value corresponds very closely to that found by SARFARÉ et al. (1963) by light-scattering measurements in dilute solutions, but is much higher than that of WATSON (1953) who used viscometric measurements on samples heated in vacuum.

The variations of the molecular parameters studied during degradation were: (i) molecular weight distributions; (ii) solute-solvent interaction constants such as k' , A_2 , and the ratio $(r^2/M_w)^{1/2}$ in light-scattering measurements; and (iii) the relationships between intrinsic viscosity and molecular weights. The study revealed that sunlight degradation produces a more branched polymer and a greater amount of low molecular weight material. Both these characteristics give a vulcanisate a greater number of free chain ends, which may account for the increased heat build-up and generally inferior properties observed in vulcanisates from sunlight-degraded rubbers as compared to other forms of degradation.

The concentrated solution behaviour of masticated and sunlight-degraded rubbers as measured by the Brookfield viscometer show similarities in their relationship between viscosity and the speed of rotation of the spindle.

Natural rubber emerging from the tree is basically an excellent elastomer, with a fair proportion of anti-oxidants and accelerators. Any inferior properties occasionally encountered in natural rubber are caused by mishandling and degradation during its processing, shipment and storage before reaching the consumer. Hence a study of some degradative agents and their effect was considered useful.

Most of the studies on characterisation of macromolecules have been conducted in the solution stage. In fact, the very proof of the macromolecular hypothesis was obtained by STAUDINGER (1920) from such studies, which are useful in that they provide a means of assessing the behaviour of individual polymer molecules. In solids, however, it is possible to study only their bulk behaviour because neighbouring molecules interfere and are probably entangled with one another. Hence studies on both dilute solutions and solids should be complementary in understanding the behaviour of polymers, and this has been the

author's approach, besides investigating concentrated solution behaviour.

Of all the physical degradative processes, mastication has been the one most thoroughly studied by many researchers on NR and other polymers. This is due to its wide application in the processing, compounding and degradation of polymers. Heat degradation has also been studied in great detail, though sunlight degradation and ultrasonics have not received as much attention. Ultrasonics has mostly been studied in the solution stage, because the cavitation effects, present in solution, have been proposed to be responsible for chain cleavage.

EXPERIMENTAL

Fractionation of the rubbers was carried out by first precipitating 6 to 7 crude fractions from toluene on to glass beads, by addition of methanol. Each fraction was extracted from the glass beads by addition of various mixtures of benzene/methanol, to give about 7 sub-fractions.

The intrinsic viscosity of a sample is taken as the average of the intercept at zero concentration of the graphs of $\log \eta_{sp}/c$ vs. c and η_r/c vs. c . A suspended-level dilution viscometer was used and all measurements were made at 30°C. Osmotic pressure measurements were conducted on a high-speed Mechrolab Membrane Osmometer Model 501. The membranes used were either cellulose film 300 or some collodion membranes conditioned for use by the following procedure:

- (a) Washed in:
- | | | |
|-----------------------|---|--------------------|
| water | — | $\frac{1}{2}$ hour |
| water/acetone (75/25) | — | " |
| " (50/50) | — | " |
| " (25/75) | — | " |
| acetone (thrice) | — | $\frac{1}{2}$ hour |
| | | each time |
- (b) Immersed in:
- | | | |
|---------|---|--------|
| toluene | — | 2 days |
|---------|---|--------|

The square roots of the reduced osmotic pressures were plotted against concentration *i.e.*, $(\pi/c)^{1/2}$ vs. c and the concentration ranges were limited to 0.002 and 0.007 g/cc to obtain the best results. At concentrations below 0.002 g/cc, plots in the form of horizontal lines (with zero gradients) are likely to be obtained and hence such concentration levels should be avoided.

A Brice Phoenix light-scattering apparatus was used to measure weight average molecular weight, M_w , radius of gyration ρ_z and related parameters. A cylindrical cell with an attachment of a set of narrow slits was used to obtain readings of scattered light from 135° to 30°. The greatest problem in these measurements was the purification of the solutions prior to light scattering. A combination of ultracentrifugation at 25 000 rev/min in a Spinco ultracentrifuge for 1 hour, and filtration through a set of filters of porosities 3, 4 and 5 was necessary to give good Zimm plots. However, in certain cases where filtration through filter of porosity 5 was slow, degradation of the rubber occurred. The solvent used in these light-scattering measurements was tetra-hydrofuran (THF) because of its high dn/dc ratio. Although cyclohexane has also high values, it was not used since it gives a great amount of gel. In concen-

tration determinations of THF solutions it was found that, at lower concentrations, values higher than expected were obtained, possibly due to polymerisation of THF by non-rubbers.

RESULTS AND DISCUSSION

A diced sample of natural rubber was sealed inside some capsules, which had been evacuated for 1 hour to a pressure of 10^{-5} mm Hg. Some of these, and some control samples, were heated to 120°C and 140°C and their number average molecular weights determined for various periods of heating. Their degrees of degradation were determined by using the relation of MONTROLL AND SIMHA (1940) derived for completely random degradation of long-chain molecules:

$$M_n/M_o(p, \alpha) = (p + 1)/(1 + \alpha p)$$

where M_n — number average molecular weight,

M_o — molecular weight of monomeric element,

p — number of monomeric units in chain,

and α — degree of degradation.

The graph of α vs. t , the time of heating at 120°C, can be represented by two straight lines (Figure 1) but only the initial line with a gradient is used in the calculation of the slope, k_1 (this slope gives the rate constant assuming that the rate of scission of chain links is proportional to the number of links present). The value of k_2 at 140°C (Figure 2) is obtained from the straight line which is an average of two sets of results. The graph of α vs. t for both temperatures in vacuum show big fluctuations.

$$k_1/k_2 = \varepsilon \frac{\Delta E}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad \dots(1)$$

Using Equation (1) where the rate constants are related to the activation energy, and

$$\text{with } T_1 = 413^\circ\text{K}, \quad k_1 = 3.01 \times 10^{-4},$$

$$T_2 = 393^\circ\text{K}, \text{ and } k_2 = 0.61 \times 10^{-4},$$

we obtain $\Delta E = 25.7$ kcal/mole.

This value agrees very closely with that determined by SARFARE *et al.* (1963) who obtained a value of 25.8 kcal/mole from their

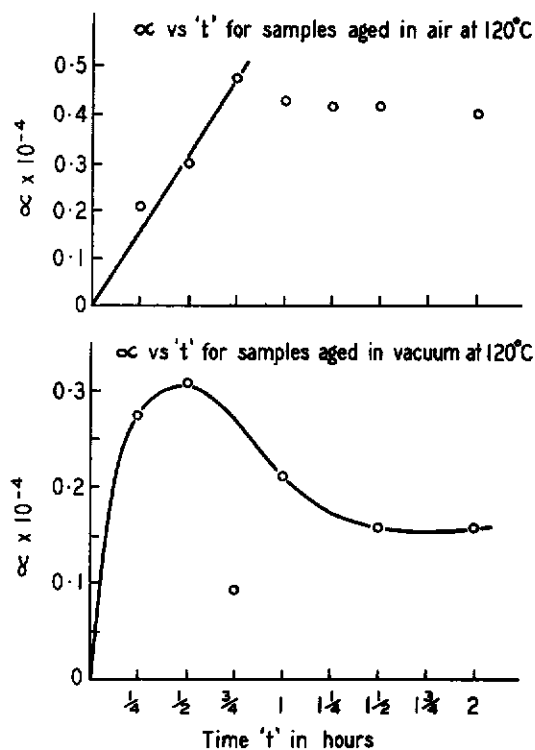


Figure 1. Degree of degradation, α vs. t (time of heating) at 120°C.

thermal degradation studies of NR in dilute solution. However, the value of 15.6 kcal/mole as obtained by WATSON (1953) through his viscometric studies of NR degraded under vacuum is very low, as may be expected due to cross-linking and branching.

Although one may expect a greater amount of cross-linking and branching in the degradation of solid rubber as compared to dilute solutions, and hence higher values for the molecular weights, it is likely that in the above determination the cross-linking and branching occurs to an equal extent at the two temperatures used, i.e., 120°C and 140°C, so that these effects cancel out. As such, the value of about 26 kcal/mole may be taken as an accurate measure of the activation energy of thermal degradation of natural rubber in air. However, this value for the activation energy of degradation is very much less than that necessary for

the breaking of a C-C or C=C bond. It is possible that some other intermediate with a different bond is formed with oxygen which has a lower bond-breaking energy, or on the other hand, this may be explained by the presence of weak links in the main chain possibly due to the postulated abnormal groups (SEKHAR, 1960) in rubber.

The value of 56–63 kcal/mole found from rate of volatilisation studies in vacuum (STRAUS AND MADORSKY, 1956) favours the hypothesis of scission of an intermediate bond with smaller bond dissociation energy rather than that of a pure C-C bond.

Molecular Weight Distribution

Natural rubber has been shown to have a multi-peaked molecular weight distribution curve which is altered by the different degradation processes (NAIR, 1966). The multi-peaked distribution is reduced by sufficient mastication on a cold mill to a unimodal distribution, while

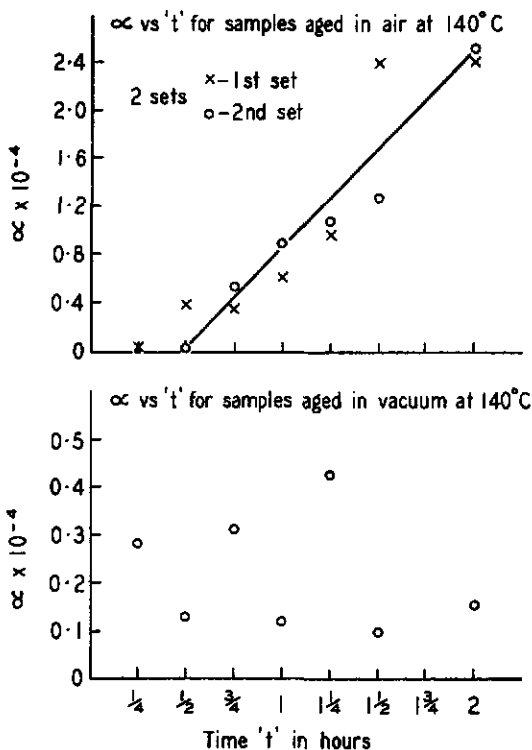


Figure 2. Degree of degradation, α vs. t (time of heating) at 140°C.

sunlight degradation (in solution) of the sample to the same extent (as given by $[\eta]$) does not reduce the number of peaks but only shifts the maxima to lower molecular weights. Heat degradation of solid rubber and ultrasonic degradation of NR solution both give a two-peaked distribution curve. These studies illustrate the selectiveness of some degradative processes like mastication and the randomness with respect to degradation of molecules irrespective of chain length of sunlight degradation. A combination of sunlight degradation and subsequent milling also produces a two-peaked molecular weight distribution curve (*Figure 3*).

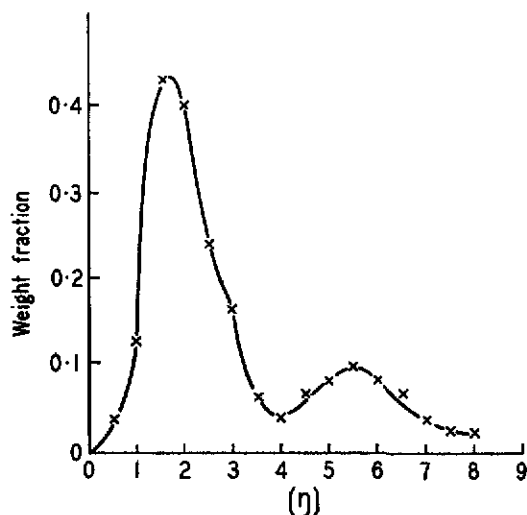


Figure 3. A sample of natural rubber after sunlight degradation and milling.

Samples of natural rubber from a common source were degraded by three different methods until the intrinsic viscosities of the degraded samples were about 4. The molecular parameters of these rubbers together with that of the control are listed in *Table 1*. The light-scattering measurements were omitted because of their distorted Zimm plots especially in the cases of heat and sunlight-degraded samples. The molecular weight distribution curves of these rubbers are compared in *Figure 4*, and it is obvious that sun-

TABLE 1. MOLECULAR PARAMETERS OF CONTROL AND RUBBERS DEGRADED BY HEAT, MASTICATION AND SUNLIGHT EXPOSURE

Sample	$[\eta]$	Osmometry	
		$M_n \times 10^{-5}$	$A_2 \times 10^4$
Control	6.80	6.12	5.11
Heat	4.30	3.30	5.49
Mastication	4.60	3.60	6.16
Sunlight	3.70	2.81	6.49

light-degraded rubber has the shortest molecular weight distribution range, followed by heat-degraded rubber. The sunlight-degraded sample has also the greatest amount of low molecular weight material with the pronounced overlapping of first and second peaks in the distribution curve. The physical properties such as tensile strength, dynamic compression set and scorch of the sunlight-degraded sample are all inferior to those of other samples. The order of potency as seen from the physical properties of both gum and filled vulcanisates is

sunlight > heat > mastication \approx control.

The higher heat build-up characteristics of sunlight- and heat-degraded rubbers is shown in *Figure 5*. Increases in heat build-up characteristics of vulcanisates prepared from raw rubbers exposed to sunlight have also been reported (O'CONNELL, 1966).

Solute-Solvent Interactions and Light-Scattering Parameters

Huggin's constant k' in viscosity measurements has been widely investigated for a number of polymers. It is affected by changes in molecular weight, molecular weight distribution, branching and nature of solvent; very often, it is impossible to determine the exact degree of influence of each of these characteristics on the k' values. Natural rubber in good solvents such as benzene and toluene has values of between 0.50 and 0.60 for k' and, since it is generally assumed that the molecule

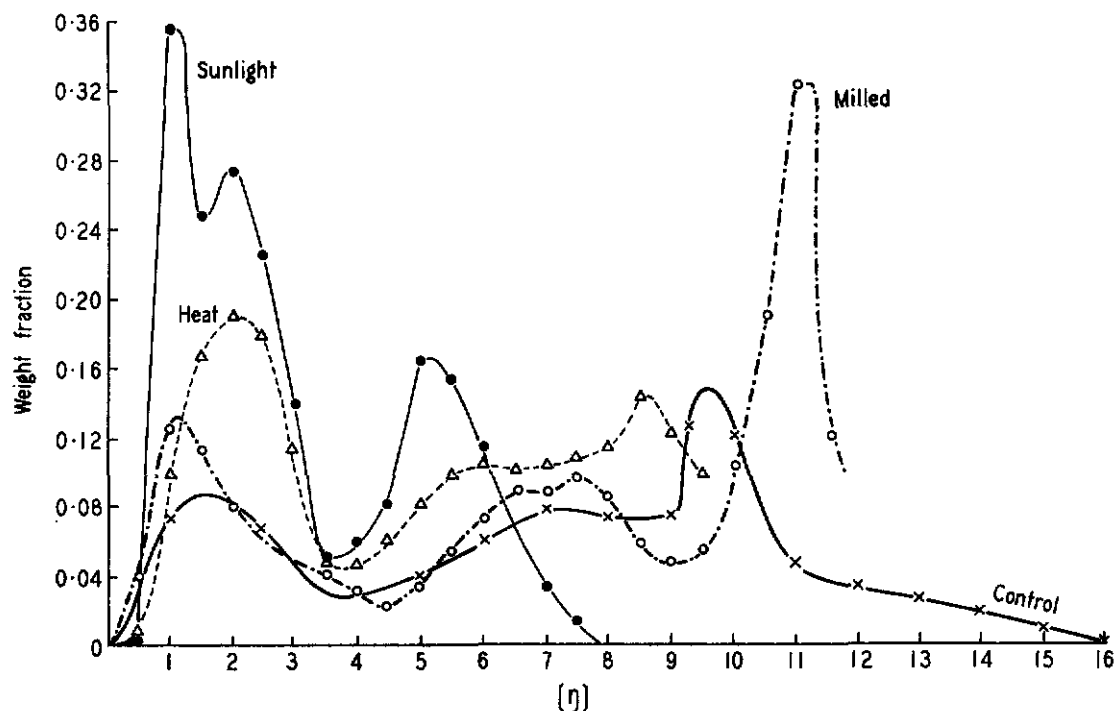


Figure 4. Molecular weight distribution of samples subjected to different methods of degradation.

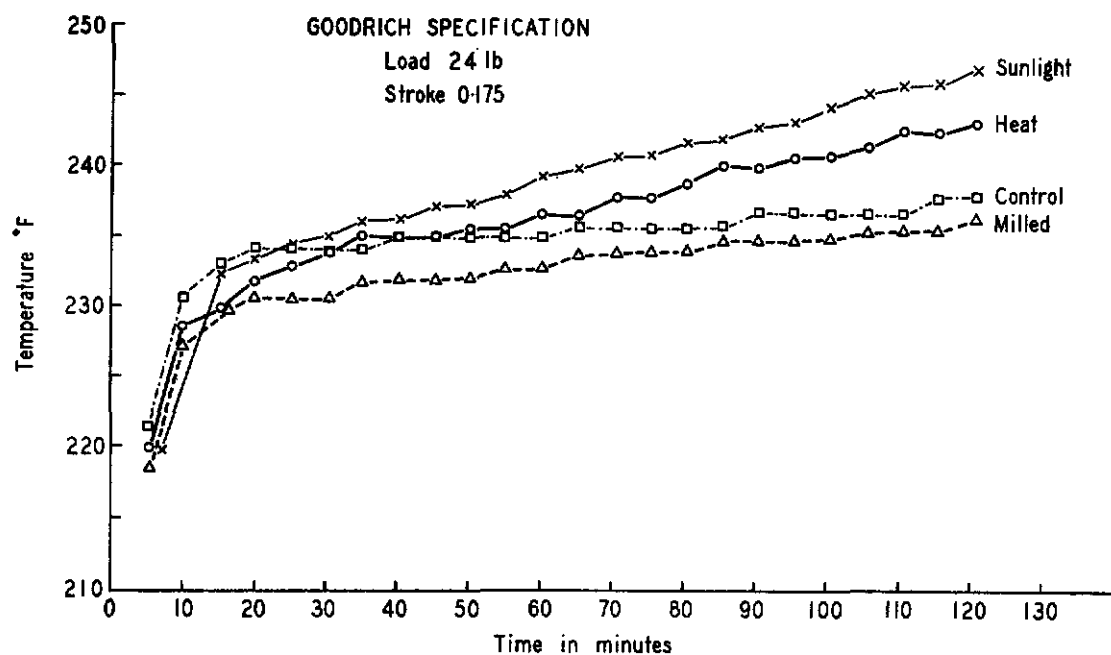


Figure 5. Heat build-up curves for degraded and control rubbers.

is essentially linear, these high values can only be attributed to the high molecular weights and the heterogeneity of its molecular weight distribution.

On cold mastication in air, the k' values of NR decrease to a constant value of about 0.28 due to the decrease in both molecular weight and the heterogeneity of the polymer. However, on mastication in an inert atmosphere (BRISTOW, 1962) or heating in vacuum (Table 2), no such decrease in k' value is observed. This is due to the re-formation of chains giving branched or cross-linked molecules because of the absence of a good chain terminator like oxygen.

TABLE 2. $[\eta]$ AND k' VALUES FOR RUBBER HEATED AT 140°C IN AIR AND VACUUM

Time (h)	Air		Vacuum	
	$[\eta]$	k'	$[\eta]$	k'
0	8.32	0.62	9.84	0.46
$\frac{1}{4}$	8.10	0.56	8.41	0.52
$\frac{1}{2}$	7.55	0.53	7.80	0.55
$\frac{3}{4}$	6.80	0.57	8.03	0.54
1	6.40	0.50	7.56	0.54
$1\frac{1}{4}$	5.90	0.50	7.78	0.51
$1\frac{1}{2}$	5.50	0.41	7.72	0.48
2	5.48	0.45	7.75	0.51

Sunlight degradation of natural rubber in solution lowers k' values but, in the solid state, k' values either increase or remain constant (Figure 6). These high values of k' for sunlight degradation of NR in the solid state can be assigned as for mastication in an inert atmosphere, to the predominant cross-linking or branching reactions. These branched molecules together with the great amount of low molecular weight molecules from sunlight degradation result in the vulcanisate having a large number of free chain ends and these could

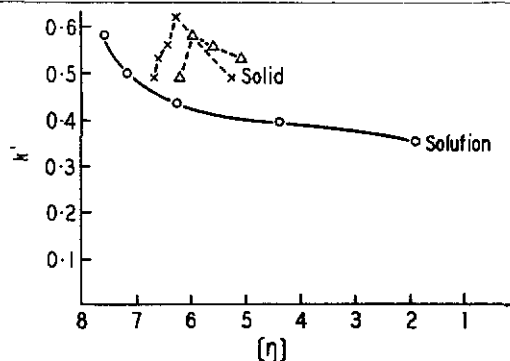


Figure 6. k' of solid rubber in comparison with solution during sunlight degradation.

account for the higher heat build-up observed. BUECHE (1957) has shown by comparing NR with GRS that the low number average molecular weight of GRS is responsible for the high heat build-up properties of this synthetic rubber.

Another possible source for the production of branched molecules is by photo-chemical breakdown of the gel and micro-gel. The difference between sunlight degradation in dilute solution and in solid state can be seen in the limits to which these samples can be degraded. In solution, it is possible to obtain $[\eta] < 0.08$ whereas, in solid, $[\eta]$ becomes 1.5 after very long exposure and starts to rise again.

These trends in k' values were also observed for NR in solid and solution, in the presence of thermal initiators like cumene hydroperoxide, benzoyl peroxide and azo-isobutyronitrile in concentrations of up to 1%. The rate of degradation was found to be faster in the presence of these initiators while in the presence of anti-degradants like hydroxylamine the rate was slower but similar trends in k' values were observed.

From Table 3, it is seen that A_2 increases with decrease of M_n for the samples heated in air, while remaining constant for vacuum-heated samples. The same behaviour is observed on milling. The A_2 values obtained from L.S. measurements do not show any trends due to

the large errors involved. In the light-scattering measurements of natural rubber in THF solutions, the Zimm plots used for the measurements of the various molecular parameters have very small intercepts on the $(HC)/\tau$ axis because of the high molecular weights. The error involved in estimating M_w is consequently high but it is found that the ratio $(r^2/M_w)^{1/2}$ has a constant value of about 1.7×10^{-8} (r^2 is the mean square distance between the chain ends of a molecule) for rubbers from different clones and different methods of preparation. This ratio is very much higher for rubbers heated in vacuum (Table 3) and for solid rubber degraded in sunlight. In both these cases we expect a more branched or cross-linked polymer to be formed and, on theoretical grounds, a lower value for the ratio $(r^2/M_w)^{1/2}$ since for a molecule of the same molecular weight a branched polymer should have a lower r^2 value. The explanation we can offer for this anomaly is that the branched or cross-linked molecules are probably trapped in the gel and are removed during the exhaustive purification procedure thus leaving only the very linear molecules.

Relations between Intrinsic Viscosity and Molecular Weights

The relation between $[\eta]$ and M_n (Figure 7) for masticated purified NR (for the greater part of the molecular weight range investigated)

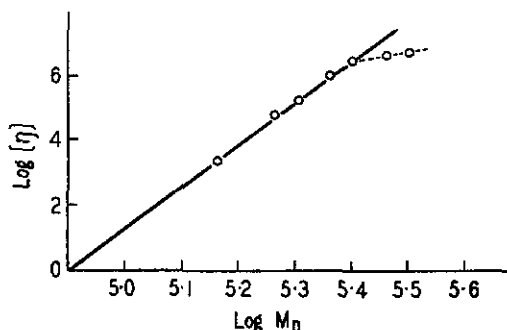


Figure 7. Relation between $[\eta]$ and M_n for masticated NR.

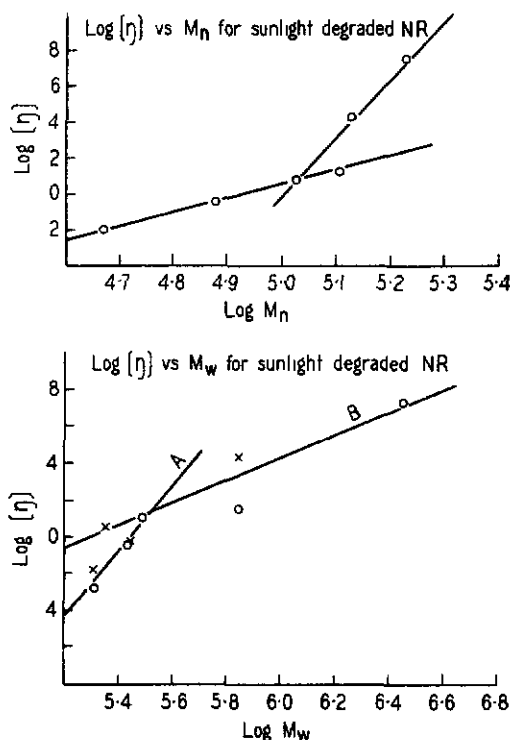


Figure 8. Relation between $[\eta]$ and M_n and M_w for sunlight-degraded NR.

is $[\eta] = 3.81 \times 10^{-7} M_n^{1.33}$ which is very close to that determined by MULLINS AND WATSON (1959). However, at the higher molecular weight range, a more horizontal line seems to give a better fit. In this relationship, the exponent of M_n is usually less than 1 for most polymers on theoretical grounds; in this case, however, we can probably attribute the high value to the high degree of heterogeneity of the polymer itself. KEMP (1967) holds the view that a universal viscosity-molecular weight relationship should apply for all polymers namely $[\eta] = KM_n$ and that the exponent of M_n should be 1. He states that all present methods of molecular weight determinations are invalid and that M_n values as determined by conventional techniques are very much higher due to the permeability of solute.

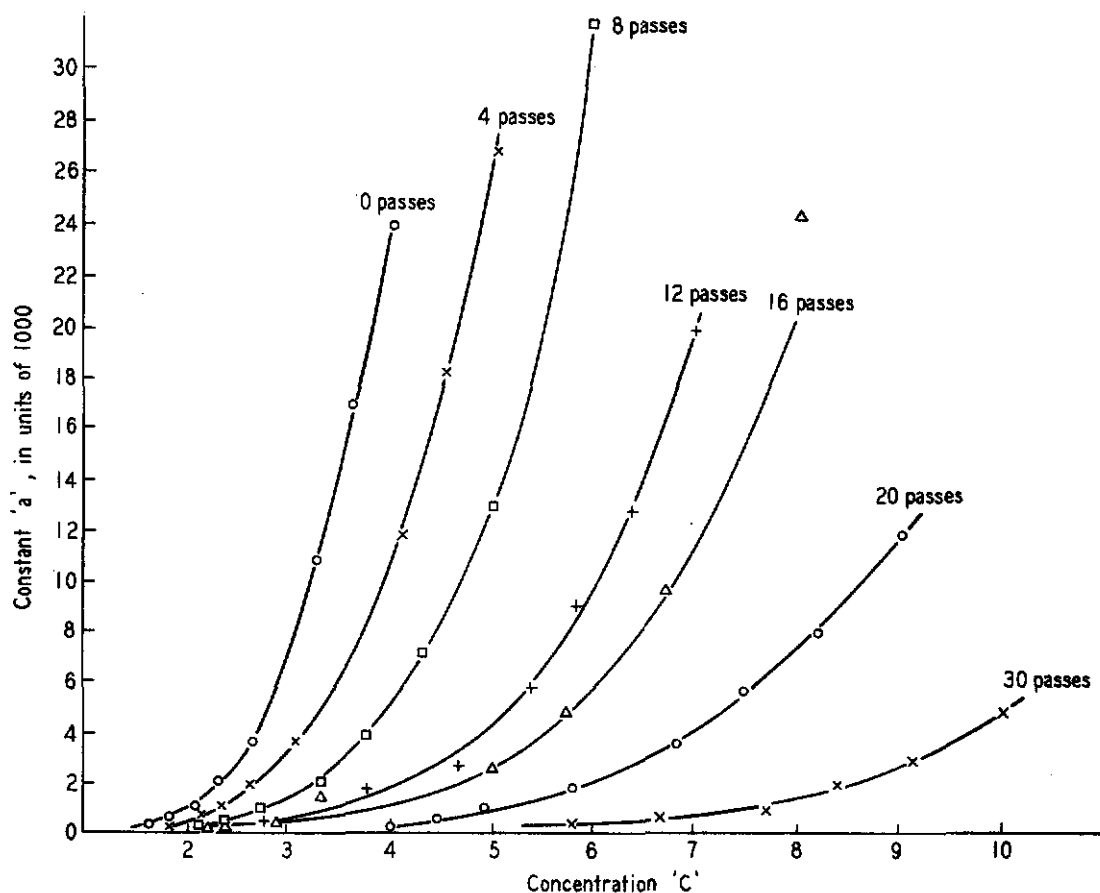


Figure 9. Relationship between 'a' (in equation $v=a-b \log x$) and concentration for Brookfield viscosity measurements of masticated NR.

TABLE 3. OSMOMETRIC AND L.S. PARAMETERS OF RUBBERS HEATED IN AIR AND VACUUM AT 120°C

Time of heating (h)	$[\eta]$		$M_n \times 10^{-5}$		$(r^2/M_w)^{\frac{1}{2}}$		A_2 (Osmo.)	
	Air	Vacuum	Air	Vacuum	Air	Vacuum	Air	Vacuum
0	8.32	8.94	7.12	8.10	1.75	2.22	4.57	4.63
$\frac{1}{4}$	8.10	8.41	5.78	7.12	1.58	2.18	5.08	4.94
$\frac{1}{2}$	7.55	7.80	5.47	6.90	1.94	2.70	5.01	4.91
$\frac{3}{4}$	6.80	8.03	5.32	6.90	1.76	2.24	5.08	4.91
1	6.40	7.56	5.18	7.12	1.84	2.16	5.15	4.94
1 $\frac{1}{4}$	5.90	7.78	3.94	6.90	Distorted Zimm plot	2.91	5.49	5.02
1 $\frac{1}{2}$	5.50	7.72	4.55	6.12	2.19	2.66	5.72	4.88
2	5.40	7.75	4.55	6.12	1.78	2.10	5.72	4.88

In the case of sunlight-degraded rubbers, the relationships between $[\eta]$ and $\log M_n$, and $[\eta]$ and $\log M_w$ consist of two intersecting straight lines (Figure 8). These pairs of lines representing the relationship between viscosity and molecular weights indicate the presence of some factor such as chain entanglements or changes in distribution or in configuration that come into play at certain molecular weights.

Concentrated Solution Behaviour

Concentrated solutions referred here are solutions with concentrations in the range of 2–10%; they are very viscous and difficult to handle. The viscosities of these solutions at different levels of degradation were measured with a Brookfield viscometer at 25°C, for different spindles and at various speeds. For both masticated and sunlight-degraded rubbers, exponential relations between v , the viscosity, and x , the speed of rotation of the spindle, were found (Figure 9) and deduced to be of the form (NAIR AND NARAYANAN, 1968),

$$v = f_1 [\eta] c^{4.54} - f_2 [\eta] c^{5.54} \log x \dots (2)$$

where v is viscosity (in centipoises)
and c is concentration.

The first term in the above relationship was found to be independent of shear while the second term was found to incorporate a function of x . Thus, it may be stated that Brookfield viscosity of natural rubber solutions is not affected by the distribution curves, since different distributions result from the different methods of degradation.

ACKNOWLEDGEMENT

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DISCUSSION

Chairman: Dr. G. F. Bloomfield

Dr. K.M. Hui asked if an Arrhenius plot was made; if it was linear, a simple rupturing would be indicated and the activation energy could be accurately estimated. Dr. Nair said this was not done yet; in answer to a further question by Dr. Hui, the author said the constants to convert the intrinsic viscosities to average molecular weights were perhaps not applicable to these studies.

Dr. F. Haas asked what allowance was made for micro- and macro-gel fractions. Dr. Nair replied gel fractions were filtered off so that only the soluble portion was used in the investigations.

Dr. P. Thirion asked if the intensity of the illumination in the light-ageing experiments had been measured or standardised, because he had found this important with vulcanisates. Dr. Nair said no quantitative measurements were made except that cloudy periods were noted.

Dr. W.F. Watson asked if the curves used to obtain the activation energy had been fitted statistically and were significant. Dr. Nair said the curves were drawn by eye and the values obtained agreed with those of BHATNAGAR *et al.* (1964). Dr. Watson suggested that the difference between the activation energies reported in this work and that of his earlier paper was caused by the different assumptions on the question of random distributions.

Dr. C.H. Tan noted that some light, especially ultraviolet, might be absorbed by the solvents, toluene and benzene, and by the glassware. Dr. Nair agreed and said that thin glassware was used.