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# Light-Scattering Measurements on Polyisoprene Solutions. II. Rubber from Fresh Natural Latex

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## INTRODUCTION

In Part I of this series it was shown that solutions of milled natural rubber contained a scattering component which could be partly removed by filtration, but at that time the possibility could not be excluded that this component was composed mainly of nonrubber constituents.[1] The primary purpose of this communication is to provide positive identification of the scattering species and to indicate its properties and origin. The investigation has been limited to samples of natural rubber from fresh latex of one clonal type.

## EXPERIMENTAL

### Rubber

Freshly tapped latex from Clone PB186, preserved with ammonia, was flown from Malaya and received in this country within 5–10 days after tapping. The latex was stored in the dark and samples of rubber were obtained by casting films on porous tiles at room temperature, and then drying them *in vacuo.* These films were dissolved in solvent overnight without shaking.

### Light-Scattering Measurements

Clarification was effected as described previously, by filtration through sintered glass filters.[1] In a few cases solutions were subjected to centrifugation in a Spinco Model L preparative ultracentrifuge. Turbidity measurements were carried out as before in a Brice-Phoenix Series 1000 photometer with the use of the blue Hg line $\lambda = 4358$ A. In the Zimm diagram measurements, tetrahydrofuran was used as solvent. The parameters tabulated are weight-average molecular weight $\bar{M}_w$, second virial coefficient $A_2$, mean square radius of gyration $\bar{S}_z^2$, and $(\bar{r}_z^2/\bar{M}_w)^{1/2}$ where $\bar{r}_z^2$, the mean square end-to-end distance of the equivalent random coil (linear chains), is equal to $6\bar{S}_z^2$.

## RESULTS AND DISCUSSION

### Experiments with Unmasticated Samples

Rubber films obtained from fresh latex and from latex which had been stored for up to three months were not fully soluble in tetrahydrofuran. Removal of the gel phase gave clear solutions which filtered easily. A typical Zimm plot is shown in Figure 1. The $c = 0$ line (whence is derived $\bar{S}_z^2$) is curved, presumably because the polymer is heterodisperse. There is also marked curvature of the $\theta = 0$ line suggesting a nonzero third virial coefficient. By analogy with the osmotic pressure equation of Flory,[2] a straight line can be obtained by plotting $(c/\tau)_{\theta=0}^{1/2}$ versus $c$ and $A_2$ evaluated from the slope of this plot. Less conveniently, equivalent $A_2$ values can be obtained from the initial slope of the $\theta = 0$ curve. (The $\theta = 0$ curve in Fig. 1 is recalculated from the square root plot.)

The Zimm curves for the untreated latex rubbers are very similar to those given by samples of crepe rubber (Fig. 2 of Reference 1). It is now suggested that the distortion, i.e., the crossing-over of the $c = 0$ and $\theta = 0$ lines, is due, at least in part, simply to the fact that the third virial coefficient is not equal to zero.

As the latex ages on storage, so the proportion of gel increases and $\bar{M}_w$ decreases (Table I). Though there is no evident correlation between $\bar{M}_w$ and the age of the latex (Table I), as a given batch of latex ages on storage $\bar{M}_w$ decreases smoothly as the gel content increases (Fig. 2). This correlation is a reflection of the fact that rubber in latex becomes progressively harder on storage. This is generally considered to be a result of a crosslinking reaction, and it has recently been indicated that this reaction is associated not only with peroxidic groups but also with the demonstrated presence of aldehyde groups.[3] Since the larger molecules will be preferentially incorporated

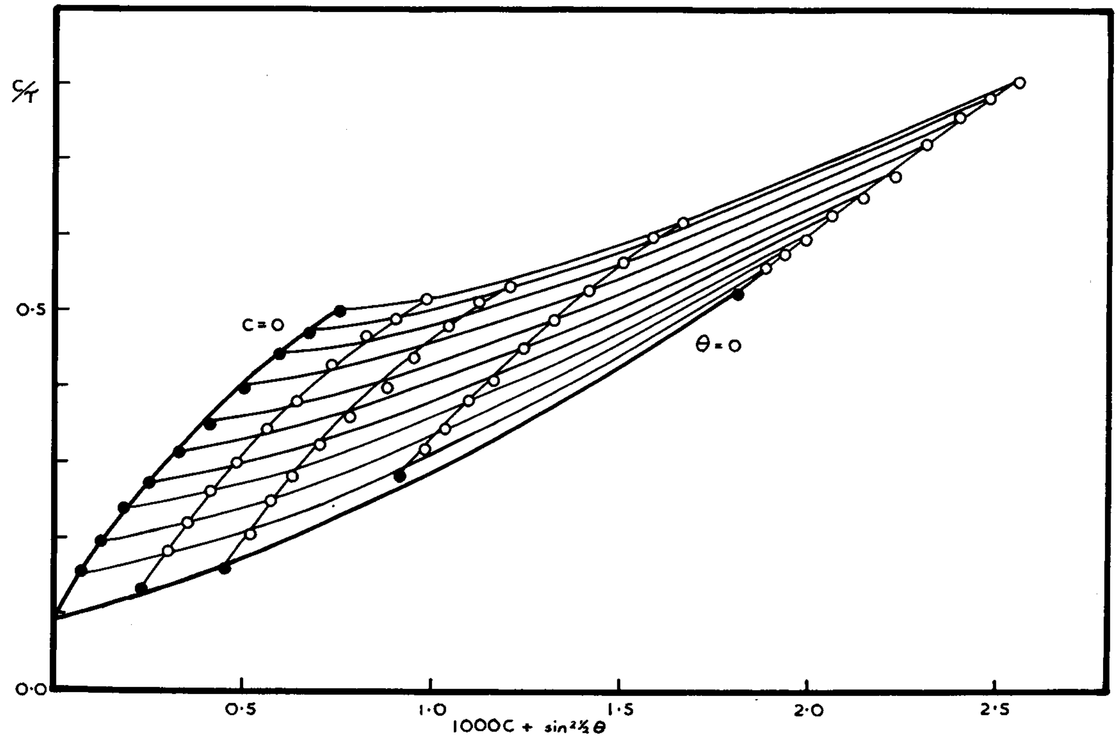

Fig. 1. Zimm diagram for unmasticated rubber from fresh natural latex.

into the network, $\bar{M}_w$ should decrease, as was observed.

Other facts shown by the data of Table I are that (*1*) purification of the latex by displacement of protein with pure sodium dodecyl sulfate[4] and (*2*) centrifugation of the rubber solution at 50,000 *g* are both without effect on the measured parameters. Since more than 95% of the nitrogen content remains in the gel phase, it would not be expected that soap purification would have any substantial effect on the properties of the sol phase. As centrifugation does not materially alter $\bar{M}_w$, it seems unlikely that the *sol phase* contains any great quantity of suspended small particles unless

TABLE I
Unmasticated Latex Rubbers

| Sample | Date of examination | Soluble matter, % | $\bar{M}_w \times 10^{-5}$ | $A_2 \times 10^4$, ml./g. | $\bar{S}_z^2 \times 10^{-5}$, A.$^2$ | $(\bar{r}_z^2/\bar{M}_w)^{1/2} \times 10^{11}$ |
|---|---|---|---|---|---|---|
| Examinations of untreated latex | | | | | | |
| Batch A, tapped 29/4/60 | | | | | | |
| | 16/5/60 | 98 | 20.1 | 4.6 | 15.1 | 2120 |
| | 10/6/60 | 73 | 13.1 | 4.2 | 12.0 | 2320 |
| | 19/8/60 | 61 | 6.7 | 6.4 | 4.5 | 2020 |
| Batch B, tapped 25/8/60 | | | | | | |
| | 2/9/60 | 80 | 13.6 | 5.5 | 15.3 | 2450 |
| | 11/10/60 | 66 | 11.2 | 5.5 | 9.4 | 2240 |
| | 4/11/60 | 52 | 7.6 | 6.4 | 5.8 | 2140 |
| Latex purified by soap displacement | | 73 | 12.3 | 4.2 | 10.2 | 2220 |
| Control | | 73 | 13.1 | 4.2 | 12.0 | 2320 |
| Latex solution centrifuged at 50,000 *g* for 90 min. | | — | 8.4 | 5.3 | 4.9 | 1870 |
| Control | | — | 6.7 | 6.4 | 4.5 | 2020 |

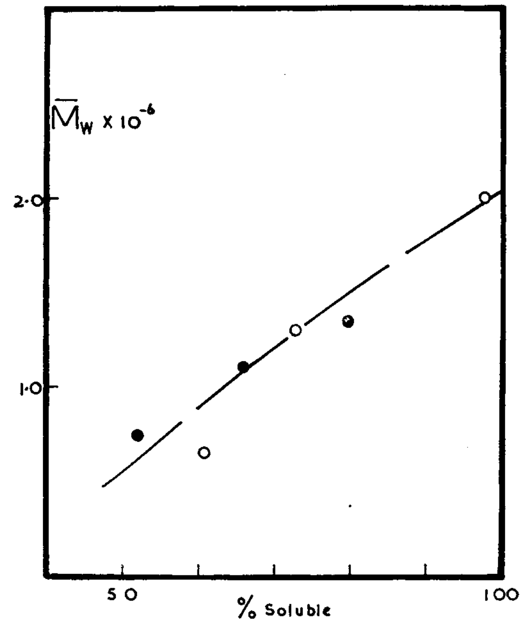

Fig. 2. The effect of storage on $\bar{M}_w$ and gel content.

these particles are either so small or so swollen with solvent that they cannot be partly removed by centrifugation. This re-emphasizes our interpretation of the distortion of the Zimm plot (Fig. 1) in terms of a nonzero third virial coefficient. Furthermore, electron-microscopical examination of films cast from the sol phase showed that they were free from particles.

The mean of the values obtained for $A_2$ corresponds to a value for the interaction parameter $\chi$ of 0.466 which should be compared with values of 0.442 and 0.452 obtained from viscosity and swelling measurements.[5]

## The Effect of Mastication

Films obtained from fresh latex as described were masticated for various times under oxygen in a laboratory masticator.[6] Solutions of the masticated polymers in tetrahydrofuran were faintly turbid and extremely difficult to filter. One such solution was subjected to centrifugation at 50,000 *g* for 2 hr. The light-scattering results are given in Table II, which shows, in addition, the effect of masticating (*1*) rubber from latex which had been purified by soap displacement and (*2*) rubber which had been freed from gel *before* mastication by dissolution in tetrahydrofuran, filtration, and reprecipitation (the unmasticated sol rubber, as expected, had properties identical with those of whole rubber).

TABLE II

The Effect of Mastication in Oxygen

| Sample | $[\eta]$, dl./g. | $\bar{M}_w \times 10^{-5}$ | $A_2 \times 10^4$ | $\bar{S}_z^2 \times 10^{-1}$ | $(\bar{r}_z^2/\bar{M}_w)^{1/2} \times 10^{11}$ |
|---|---|---|---|---|---|
| Rubber masticated for various periods of time | 8.05 | 13.1 | 5.5 | 12.0 | 2320 |
| | 5.32 | 10.0 | 4.2 | 5.1 | 1890 |
| | 2.66 | 6.0 | 2.5 | 3.5 | 1880 |
| | 1.43 | 3.7 | 1.1 | 1.2 | 1430 |
| Last sample, after ultracentrifugation | 1.24 | 1.5 | 8.1 | 0.8 | 1800 |
| Sol rubber | 1.01 | 2.1 | 7.0 | 1.1 | 1770 |
| Rubber from purified latex | 1.17 | 3.0 | 0.8 | 1.6 | 1660 |

The effect of increasing severity of mastication is to lower progressively both $A_2$ and $(\bar{r}_z^2/\bar{M}_w)^{1/2}$. This underlines the experiments reported in Part I of this series, which gave, for milled commercial pale crepe, $A_2 \approx 0$ and $(\bar{r}_z^2/\bar{M}_w^{1/2}) = 1290 \times 10^{-11}$, representing, in effect, even more extreme conditions than those of Table II. Removal of about four fifths of the nitrogenous impurities by soap displacement is without effect. Removal of the gel phase, on the other hand, gives a sol rubber which behaves normally on mastication, displaying a slightly enhanced value of $A_2$, probably resulting from the great reduction in $\bar{M}_w$.

It is quite evident that these solutions of masticated rubbers (except for the case where the gel phase has been removed) contain particulate scattering inclusions. Qualitatively this is revealed by the filtration difficulties, which were absent with unmasticated samples. If a part of the rubber in a solution exists not as dissolved molecules but as spherical particles, then $A_2$ will be lowered because, for a suspension of spheres, $\tau \propto c$ and hence $A_2 = 0$. Values of $A_2$ intermediate between zero and the value expected for soluble molecules will result from a mixture of spheres and molecules. Similarly, $\bar{M}_w$ will be increased. A quantitative treatment of these effects is given in the Appendix, where it is shown that the data of Table II are in agreement with this hypothesis.

If a part of the rubber exists as particles rather than as molecules, then this part should be removable by centrifugation, though the ease with which this can be done will depend both on the sizes of the particles and on the density difference between the swollen particles and solvent. Centrifugation for 2 hr. at 50,000 *g* is evidently sufficient to remove substantially all the particles, giving a solution the value of $A_2$ for which is almost identical with that for the sol (particle-free) rubber and very similar to values obtained for synthetic *cis*-polyisoprenes, which are also believed to be free from particles.[7] Thus, polymer of equivalent light-scattering qualities can be obtained either by removal of the gel phase before mastication or by removal of the particles after mastication, and it is evident that the particles originate from within the gel phase.

An interpretation of the reduction in $(\bar{r}_z^2/\bar{M}_w)^{1/2}$ accompanying mastication is less simple. It is true that a mixture of particles and molecules will give a lower value for this quotient than will molecules alone. There is a similar diminution upon mastication of synthetic polyisoprene,[7] most likely due to a sharpening of the molecular weight distribution by the preferential scission of large molecules. This will reduce $\bar{r}_z$ relatively more than $\bar{M}_w$. Probably a part of the diminution shown in Table II results from this effect, and part from the addition of scattering particles. In agreement with this, centrifugation results in a slight increase of $(\bar{r}_z^2/\bar{M}_w)^{1/2}$ to a value which is still lower than that for the unmasticated rubber.

## Identification of the Scattering Component

The particles whose presence in masticated samples of rubber cause the effects described in the last section originate from the gel phase. Since this phase contains virtually all the nitrogenous impurities, the suspicion arose that these particles might be composed mainly of nonrubber components. In this section we describe two independent methods by which it was established that the particles are, in fact, composed mainly of rubber.

Examination in the electron microscope of thin films cast from solutions of masticated samples revealed the existence of dark (i.e., thicker) regions separated by clear areas. The electron diffraction pattern given by the dark regions was indistinguishable from that of the clear regions and was identical with the amorphous pattern normally given by natural rubber. Solutions of masticated sol rubber were free from dark areas.

The other identification method started with the observation that solutions of masticated samples in hexane were invariably cloudy, whereas benzene solutions were clear. Examinations of solutions in a range of solvents showed that their turbidity depended solely on the solvent refractive index. It will be apparent that the turbidity of a dispersion of scattering particles will depend on the difference in refractive index between particles and solvent, being zero when this difference is zero. For spherical particles, for instance, the equation is that derived by Rayleigh, viz.:

$$\tau/c = \frac{4\pi}{\rho\lambda'}\alpha^3\left(\frac{m^2-1}{m^2+2}\right)^2 \quad (1)$$

where

$$\alpha = 2\pi r/\lambda'$$

$\rho$ being the particle density, $r$ its radius, and $m$ the ratio of refractive index of the particle to that of the solvent.

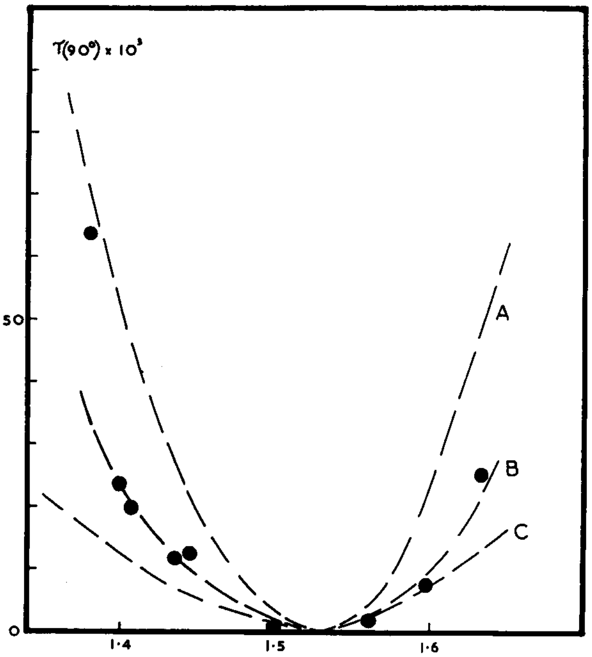

Fig. 3. The turbidity ($c$ = 2 × $10^{-3}$ g./ml., $\theta$ = 90°) of a masticated sample in solvents of varying refractive index $n$.

Figure 3 shows the turbidities (at $\theta$ = 90°) of a masticated rubber in various solvents at a concentration of 2 × $10^{-3}$ g./ml., plotted as a function of solvent refractive index. The solutions were filtered, not through the fine filters used for molecular weight measurements, but through coarse filters to remove dirt, etc. The turbidities are, as a result, very much larger than those recorded for the data of the preceding section and it is evident that the fine filters can remove a large proportion of the scattering matter. The significance of the broken lines is described later.

From the curve of Figure 3 the turbidity is seen to be zero for $n \approx 1.53$, and this is the refractive index of the scattering component. A value for the refractive index of natural rubber at the wavelength used (4358 A.) can be obtained from values of the refractive index increment $dn/dc$ in various solvents given by Altgelt and Schulz.[8] A plot of $dn/dc$ is linear, in accordance with the Gladstone-Dale rule, and the value of $n$ for which $dn/dc$ is zero is 1.535. This is so close to the value derived for the refractive index of the scattering component as to leave no doubt that this component is rubber.

## The Effect of Fractionation of the Latex

An aliquot of latex was separated into three fractions of differing particle size by creaming with ammonium alginate. From the concentration of ammonium alginate used to prepare each fraction it was possible to estimate the ranges of particle diameters[9] as 12,000 A. (fraction I), 7,000–12,000 A. (fraction II), and 2,000–7,000 A. (fraction III). Whole latex contains particles ranging down to ~500 A., and therefore the smallest particles, representing a very small weight fraction, are not included in fraction III. Electron microscopic examination of cast films confirmed this fact.

Films cast from the latex fractions were dissolved in tetrahydrofuran for light-scattering measurements (Table III). In addition, a sample of each film was masticated to give $[\eta] \approx 1.0$ dl./g. and the turbidity at $\theta = 90°$ of hexane solutions ($c = 2 \times 10^{-3}$ g./ml.) was measured. For the unmasticated films there are no significant differences between the fractions. This is in accord with the findings of van Essen,[10] whereas Hessels[11] has reported that as latex ages changes take place which result in the smaller particles, having lower molecular weights than the larger particles.

The turbidities of the masticated samples show an interesting trend. For the whole latex the corresponding turbidity (Fig. 3) is $64 \times 10^{-3}$. The larger particles make only a small contribution to this and even for fraction III the turbidity is less than that for the whole latex. The inference is that the scattering component is associated mainly with the smallest particles in the latex, those with diameters below ~2000 A. One should note that in the fractionation process the very small particles are lost and that the inclusion of these in fraction III would presumably have raised the turbidity.

TABLE III
Latex Fractions

| Fraction | $\bar{M}_w \times 10^{-5}$ | $A_2 \times 10^4$, ml./g. | $\bar{S}_z^2 \times 10^{-5}$, A.$^2$ | $(\bar{r}_z^2/\bar{M}_w)^{1/2} \times 10^{11}$ | Turbidity (90°) $\times 10^3$, cm.$^{-1}$ |
|---|---|---|---|---|---|
| I | 12.3 | 5.5 | 7.9 | 2290 | 17.3 |
| II | 11.2 | 6.0 | 8.9 | 2180 | 16.3 |
| III | 11.9 | 5.2 | 9.5 | 2190 | 31.6 |

## Estimates of Particle Size

It is in principle possible to measure the size of the particles from light-scattering measurements, since, under conditions corresponding to Figure 3, the greater part of the measured turbidity arises from the particles rather than from the concomitant dissolved rubber molecules. The applicability of the Rayleigh-Debye equations to this case is legitimate if the particles are reasonably small and if the ratio of particle to medium refractive indices is not too large.[12] These conditions are fulfilled here.

The most direct way of measuring the particle diameter is to carry out a normal Zimm diagram procedure using as sample a masticated rubber which has been through a coarse filter only. This gives $\bar{M}_w$ with which, assuming sphericity, the particle diameter is calculable from

$$\bar{M}_w/N = \pi D^3 \rho/6 \qquad (2)$$

where $N$ is Avogadro's number and $\rho$ the particle density. The $D$ so obtained is a weight-average diameter, $(\bar{D}_w^3)^{1/3}$.[13]

The chief difficulty with this approach is that the precise concentration of scattering particles is not known. An estimate can be made from the fact that ultracentrifugation of a hexane solution of a masticated sample reduced the turbidity by 95% while the polymer concentration was reduced by only 7%. Hence one can take the particle concentration to be 0.07 of the polymer concentration. The Zimm plot gave (as expected) $A_2 = 0$ and, with the concentration corrected in this way, $\bar{M}_w \approx 2 \times 10^8$ whence $(\bar{D}_w^3)^{1/3} \approx 900$ A. This must be regarded as very approximate.

Another method of computing an average particle diameter is from the dissymmetry, i.e., the ratio $Z$ of turbidities at two angles equidistant from 90° (usually 135° and 45°). The type of average given depends on the distribution but is presumably analogous to a $z$-average value. This method has the attraction that knowledge of the particle concentration is not needed since it was found that the dissymmetry did not vary appreciably as the total

TABLE IV
Particle Diameters from Dissymmetry

| Solvent | $Z_{45°}/_{135°}$ | Mean diameter, A. |
|---|---|---|
| Hexane | 2.20 | 1140 |
| Di-*n*-butyl ether | 1.81 | 990 |
| Tetrahydrofuran | 1.99 | 1070 |
| Chloroform | 1.99 | 1030 |

concentration (molecules + particles) was varied. Dissymmetries and particle diameters computed therefrom are shown in Table IV for a masticated sample in four solvents.

Two points emerge from the data of Table IV. The computed particle diameter is very close to that (900 A.) estimated from the Zimm plot. The diameter does not significantly depend on the solvent power, chloroform being a very good and di-*n*-butyl ether a poor solvent for rubber. This suggests that the particles cannot be very swollen for, if they were, their size would vary with swelling efficiency of the solvent.

Since the particles are comparatively small it is to be expected that Rayleigh's equation (1) should be applicable. With the particles assumed to be unswollen (i.e., with refractive index of 1.53) and of diameter 1000 A., eq. (1) predicts a value for $(\tau/c)$ of $2.15 \times 10^3$ with hexane as solvent. The measured value for $(\tau/c)$, corrected from $\theta = 90°$ to $\theta = 0°$ by means of the particle scattering factor, is $\sim 2.0 \times 10^3$, assuming as before that the particles represent 7% of the total polymers. The agreement is excellent.

Quantitative significance can now be given to the data of Figure 3. Assuming $r$ to be 500 A. it is possible to compute $\tau$ from eq. (1) as a function of the refractive index of the medium, making the same assumption as before concerning the particle concentration and correcting the turbidities from $\theta = 0$ to $\theta = 90°$. Curve A in the figure is calculated on the basis that the particle refractive index is 1.53, i.e., that the particles are unswollen. Curves B and C are calculated for solvent/rubber swelling ratios of 0.5:1 and 1:1, respectively. Bearing in mind that the exact location of the theoretical curves is very dependent on the value chosen for $r$ as well as on the assumed swelling ratio, it is apparent that the turbidity data fit the Rayleigh–Debye treatment with $r \approx 500$ A. and that the particles are very little swollen, as previously deduced (Table IV).

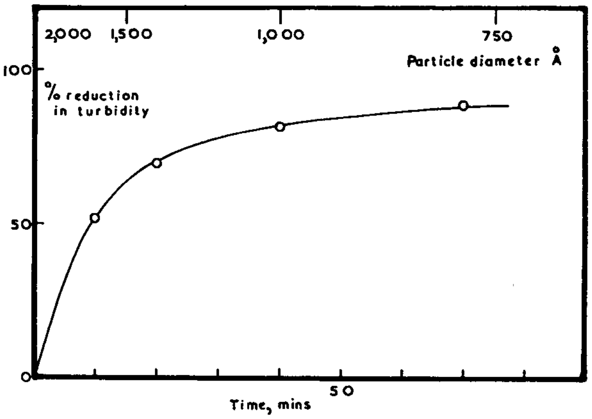

Fig. 4. Centrifugation at 9000 $g$ of a masticated sample.

A further source of information on particle size is the behavior in centrifugation. It is not possible to obtain a precise measure of size because, again, calculated diameters are dependent on the differences between particle and medium densities and hence on the degree of swelling. On the other hand, by measuring turbidity as a function of centrifugation time some idea can be obtained as to the approximate range of particle diameters without invoking any estimate of particle concentration since, for spheres, the turbidity is proportional to the particle concentration. Figure 4 shows the result of an experiment in which a hexane solution was centrifuged at 9000 $g$ and the turbidity was measured at intervals. An approximate diameter scale is shown. This is calculated from the geometry of the centrifuge with the assumption that the particles are unswollen. The particle diameters ranged from over 2000 A. to below 750 A., the system being very heterodisperse. The material collected at the bottom of the centrifuge tubes was elastic and clearly had a substantial content of rubber, the existence of which was confirmed by infrared spectroscopy.

Attempts to measure the particle diameter by means of electron microscopy were not very satisfactory. As stated before, examination of thin films revealed the existence of dark patches. These were almost certainly not individual particles, being far too large (up to 10,000 A.) and having ill-defined boundaries. When solutions were brominated to a bromine content of 20–40% (based on the rubber), well-separated particles could be seen. These were not perfectly spherical and had an unusual appearance; moreover, they gradually faded on exposure to the electron beam. In size they were very heterodisperse. A rough estimate of $(\bar{D}_w^3)^{1/3}$ gave a figure of 1000 A., close to that deduced from light-scattering measurements.

### Swelling of the Particles

Since the diameter of the particles is independent of the solvent power of the medium (Table IV) it has been inferred that the particles are swollen very little, even in good solvents. A similar conclusion has been drawn from the absolute turbidity values (Fig. 3). An exact value for the swelling ratio cannot be obtained, but a figure of $\sim 1:1$ would be in accord with the data.

If this very low degree of swelling were to be attributed to crosslinking, then the crosslink density would have to be very high and the rubber quite hard. Examination of the centrifuged particle fraction showed it to be soft. Precise measurement of the swelling in hexane of this centrifugate was not possible on account of the small quantity available; rough estimates gave values ranging up to $\sim 7:1$, i.e., much greater than that calculated from the light-scattering data and in agreement with the softness of the material.

This discrepancy is probably due to the fact that the swelling of small particles is considerably less than that of bulk material crosslinked to the same extent, because swelling is opposed by the interfacial free energy between particle and medium.[14] The effect has been demonstrated for polystyrene[14] and natural rubber latices.[15] The free energy equation is

$$\Delta G = \Delta G_{\text{osm}} + \Delta G_i + \Delta G_{\text{el}} \qquad (3)$$

where

$$\Delta G_{\text{osm}} = RT\,\{\ln(1 - v_2) + v_2 + \chi v^2\}$$

and

$$\Delta G_i = 2V_1\gamma/r$$

and $\Delta G_{\text{el}}$ is the contribution from rubber elasticity.[2] $v_2$ is the volume fraction of polymer in the swollen system [the swelling ratio is $(1/v_2) - 1$], $V_1$ is the molar volume of the solvent, $\gamma$ the interfacial free energy, and $r$ the particle radius.

Assuming that $\Delta G^{\text{el}}$ is not affected by the subdivision of the bulk material into particles and taking $v_2$ for the bulk material to be 0.1 (swelling ratio 9:1) it is found that, for $r = 500$ A., a value for $v_2$ (particles) of 0.5 (swelling ratio 1:1) corresponds to an interfacial energy $\gamma$ of 15 dynes/cm. $\gamma$ is unlikely to be greater than this and may well be considerably less, in which case the reduction in swelling is even greater.

## CONCLUSIONS

Solutions of masticated samples of rubber from fresh latex contain particles of rubber. A precise assessment of their size is complicated by the fact that neither their concentration nor their swelling can be estimated precisely. All the evidence indicates that they are small (of mean diameter $\sim$1000 A.) and, as a result, are swollen very little in good solvents.

These particles are associated with the gel phase, since mastication of samples from which the gel phase has been removed produces particle-free solutions. One matter which remains unsettled is whether the particles exist as such within the gel phase (being liberated into solution when the gel is broken down) or whether they are formed by the mastication process. It is not yet possible to exclude the latter possibility but it seems more likely that the particles are, in fact, small latex particles which have survived intact the processes of film formation and of mastication. Their survival could be linked with the fact that the gel phase contains most of the nitrogenous impurities and so these particles are likely to be heavily protected by protein surfaces. The rubber within the particles is presumably crosslinked.

The existence in very fresh rubber latex (straight from the tree) of small particles has previously been postulated.[16,17] The primary evidence for their existence was that solutions of very fresh rubber suffered a measurable loss in concentration on treatment with various inorganic powders or on centrifugation. Since the viscosity was not altered, it was deduced that part of the rubber existed in the form of small particles. These particles were designated "microgel," defined[18] as internally crosslinked molecules comparable in size with latex particles. The concentration in latex of such microgel was found to vary considerably from one clonal type to another and to be greatest in trees which had not been tapped for some time. It is to be noted that the clonal type used in the present work, PB186, was found to contain only a very small amount of microgel.[17] It is not clear whether the microgel particles so studied are to be identified with the particles whose existence in masticated rubber has been revealed by light scattering. These latter particles are not removed from solution by treatment with inorganic powders such as calcium sulfate, and it seems likely that they differ in some way from the microgel in freshly tapped latex.

## APPENDIX

### The Turbidity Equation for Mixtures of Spheres and Molecules

The Debye equation for light scattering by solutions of polymer molecules at zero angle of scatter is

$$c/\tau = 1/HM + 2A_2c/H \tag{4}$$

For spheres conforming with the restrictions previously described, the turbidity is given by eq. (1) which can be written

$$c/\tau = k \tag{5}$$

If $\beta$ is the fraction of the polymer which exists in the form of spherical particles, $(1 - \beta)$ being the fraction existing as molecules, then by summing the turbidities given by eqs. (4) and (5) and rearranging, we have

$$c/\tau = \frac{k\{1 + 2A_2M(1 - \beta)c\}}{\beta\{1 + 2A_2M(1 - \beta)c\} + k(1 - \beta)HM} \tag{6}$$

The apparent molecular weight $M^*$ is given by

$$1/M^* = H(c/\tau)_{c=0} = \frac{kH}{\beta + k(1 - \beta)HM} \tag{7}$$

Curves of $c/\tau$ versus $c$ computed from eq. (6) show that the relation is approximately linear so that values of $A_2^*$, the apparent second virial coefficient, can be obtained from the slopes. As $\beta$ is increased (over the range of 0 to 0.02), $M^*$ increases and $A_2^*$ decreases. The full line of Figure 5 shows $A_2^*/A_2$ as a function of $M/M^*$, computed for $k = 10^{-2}$ and $M = 10^5$. The curve is not affected by varying $k$ between $10^{-1}$ and $10^{-3}$.

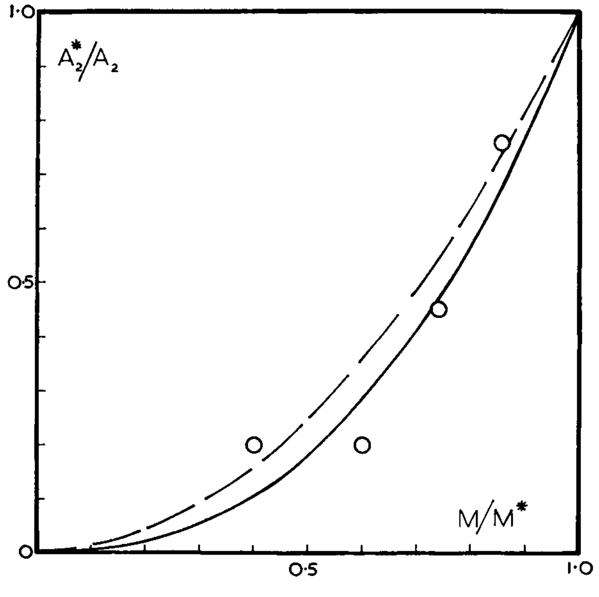

Fig. 5. Relation between $A_2^*/A_2$ and $M/M^*$.

An approximate explicit relation between $M/M^*$ and $A_2^*/A_2$ can be obtained by rearranging eq. (6) and expanding in powers of $c$:

$$c/\tau = \frac{k}{k\gamma + \beta} + \frac{k^2\alpha}{(k\gamma + \beta)^2}c - \frac{k^2\alpha^2\beta}{(k\gamma + \beta)^3}c^2 + \ldots \tag{8}$$

where

$$\alpha = 2A_2M(1 - \beta),\ \gamma = (1 - \beta)HM$$

This series is reasonably convergent for values of $M$ up to about $10^6$; above this the term in $c^2$ becomes appreciable. Since $M^*$ and $A_2^*$ are defined by $Hc/\tau = 1/M^* + 2A_2^*C$, it follows from this and from eq. (8) that

$$A_2^*/A_2 = (M/M^*)^2(1 - \beta)^2 \tag{8}$$

and if $(1 - \beta) \approx 1$, as is the case here, $A_2^*/A_2 = (M/M^*)^2$. This simple relation is indicated by the broken curve in Figure 5; it is a fair approximation to the curve obtained by direct computation.

The addition of scattering particles to a polymer solution lowers $A_2$ and increases $M$. For a given concentration of particles the effect is greater on $A_2$ than on $M$. An approximate test of the applicability of this treatment to the data of Table II has been made in the following way. It was assumed that $M$ (i.e., the true value of $\bar{M}_w$) could be obtained from the intrinsic viscosity through the $[\eta]$–$\bar{M}_w$ relation obtained previously[1] for synthetic polyisoprene. The ratio of this quantity to the measured values for $\bar{M}_w$ (Table II) gives $M/M^*$. To compute $A_2^*/A_2$ it was further assumed that $A_2$ is independent of molecular weight and given by the value found for the unmilled sample, $5.5 \times 10^{-4}$. In this way values of $A_2^*/A_2$ versus $M/M^*$ were obtained. An additional point was obtained by comparing the centrifugation data (which gives $A_2$ and $M$) with the results for uncentrifuged samples of equal intrinsic viscosity. The points so obtained are somewhat approximate but fit the theoretical curves fairly well.

The above derivation and treatment of the data has assumed that $A_2$ is independent of molecular weight. In fact, $A_2$ should increase somewhat as $\bar{M}_w$ diminishes.[2] Examination of Table II shows that, for particle-free samples, this is so with $A_2$

increasing from $5.5 \times 10^{-4}$ to $7\text{-}8 \times 10^{-4}$ as $\bar{M}_w$ diminishes from $1.3 \times 10^6$ to $1.5 \times 10^5$. This change is of the expected magnitude.

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## Synopsis

The value of $\bar{M}_w$ for a sample of natural rubber from fresh latex of one clonal type is $\sim 2 \times 10^6$. As the latex ages, $\bar{M}_w$ diminishes and the gel content increases. Solutions of samples which have been masticated in oxygen contain very small particles of rubber, the existence of which is demonstrated by both light-scattering and electron-microscope measurements. The particles are heterodisperse and have a mean diameter of about 1000 A. As a result of their small size they are swollen very little in good solvents. They originate from the gel phase and either they are a product of mastication or, more probably, they are latex particles which have survived mastication.

## Résumé

Pour un échantillon de caoutchouc naturel provenant de latex frais, la valeur de $\bar{M}_w$ est de $\sim 2 \times 10^6$. Quand le latex vieillit, $\bar{M}_w$ diminue et le pourcentage de gel augmente. Des solutions d'échantillons, qui ont été mastiqués en présence d'oxygène, contiennent de très petites particules de caoutchouc, dont l'existence a été démontrée par des mesures de diffusion lumineuse et par des mesures au microscope électronique. Les particules sont hétérodispersées et ont un diamètre moyen d'environ 1.000 Å. En égard à leurs petites dimensions, elles sont très peu gonflées dans les bons solvants. Elles proviennent de la phase gel, et sont, ou un produit de la mastication, ou plus probablement des particules de latex ayant survécu à la mastication.

## Zusammenfassung

Der Wert für $\bar{M}_w$ für eine Probe von Naturkautschuk aus frischem Latex einer bestimmten Type beträgt $\sim 2 \times 10^6$. Bei Alterung des Latex fällt $\bar{M}_w$ und der Gelgehalt steight an. Lösungen von Proben, die unter Sauerstoff mastiziert wurden, enthalten sehr kleine Kautschukteilchen, deren Vorhandensein sowohl durch Lichtstreuungs- als auch durch elektronenmikroskopische Messungen gezeigt wurde. Die Teilchen sind heterodispers und haben einen mittleren Durchmesser von ca 1000 Å. Infolge ihrer geringen Grösse sind sie in guten Lösungsmitteln nur wenig gequollen. Sie stammen aus der Gelphase und werden entweder bei der Mastizierung gebildet oder sind, noch wahrscheinlicher, Latexteilchen, die die Mastizierung überlebt haben.

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