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The Gel Phase in Natural Rubber

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INTRODUCTION

It is a matter of common knowledge that a proportion of any commercial sample of unmilled *Hevea* rubber is insoluble in rubber solvents, this portion being described as the gel phase. A considerable amount of information as to the properties of this phase was published over twenty years ago, when it was established that the gel content varied with the source and type of rubber and with the nature of the solvent.[1] Although there was rather limited information on this latter point, one must draw special attention to it, since it establishes one fact. If the gel phase is a simple, crosslinked network then it should be insoluble in all solvents, provided that degradative scission of crosslinks does not occur. Since the gel phase is partially soluble in some solvents, it cannot be a crosslinked phase, but must have a more complex structure. The gel phase contains the greater part of the nitrogenous impurities, and the idea emerges that it is an important feature of *Hevea* rubber, reflecting its botanical origins and being perhaps in some way connected with the microgel phase which occurs in fresh latex.[2,3] Synthetic *cis*-1,4-polyisoprene does not possess such a phase, though gel components in synthetic elastomers are far from unknown. These are certainly crosslinked portions, arising as a result of side-reactions during polymerization.

In the present work an examination is presented of the behavior of the gel phase in natural rubber, with the use, *inter alia*, of the light-scattering techniques which have been described in earlier papers.[4,5]

EXPERIMENTAL

Throughout this work a sample of pale crepe rubber (International No. 1X) was used. The intrinsic viscosity in toluene at 25°C. of the soluble component was about 6 dl./g. and its nitrogen content was 0.42%.

Gel contents were determined by immersing samples of rubber in solvent for the stated times in the dark without shaking or stirring, a small quantity of antioxidant (Topanol OC, Imperial Chemical Industries Ltd.) being added. Aliquots were removed and their concentrations determined, after filtration, by evaporation to dryness. It was assumed that the

soluble polymer concentration was uniform throughout the gel and liquid phases.

Light-scattering measurements were carried out as previously described.[4]

Rates of swelling of peroxide-cured vulcanizates were performed in a voluminometer identical with that described by Hauser, Walker, and Kilbourne.[6]

RESULTS AND DISCUSSION

Gel Contents

The conventional method for determining gel content is to immerse the sample in the liquid for ca. 48 hr. Values so obtained for the pale crepe in a range of solvents at room temperature are recorded in Table I and are described as apparent gel contents. In this table the solvents are arranged in order of decreasing solvent power, as indicated by the values of the Flory-Huggins parameter χ obtained from swelling measurements.[7] For comparison, the table also includes gel contents similarly measured for an artificial mixture (prepared by cold milling) of peroxide-cured crepe with *cis*-1,4-polyisoprene (gel-free); this mixture contained 25% of crosslinked material. This comparison is made in order to emphasize the point that gel contents of mixtures of crosslinked material with soluble polymer are constant and do not vary with solvent power. By contrast, the apparent gel contents for the pale crepe vary widely and bear no relation to the values of χ.

TABLE I
Apparent Gel Contents in Various Solvents

Solvent	χ	Apparent gel content, %[a]	
		Pale crepe	Artificial mixture[b]
Carbon tetrachloride	0.334	29	24
Chloroform	0.383	22	25
Toluene	0.391	18	24
Cyclohexane	0.399	46	26
Tetrahydrofuran	0.452	16	22
2,2,4-Trimethylpentane	0.513	40	22
n-Butyl acetate	0.561	30	23
n-Propyl acetate	0.649	68	24

[a] The error in % gel content is computed to be ca. ±2.

[b] 25% Crosslinked pale crepe + 75% *cis*-1,4-polyisoprene.

For three solvents gel contents were determined at intervals for periods up to 16 days (Fig. 1). Equilibrium is not established in 48 hrs., and there is continued slow dissolution of the rubber. Nevertheless, the order of action of the solvents is the same as in Table I.

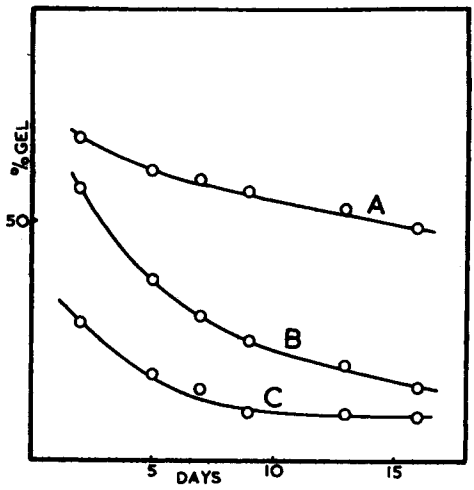


Fig. 1. Variation in apparent gel content with time of extraction for: (*A*) *n*-propyl acetate; (*B*) cyclohexane; (*C*) toluene.

It is of great importance to establish that this process of continued solution is not due to degradation, since no attempt was made to exclude oxygen. Table II gives some values of intrinsic viscosity for the soluble material in various solvents (containing Topanol antioxidant) and for various extraction periods. These include some experiments conducted at higher temperatures to which reference is made later. The data show that there is little degradation, and it is our experience that rubber solutions can be stored almost indefinitely in the dark, whereas exposure to daylight provokes a rapid reduction in viscosity.

TABLE II
Stability of Rubber Solutions

Solvent	Extraction time, days	Temperature, °C.	Intrinsic viscosity (toluene, 25°C.)
Toluene	16	room	5.5
	61	room	5.4
Cyclohexane	3	room	5.4
	15	room	5.7
	2	40	5.6
	24	40	5.9
n-Propyl acetate	4	40	6.0
	13	40	6.0

A further point must be made. Whereas the initial dissolution of the soluble fraction is very slow (Fig. 1), re-solution of soluble fractions in any solvent is quite rapid (<24 hr.). This suggests that the initial process of solution involves the disintegration of some structure, or that the soluble

phase is connected in some way to the gel phase or protected by nonrubber substances. Once the soluble phase has been separated from the gel phase, its subsequent solution is facile. Further strength to this idea is given by the effect of adding small amounts of alcohols to rubber solvents. It has been known for many years that the addition of small quantities of ethanol to various solvents greatly facilitates solution.[1] This effect has been found to be most marked with cyclohexane, the addition to which of 10% ethanol reduces the apparent gel content from 46% to 15%. The intrinsic viscosity of the rubber extracted in this way was somewhat higher (6.64 dl./g.) than that extracted by cyclohexane alone (6.00 dl./g.). One supposes that the effect of alcohol is to assist disintegration of a polar structure.

The nitrogenous impurities remain substantially in the gel phase, the soluble fractions having low nitrogen contents of the order of 0.05%. This is true even when the proportion of soluble material is greatly increased by the addition of small amounts of alcohol, as described in the last paragraph.

Thus so far it has been shown that the material which slowly dissolves in a variety of solvents is of approximately constant viscosity and free from gross contamination with nitrogenous impurities. Further investigations of the soluble phase have been carried out with the light-scattering method with cyclohexane as solvent. The extraction procedure was as described. Aliquots of solution were removed at intervals and their concentrations were determined. After filtration through a coarse (Pyrex grade 3) sintered glass filter to remove gross scattering impurities, the dissymmetry ($z_{45°/135°}$) was measured. Values obtained were 1.31 (2 days), 1.30 (4 days), 1.28 (8 days), 1.27 (15 days), and 1.31 (38 days), the values being effectively constant. This shows that the extracted material does not contain any appreciable amount of particulate scattering material, for these would give dissymmetries greater than 3. The significance of this will be seen later.

Measurement of gel contents at temperatures above room temperature is not easy to achieve, principally because of enhanced solvent volatility. Some experiments with cyclohexane as solvent showed that the gel content fell to 15% in 2 days at 45°C.; this value of gel content is achieved at room temperature only after 15 days (Fig. 1). Experiments with *n*-propyl acetate at 40° were particularly revealing, in that the gel content fell to ca. 15% after several days, whereas at room temperature the gel content remains very high even after prolonged extraction. For this experiment the nitrogen balance was measured, the figures being: original crepe, 0.41% N, soluble phase, 0.05% N, gel phase 2.57% N. These values are consistent with a gel content of 15%. It has already (Table II) been shown that there is little degradation, even at 40°C.

In summary, the experiments of this section show that the extraction of pale crepe results in the removal of soluble polymer the molecular weight of which does not vary significantly over protracted extraction periods;

this polymer does not contain particulate scattering material. The fraction of extractable polymer increases both with time of extraction and with temperature under conditions where little or no degradative scission occurs. Although it is not possible to decide clearly whether a final limiting gel content is every reached, the data, especially at higher temperatures, suggest that about 10% of the crepe remains insoluble even under the most severe conditions of extraction. This is to be regarded as the true gel phase. The effectiveness of different solvents in extracting soluble material bears no relation to their thermodynamic powers (Table I). Three problems, then, are posed by the data: (*1*) what property of a rubber solvent determines its effectiveness in removing soluble polymer from crepe rubber? (*2*) what is the reason for the slow dissolution of the soluble fraction? (*3*) what is the nature of the true gel phase which remains after prolonged extraction?

Diffusion Coefficients

The results of the last section suggested that apparent values of the gel content (Table I) might be governed by diffusion effects. To test this idea measurements were undertaken of the mean diffusion coefficients into rubber of the various solvents. Such measurements should ideally be carried out using raw pale crepe, but there are considerable experimental difficulties. The simplest way of obtaining mean diffusion coefficients is by measurement of rate of swelling. This is most conveniently done with crosslinked rubber, and in this work we have used sheets (2 mm. thick) of peroxide cures of the same pale crepe as that used in the gel content experiments. The justification of this approach is that it is essentially the difference in diffusion properties between the various solvents relative to rubber which is of interest. It is probable that a different sample of rubber

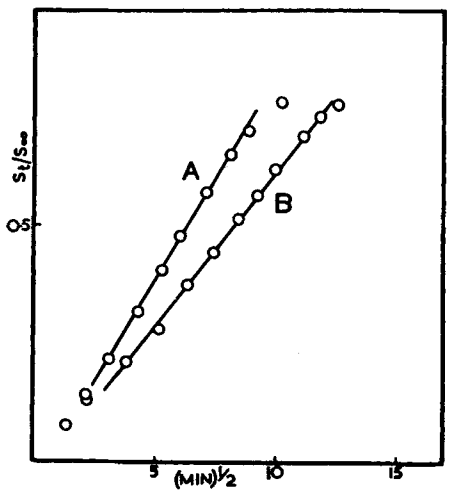


Fig 2. Dependence of swelling ratio on time, plotted according to eq. (1).

TABLE III
Values of the Mean Diffusion Coefficient D at 25°C.

Solvent	$10^6 \times \bar{D}$, cm.²/sec.
Carbon tetrachloride	2.16
Chloroform	3.90
Toluene	3.28
Cyclohexane	2.05
Tetrahydrofuran	3.85
2,2,4-Trimethylpentane	2.34
n-Butyl acetate	2.50
n-Propyl acetate	2.05

would have given different values for diffusion coefficients but we assume that the relative order for the solvents would remain unchanged.

Swelling uptakes were measured in a simple voluminometer[6] at 25°C. Mean diffusion coefficients $\bar{D}$ were evaluated by means of the equation[8]

$$S_t/S_\infty = 2(\bar{D}t/\pi l^2)^{1/2} \quad (1)$$

where S_t is the solvent uptake at time t, S_∞ is the equilibrium value (after ~24 hr.) and l is the sample thickness. Figure 2 shows two typical plots of S_t/S versus $t^{1/2}$, from the slopes of which values of $\bar{D}$ are evaluated. There is slight curvature at the start of swelling and then curvature towards the equilibrium. Table III lists the values that were obtained.

The differences between the values of $\bar{D}$ for the various solvents are not very large; nevertheless, the values are quite reproducible. Figure 3 shows the apparent gel contents of Table I plotted as a function of $\bar{D}$. There is little doubt that there is a correlation between the two properties. Since the values of apparent gel content reflect the rate of solution of the soluble component, it is evident that the rate of solution is governed by the diffusion coefficient.

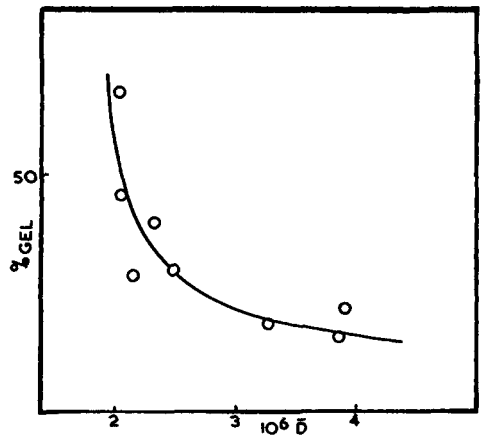


Fig. 3. Correlation between apparent gel content and mean diffusion coefficient.

One factor responsible for the variations in $\bar{D}$ from solvent to solvent is the viscosity. Examination of the data in Table III shows that there is a rough correlation between $\bar{D}$ and solvent viscosity. Thus the viscosities of cyclohexane and carbon tetrachloride are the highest of this series of solvents and their diffusion coefficients are among the lowest. However, the correlation is not very good, and there must be other solvent properties which are responsible for the variations in $\bar{D}$ and hence in apparent gel content.

Effect of Mastication

On mastication of pale crepe in oxygen the amount of gel component is progressively reduced until the rubber becomes completely soluble. Solutions of such masticated rubbers are frequently quite turbid. Previously this turbidity had been attributed to suspended nonrubber components.[1] Recently, however, we have shown that this turbidity is caused by the presence of small particles of rubber, with a mean diameter of ca. 1000 A.[5]

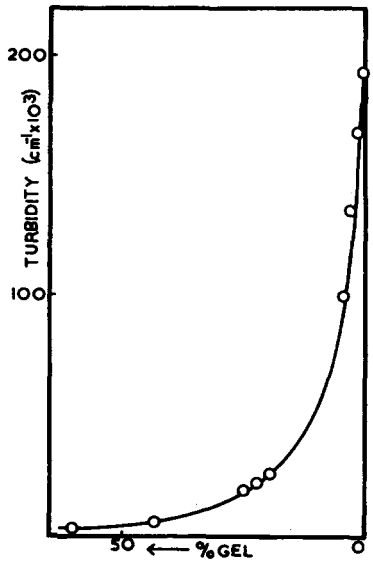


Fig. 4. Turbidity of solutions (0.2% in *n*-hexane) of crepe masticated for various times, plotted as a function of apparent gel content.

Figure 4 shows the turbidity (measured at a scattering angle of 90° for 0.2% solutions in *n*-hexane) as a function of the gel content for a series of masticated samples. There is a sudden and rather sharp increase in turbidity as the gel content approaches 20–10%. The limiting turbidity reached is comparable with that previously reported.

Further observations were made on *n*-hexane solutions of masticated crepe. In addition to the turbidity, measurements were made of the dissymmetry ($z_{45°/135°}$). The concentration of each solution was measured

before and after centrifuging at ~50,000G for 2 hr., the difference between the two values being the amount of centrifuged material (per cent centrifugate), expressed as a percentage of the total (sol + gel) rubber. Figure 5 shows the three parameters as a function of time of mastication.

At a mastication time of 8–9 min. there is an abrupt increase in turbidity. This corresponds to ca. 15% gel (cf. Fig. 4). At this point, also, the amount of centrifugable material rises sharply. The per cent centrifugate associated with unmasticated crepe (i.e., at zero time) presumably represents dirt and nonrubbers. The difference in the values before and after the abrupt change must correspond to that entity responsible for the turbidity and its concentration is thus estimated to be ~17%. This figure is probably subject to some error. The dissymmetry rises smoothly to a

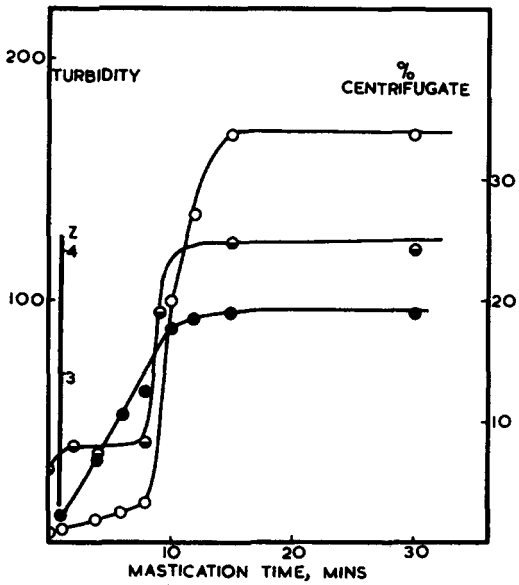


Fig. 5. Plots of (O) turbidity, (◒) per cent centrifugate, and (●) dissymmetry z as a function of time of mastication.

limiting value of ~3.5. An abrupt increase in this parameter is not to be expected, since it is not very concentration-dependent. The equilibrium value of z corresponds to a particle diameter of 1200 A.

The results of Figures 4 and 5 show clearly that, when pale crepe is masticated in oxygen, a point is reached at which there is a sudden production of particulate scattering material (previously identified as rubber[5]). For the sample of pale crepe this material represents about 17% of the total rubber and has a particle diameter of ca. 1200 A. It has already been shown that this component originates from the gel phase and it had been postulated that it consists of microgel particles which have preserved their identity throughout the commercial process of latex coagulation and drying. The following experiments strengthen this view.

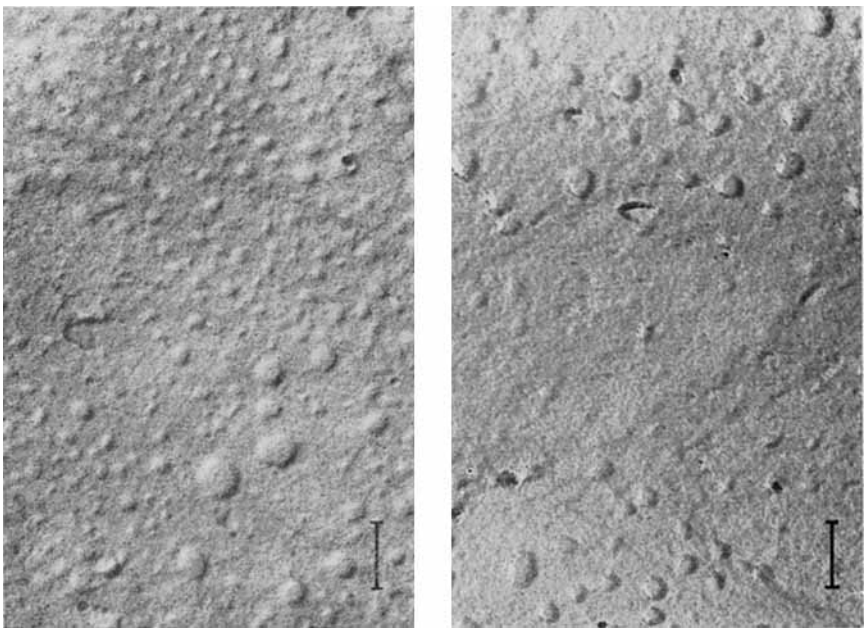
Microgel particles are internally crosslinked latex particles.[3] It is possible to make a synthetic microgel latex by artificially crosslinking a fully soluble latex rubber. A sample of rubber from fresh Malayan latex (Clone PB 186) was found to be fully soluble in hexane (this is not usually the case and gel contents of up to 25% are often found). An aliquot of the latex was treated with *tert*-butyl hydroperoxide and tetraethylenepentamine (1% of each, based on the rubber content). After standing for several days at room temperature the rubber contained (in hexane) 90% gel. It is reasonable to suppose that the treated latex contained individually crosslinked particles, analogous to microgel. This material was masticated for 30 min. in oxygen, and a 0.2% solution of the product was found to have the characteristically high turbidity displayed by masticated pale crepe (Figs. 4 and 5). The actual value of the turbidity was 535×10^{-3} cm.$^{-1}$, and the dissymmetry was 4.3. These figures are somewhat higher than those recorded for the pale crepe, probably because the gel content is much higher, and therefore the concentration of scattering material will be greater.

This experiment shows that the mastication of rubber from artificially crosslinked latex produces scattering particles with the expected properties. Alternatively, one can crosslink solid rubber and demonstrate that its behavior is quite different. A sample of soluble crepe (extracted from pale crepe with cyclohexane) was crosslinked at 140°C. with dicumyl peroxide to a gel content of 25%. Mastication of this material for 30 min. gave a product whose turbidity in hexane (0.2%) was only 6×10^{-3} cm.$^{-1}$, almost identical with that given by masticated noncrosslinked rubber. This low turbidity is that to be expected for dissolved rubber molecules (rather than microgel particles) at this concentration.

Mastication produces the particulate component (microgel) only when the crosslinked regions are separated as they are in crosslinked latex. This component, then, is not merely the result of fragmentation of crosslinked molecules, for it is not produced by mastication of crosslinked solid rubber. It seems likely that latex particles, when crosslinked, possess sufficient individuality to retain their character while being masticated. This may be a result of their surface structure.

Structure of the Gel Phase

The inference from the experiments described is that the true gel phase in pale crepe (i.e., that which remains after prolonged extraction) consists of small particles derived from the parent latex. Direct proof of this has been obtained by electron microscopy. A piece of the pale crepe was extracted with *n*-propyl acetate for 17 days at 40°C., after which the gel content was ~10%, indicating that all the soluble material had been removed. A two-stage replica (gelatine/carbon) was made of the surface, which was then shadowed with gold/palladium and examined at 40,000 × in an electron microscope. Figure 6*a* shows the result. The particulate nature of the surface is seen quite clearly. It is not possible to make



a *b*

Fig. 6. Electron micrographs 42,400× of replicas of the surfaces of (*a*) gel phase and (*b*) masticated crepe. The scale is 2000 A.

precise measurements of particle diameters from such photographs, but examination shows that the larger particles have diameters of ~1300 A., ranging down to about half this size. This is in excellent agreement with the size estimated from light-scattering dissymmetry measurements which yielded a weight-average diameter of ca. 1200 A.

Figure 6*b* shows the surface of masticated pale crepe. Again the microgel particles are visible, but at a somewhat lower density, because they are diluted with the soluble phase. This confirms that mastication does not destroy the particles nor greatly alter their size.

Conclusions

The gel phase in natural rubber could be formed (*1*) in the tree; (*2*) in the latex after tapping and before coagulation; (*3*) during coagulation; (*4*) after coagulation. With respect to (*4*) it is a well-known fact that crepe rubber undergoes hardening on storage,[9] and it has been indicated that this process is the result of a crosslinking reaction, possibly involving aldehyde groups.[10] There is rather scanty evidence that the apparent gel content increases during storage hardening.[9] In the present work it has been shown that the true gel content after prolonged extraction is quite low. The properties of this true gel phase suggest strongly that it is composed of small latex particles and we infer, therefore, that this phase originates as (*1*) or (*2*) above. The possibility is not excluded that in some samples

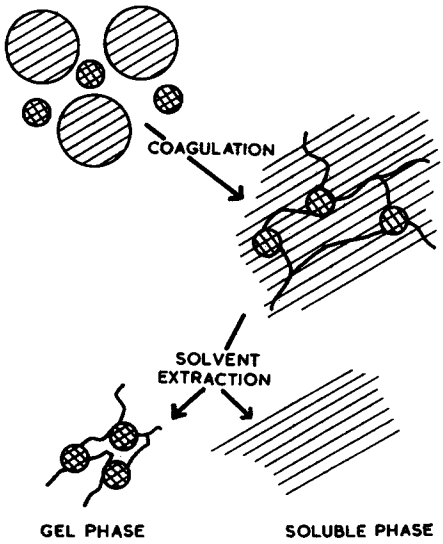


Fig. 7. Schematic representation of the processes of latex coagulation and solvent extraction. The hatching indicates soluble material, and the crosshatching crosslinked material.

of crepe rubber additional gel may be present as a result of continued crosslinking during storage; this does not appear to be the case here.

The following description of the formation of microgel and its conversion into the gel phase is speculative. Rubber from very fresh latex is normally completely soluble in rubber solvents, provided that the tree is in regular tapping. Immediately after tapping a crosslinking reaction sets in. If we postulate that the rate of the crosslinking reaction is governed by the rate of entry of some component into the particles, then the extent of crosslinking will be greatest in the smallest particles. This postulate is necessary to account for the fact that the microgel particles are found, both by light scattering and electron microscopy, to have a mean diameter of 1000–1500 A., considerably smaller than the mean diameter of all the particles in a typical natural latex.

Before coagulation, then, the latex will contain a proportion of crosslinked particles. One factor responsible for variations in this proportion will be the age of the latex, for it has already been shown that, as latex ages, so the amount of insoluble material increases.[5] In this connection it is interesting to note that latex from "rested" trees and latex which has been taken from a point on the tree distant from the tapping cut is often completely insoluble.[2] Such latex may be regarded as having aged within the tree.

Reference to Figure 7 will facilitate understanding of the following discussion. Before coagulation there exist in the latex crosslinked small particles and uncrosslinked large ones, all the particles being covered with surfaces containing proteins, etc. On coagulation, the large particles will

essentially fuse together to form a continuous matrix containing within it the remains of the original surfaces. It may be supposed that there is some degree of chemical interaction between this protein-containing network and the rubber molecules. The small, microgel particles do not fuse together because the rubber inside them is crosslinked and because their small size gives them greater stability. Prolonged extraction of this system with solvent leaches out the uncrosslinked rubber, leaving behind the microgel particles which are held together in an aggregate by the residual surface material. This is the true gel phase, and it contains nearly all the nitrogenous impurities.

It has been inferred that the rate of solution of the soluble phase is controlled by the rate of diffusion of solvent. This is not the whole story, for, as has been described, subsequent re-solution of the soluble phase is much more rapid. It seems likely that, in order to dissolve out the soluble rubber from the protein matrix, not only must solvent diffuse with the system, but work must be done to detach it from the matrix; hence the suggestion that there may be chemical interaction between the rubber molecules and the matrix. The effect of added alcohol is presumably to facilitate disruption of the system.

Estimates of the microgel content from gel content measurements and from centrifugation experiments are in fair agreement. For the sample of pale crepe used, gel content measurements indicated that ca. 10% of the rubber remained insoluble after prolonged extraction. Centrifugation of solutions of masticated crepe gave a figure of ~17% for the amount of centrifugable particles. These values will, of course, vary from sample to sample, depending on the type and age of the parent latex.

This work serves to emphasize the complexity of *Hevea* rubber which is far from being a simple polyisoprene and which differs considerably in these properties from synthetic *cis*-1,4-polyisoprene. It is not unlikely that this difference is a contributing factor to the known differences in the processing behavior of the two elastomers.

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References

1. Kemp, A. R., and H. Peters, *J. Phys. Chem.*, **43**, 923 (1939); *Ind. Eng. Chem.*, **33**, 1391 (1941).
2. Bloomfield, G. F., *J. Rubber Res. Inst. Malaya*, **13**, 271 (1951).
3. Freeman, R., *Proc. Rubber Technol. Conf., 3rd, London*, 3 (1954).
4. Allen, P. W., and G. M. Bristow, *J. Appl. Polymer Sci.*, **4**, 237 (1960).
5. Allen, P. W., and G. M. Bristow, *J. Appl. Polymer Sci.*, **5**, 510 (1961).
6. Hauser, R. L., C. A. Walker, and F. L. Kilbourne, *Ind. Eng. Chem.*, **48**, 1202 (1956).
7. Bristow, G. M., and W. F. Watson, *Trans. Faraday Soc.*, **54**, 1731 (1958).
8. Crank, J., *The Mathematics of Diffusion*, Oxford University Press, 1956.
9. Wood, R. I., *J. Rubber Res. Inst. Malaya*, **14**, 20 (1952).
10. Sekhar, B. C., *Rubber Chem. Technol.*, **31**, 425, 430 (1958); *Proc. Nat. Rubber Res. Conf. Kuala Lumpur*, 512 (1960).

Synopsis

Evidence is presented which suggests that the true gel phase in natural rubber is composed of small crosslinked latex particles (microgel), whose presence is revealed by light scattering and by electron microscopy. These are combined into a matrix with soluble rubber molecules, forming the apparent gel phase. The rate of solution (and hence the apparent gel content) of this phase varies with solvent and is governed by the diffusion rate of solvent into rubber. Prolonged extraction removes the soluble component. Since the redissolution of the soluble component is very rapid, it is inferred that it is initially bound to the microgel particles by specific forces which have to be overcome by the diffusing solvent. Mastication of crepe breaks up the matrix, leaving microgel particles whose presence can be detected in solution.

Résumé

On met en évidence certains faits qui suggèrent que la véritable phase du gel dans le caoutchouc naturel est constituée de petites particules de latex ponté (microgel), dont la présence a été mice en évidence par diffusion lumineuse et par microscopie électronique. Ces particules sont insérées dans un réseau de molécules de caoutchouc soluble qui forment la phase apparent de gel. La vitesse de solubilisation (et donc la teneur apparente en gel) de cette phase varie avec le solvant et est régie par la vitesse de diffusion du solvant à travers le caoutchouc. Une extraction prolongée enlève la constituant soluble. Etant donné que la redissolution du constituant soluble est très rapide, on suppose, qu'initialement, il est lié aux particules du microgel par des forces spécifiques qui sont décruites par la diffusion du solvant. La mastication du crêpe détruit le réseau en libérant des particules de microgel dont la présence peut être détectée en solution.

Zusammenfassung

Es werden Tatsachen angeführt, die für den Aufbau der wahren Gelphase in Naturkautschuk aus kleinen, vernetzten Latexteilchen (Mikrogel) sprechen, deren Vorhandensein durch Lichstreuungs- und elektronenmikroskopische Messungen erwiesen wird. Diese sind mit löslichen Kautschukteilchen zu einer Matrix verbunden und bilden so die "scheinbare" Gelphase. Die Lösungsgeschwindigkeit (und somit der scheinbare Gelgehalt) dieser Phase ist vom Lösungsmittel abhängig und wird durch die Diffusionsgeschwindigkeit des Lösungsmittels in den Kautschuk bestimmt. Lang dauernde Extraktion entfernt die lösliche Komponente. Da die Wiederauflösung der löslichen Komponente sehr rasch verläuft, kann man schließen, dass sie ursprünglich an die Mikrogelteilchen durch spezifische Kräfte gebunden ist, die durch das diffundierende Lösungsmittel überwunden werden müssen. Mastizierung von Crepe zerstört die Matrix und es bleiben Mikroteilchen zurück, deren Vorhandensein in der Lösung beobachtet werden kann.

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