THE STRUCTURE OF RUBBER AND OTHER ELASTIC COLLOIDS

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Efforts have been made in recent years to ascertain the structure of rubber and explain its properties, by consideration particularly of (a) the structure of the globules in rubber latex, (b) the behaviour of rubber towards swelling agents (especially ether), (c) the X-ray diagram given by rubber under certain conditions. The purpose of the present paper is to consider current views concerning the structure of rubber, and also to point out that, since other colloids are known which exhibit in greater or less degree elastic properties similar to those exhibited by rubber, any general view of the structure of rubber can—it must be assumed, unless cogent reasons to the contrary are adduced—be regarded as acceptable only if it is also applicable to such other colloids. Its purpose is, further, to suggest that a study of such other elastic colloids is helpful in elucidating the structure of rubber.

A microscopical study (using the micromanipulator) of the globules in *Hevea* latex led Freundlich and Hauser[1] to conclude that the globules consist of rubber in two distinct forms: that they are composed of "a viscous liquid surrounded by an elastic shell".[2] The inner portion of the globule was considered as being caoutchouc in a lower and the outer as caoutchouc in a higher state of polymerization. The two forms of rubber hydrocarbon which these authors believed to be recognizable in the globules were at first assumed[3] to be identical with the parts, sol and gel, obtainable from raw rubber by the ether diffusion process (*vide infra*), but more recently Hauser has apparently modified this opinion.[4]

Von Weimarn[5] has concluded that the microscopical phenomena presented by rubber latex cannot be interpreted as proving the presence of a solid shell of rubber on the outside of the globules; and the present writer's observations, using the micromanipulator, are in agreement with this conclusion.

Leaving aside the question of the structure of the globules in rubber latex, a two-phase structure of a lower order, not recognizable by microscopic examination, has been considered to be present in rubber by many recent writers and has been made the basis of explanations of many of the properties of rubber. The two phases in question are usually known as sol and gel rubber and are distinguished by the fact that they are respectively soluble and insoluble in ether.

In point of fact the idea that raw rubber consists of two parts, identical in proximate composition, but one soluble and the other insoluble, is an old idea which has been lately revived and made the basis of explanations of some of the more striking modern phenomena observed with rubber, especially by means of X-rays. The idea was expressed by Payen,[6] Herbst,[7] Gladstone and Hibbert[8] and Weber.[9] Caspari,[10] by treating raw rubber with petrolic

ether, separated it into a soluble and an insoluble portion, the latter of which he referred to as the "pectous" form of rubber. He believed that it was possible to make a definite separation of rubber into the two forms, and that the proportions in which they occurred varied from sample to sample, and could be determined quantitatively. Stevens[11] reported, however, that, on repeating Caspari's experiments, he had been unable to obtain concordant results in repeat experiments. "The proportion of soluble to 'pectous' appeared to depend on the period of extraction." "Moreover," he said, "I find that the 'pectous fraction', if allowed to stand sufficiently long in cold petroleum spirit, dissolved wholly, with the exception of a small quantity of slimy nitrogenous matter which settled to the bottom of the containing vessel."

In recent years Caspari's views concerning the twofold nature of rubber have been revived; in the first place by Feuchter,[12] who applied ethyl ether instead of petrolic ether for the separation of the two parts. The portion of raw rubber which diffuses into ether when the rubber is allowed to stand in that liquid, and which corresponds to Caspari's "soluble" rubber, Feuchter designated Diffusion or D-rubber, while the portion which remains, and which corresponds to Caspari's "pectous" rubber, he designated as the gel skeleton. These two parts are now commonly known as sol and gel rubber, respectively, although Hauser[2] prefers the terms alpha- and beta-rubber. According to present usage, sol rubber is such portion of raw rubber as diffuses from the swollen mass into the solvent when rubber is allowed to stand in ethyl ether, whereas gel rubber is such portion as remains behind.

The view that rubber consists of two parts sharply separable by means of ether has been much in the foreground in recent years. Several writers,[13] among whom Hauser is prominent, have seen in the presence of sol and gel portions in rubber an explanation of the X-ray diffraction phenomena which rubber shows when stretched. It has also been called upon to explain the behaviour of rubber on mastication,[14] the Joule effect,[15] and the elastic behaviour of rubber generally; and, further, has been made the basis of an explanation of vulcanization.[16]

Although in its normal unstretched condition, raw rubber, when examined by X-rays, gives only an amorphous ring, it gives a fiber diagram with X-rays when strained beyond about 80 per cent.[17] If the amount of strain is gradually increased to say 1000 per cent, the interference spots on the X-ray diagram gradually increase in intensity but do not change in position. It has been supposed that the appearance of a diffraction pattern on stretching rubber is due to the occurrence of a "de-swelling" of the gel by the sol phase. Such a de-swelling seems to the present writer improbable. Assuming that the phases are to be regarded as imbibed each by the other, they are in the normal condition swollen to an extent far short of their maximum capacity for swelling, and it seems unlikely that mere extension would produce a syneresis. Elastic colloids (e.g. vulcanized rubber), after being caused to imbibe ten or more times their own weight of a liquid, can be stretched without any apparent occurrence of syneresis. And it does not seem likely that a syneresis on

stretching would occur in raw rubber, where, on the view under consideration, the higher polymeric phases are swollen only slightly and where the "swelling agent" is itself a solid, namely the lower polymeric phase.

If raw rubber is kept for a considerable time at a low temperature, until it becomes "frozen," it then gives with X-rays a Debye-Scherrer diagram in the unstrained condition. This has been attributed to an increase in the gel component at the expense of the sol component during the period of storage at a reduced temperature. Conversely, it has been supposed that on subjecting rubber to heat or mechanical working a change of gel to sol takes place, and that on keeping rubber which has been so treated the change gradually reverses itself, the rubber tending to regain its original properties.[18]

X-ray studies of stretched elastic colloids cannot yet be said to have solved the problem of the cause of elasticity in such materials. It is true that raw rubber, when stretched to moderate elongations, gives an X-ray diffraction pattern, which indicates that certain parts of the material have assumed a definite configuration, but vulcanized rubber, which has better elastic properties, requires to be stretched much further before it gives a pattern, while polyvinyl acetate shows no pattern at 1500 per cent elongation and polystyrene none at 1300 per cent elongation.[19] It would seem that the regular orientation of parts which an X-ray diffusion pattern connotes is not essential to the possession of elastic properties. Indeed, the occurrence of such a pattern is rather to be regarded as indicating that the material is assuming the character of an inelastic fiber.

The assumption of a fibrous character by rubber when it is stretched can be readily demonstrated, as Hock[20] showed, by cooling stretched rubber until it becomes brittle and shattering it by a blow. Other writers[21] have shown that when rubber is stretched and then cooled until almost inextensible, the tensile strength is higher the greater the original stretch. Thus Mark and Valko[22] found that a sample of raw rubber which had a tensile strength of 360 kg./cm.[2] at 195°, had a tensile strength of 2470 kg./cm.[2] if stretched 700% before cooling. This is in accord with the general property of fibers, first demonstrated by Herzog[23] for rayon, that the greater the degree of orientation of the elements of the fiber, the greater is the tensile strength.

Experimental evidence, some of which will be outlined in what follows, clearly shows that rubber and other elastic colloids are highly heterogeneous. Hence, in the opinion of the present writer, the view that rubber consists of two parts, "sol" and "gel," represents far too great an initial simplification of the issues involved in describing the nature of rubber and explaining its elastic behaviour. In the writer's view rubber does not consist of caoutchouc in merely two states of polymerization but is a mixture of an unbroken series of polymers representing a rather wide range of degrees of polymerization.

That the X-ray diffraction pattern given by stretched rubber is not due to the presence of two forms of rubber, one diffusible into swelling agents and the other not thus diffusible, is shown by the fact that diffusion-caoutchouc itself gives a pattern. A sample of diffusion-caoutchouc, prepared by removing the resin from raw rubber by cold extraction with a petrolic ether-

acetone mixture (3:7) and then allowing the rubber to stand in benzene until a portion of it had diffused into the solvent, was examined at extensions of 300% and 1800% . At both it gave a diffraction diagram, the diagram at the latter extension being remarkably sharp.[24]

In other respects too, diffusion-caoutchouc shows all the normal behaviour of rubber. Naturally, its behaviour is not quantitatively identical with that of the original rubber from which it is obtained, since it represents only a fraction of the latter and the range of polymeric states in it is not identical with that in the original rubber. It can, however, be vulcanized, especially if small proportions of fatty acids are added to replace those removed in freeing the rubber from "resin" before diffusion; it shows "racking" phenomena (cf. infra); it requires breaking down on a mill in making up a stock, and the ease of breakdown is not strikingly different from that of the original rubber. The last-mentioned observation is opposed to the attempts which have been made to describe the phenomena involved in the mastication of rubber on the basis of its supposed dual nature. The fact that rubber must be "broken down" by mastication on a hot mill in order to render it plastic has been ascribed to the necessity of rupturing the shells supposed to surround the liquid centres of the latex globules or more generally to producing a dispersion of the gel rubber in a continuous medium of sol rubber.

If the diffusion of a portion of raw rubber into a solvent is allowed to proceed only a short way, the diffusion-caoutchouc isolated is still an elastic solid substantially similar in physical consistency to the original rubber. If there were a liquid phase in rubber, it would be expected that this would appear first on extraction. The fractional extraction of rubber affords, however, no indication of the presence of a liquid phase.

A study of the behaviour of rubber towards solvents[25] clearly indicates that the degree of heterogeneity of rubber is much greater than that suggested by the sol-gel conception. The latter conception, as already stated, came to the fore as a result of Feuchter's separation in 1925 of rubber into a portion soluble and a portion insoluble in ether. Experiments started by the writer in 1923 on the behaviour of rubber in some 400 organic liquids show that rubber cannot be separated sharply into a soluble and an insoluble part, but that the portion which passes into solution depends greatly on the nature of the liquid employed, the length of time over which the solution or diffusion process is allowed to proceed, and other circumstances. It was early observed that when weighed pieces of raw rubber are placed in organic liquids, and the imbibition followed by weighing the pieces at intervals, in a large number of cases the weight at first rises and the later falls. That the fall is due to diffusion of part of the rubber from the swollen mass into the liquid can easily be shown by adding alcohol or other precipitant to the latter, when the diffused rubber is thrown out. The process of diffusion of rubber from the swollen gel goes on gradually over a long period and does not apparently ever come to a sharp end. Some of the samples were kept under observation for four years, and in many such cases the whole of the rubber with the exception of the protein ultimately became dispersed in the liquid. Even in relatively poor swelling

agents (see, e.g., o-tolualdehyde, octylene, isoamyl oxalate, chloracetal, cyclohexanone in Table I), the dispersion process was often observed to have completed itself after 3-4 years. The general impression made by the mass of data which has been secured on the swelling of raw rubber is that in general the process of diffusion never comes to a definite end or allows of a sharp separation of the rubber into a "sol" and a "gel" portion. A little of the data is quoted in Table I.

TABLE I

Imbibition of Organic Liquids by Smoked Sheet (Original Weight: 1)

Liquid	Weight after periods of days						
	1	2	3	7	31	62	4 years
							Completely
Octylene	6.68	4.46	4.22	3.31	—	—	dispersed.
o-Tolualdehyde	3.67	4.66	4.88	4.00	1.65	—	"
Chloracetal	5.99	5.57	4.71	2.50	1.18	—	"
Cyclohexanone	6.14	4.84	2.83	1.40	—	—	"
n-Valeric anhydride	1.84	2.44	2.95	3.39	—	—	"
Isoamyl oxalate	1.51	2.13	2.76	3.40	—	—	"
Ethyl-m-toluate	7.98	8.39	8.25	6.07	2.92	2.36	
Isobutyl acetate	9.00	8.90	6.96	3.10	1.61	—	
p-Tolualdehyde	2.83	3.59	4.15	4.24	2.41	0.87	
o-Tolunitrile	5.67	7.10	7.79	7.43	4.82	2.43	
n-Propyl ether	5.98	5.25	4.29	3.03	2.27	1.87	
Safrole	9.51	11.60	12.01	10.36	5.86	4.51	
p-Cresyl ethyl ether	13.18	14.85	13.16	9.02	5.66	4.81	
Butyrophenone	4.83	5.95	6.18	4.30	—	1.60	
Allyl isothiocyanate	7.44	9.60	9.65	5.63	2.82	—	
Lauryl chloride	7.49	8.52	7.86	5.76	3.02	—	
Phenyl ethyl bromide	7.23	9.03	9.26	5.36	2.91	—	
Nonylic acid	3.37	5.00	6.50	6.91	1.58	—	
Tripropylamine	9.50	7.02	5.45	4.09	2.85	2.12	

The examples quoted in Table I have been chosen to represent liquids belonging to a considerable number of different chemical types. The figures show the weight of the swollen mass after various periods of time, the initial weight being taken as 1. In some but not all cases the samples were examined after a lapse of four years. Most of the liquids are not among the most powerful swelling agents. With such powerful swelling agents the swollen mass is usually too weak to handle for the purpose of weighing after one day. It may be mentioned for purposes of comparison that the weight of e.g. benzene imbibed in one day by the specimen of rubber in question was 24.22 parts; of ether, 11.10 parts.

If the point at which the process of diffusion becomes very slow were to be taken as the end point, the proportions of "sol" and "gel" which it would be concluded that the rubber contained would undoubtedly vary greatly with the solvent used.

Although there is no sharp end to the diffusion process, the ease with which diffusion occurs and the proportion which will diffuse into the solvent with reasonable rapidity, vary in different liquids, and are apparently influenced by (a) the swelling power of the liquid, (b) its viscosity. Even in a given liquid the proportion of caoutchouc which will diffuse in a reasonable time from a given sample of rubber can be greatly modified. Such modification can be brought about by (among various means) adding small quantities of certain agents, especially strong organic bases and acids, which increase the amount of the liquid imbibed by the rubber. When studying the electro-viscous effect in rubber sols in 1924, the author employed diffusion into ether and petrolic ether for the purpose of securing acoutchouc free from protein and observed that the addition of small amounts of piperidine, diethylamine, sodium ethoxide and ammonia greatly increased the proportion of diffused caoutchouc obtained from a given sample of raw rubber. Previously it had been found that small amounts of piperidine increase the swelling of vulcanised rubber in benzene.[26]

The influence of bases on the swelling and dispersion of raw rubber may be illustrated by the following data:—

Smoked Sheet in Petrolic Ether (B.P. 25-45°).

	A	
	Pet. ether alone	Pet. ether containing 5 drops piperidine per 10 ccs.
Weight originally	0.1317 grms.	0.1075
Weight after swelling 24 hours	1.0925 grms.	1.7435 grms.
Increase in weight	735 per cent	1520 per cent

	B	
	50 ccs. pet. ether	40 ccs. pet. ether + 10 ccs. ethereal solution NH_3
Weight originally	0.60 grms.	0.60 grms.
Weight of diffused caoutchouc pptable after 8 days' standing	0.05 grms.	0.31 grms.

In a good swelling agent such as benzene the proportion of caoutchouc which will readily diffuse from a sample of smoked sheet is greater than in a poorer swelling agent such as ether or especially petrolic ether. Thus, for example, in an experiment in which 3.83 grms. smoked sheet was left in 190 ccs. benzene with occasional very gentle agitation, 75.5 per cent of the rubber has dispersed in 7 days.

A study of the behaviour of vulcanized rubber in swelling agents also fails to afford any evidence of the presence of two sharply distinct parts. In current writings on the structure of rubber less attention has been given to vulcanized than to raw rubber, although the elastic properties which any

theory of the structure of rubber must ultimately endeavour to explain are exhibited in much greater perfection by the vulcanized than by raw material. It, however, the X-ray diffraction phenomena shown by raw rubber are ascribed, as they currently are, to its two-fold (sol-gel) nature, then it is natural to assume that, since vulcanized rubber shows similar X-ray phenomena, it too consists of two parts, although the proportion in which the two parts occur may be regarded as different, owing to the conversion during vulcanization of a portion of the sol into the gel form. (Cf. Hauser: Trans. Inst. Rubber Ind., 1926, p. 243:—"During vulcanization the liquid rubber phase is more or less gelled or polymerised.")

Observations on the behaviour of vulcanized rubber in swelling media show, as in the case of raw rubber, no evidence of the presence of two clearly distinct parts. It is usually said that vulcanized, in contradistinction to raw rubber, is insoluble in all liquids. The writer has, however, found that, by leaving fully-vulcanized rubber in swelling agents for periods up to four years in the dark, the rubber gradually dispersed in many cases, Further, the rubber dispersed completely or substantially so, and there was no indication of the presence of a soluble and an insoluble phase. Examples of liquids in which vulcanized rubber was observed to disperse completely in the course of time are ethyl benzoate, butyl acetate, butyl oxalate, ethylene glycol dipropionate and twenty-one other esters; methyl iodide, bromoform, isobutyl chloride, o-chlorotoluene and twelve other halogenated hydrocarbons; benzene, valeric acid, ethyl propyl ketone, cyclohexanone, butyl isothiocyanate, hexyl alcohol, and o-tolualdehyde, diisolbutylamine, n-propyl ether.*

A number of artificial colloids which show elastic and colloid properties fundamentally similar to those of raw rubber can readily be shown to be highly heterogeneous. Such materials, although less important industrially than rubber, are more tractable than rubber and a study of them is capable of throwing light on the structure and behaviour of rubber, not only in regard to the question of heterogeneity but also in other respects.

Examples of artificial elastic organic colloids are synthetic caoutchoucs from conjugated dienes of low molecular weight, reaction-products from fatty oils and sulphur, polymers of methyl acrylate and similar esters, polymers of styrene, vinyl acetate and ethyl itaconate, caoutchouc hydrochloride, the reaction product from isoprene and sulphur dioxide. The first three of these examples are elastic at room temperature; the others, when warmed or swollen. Of these materials polystyrene and poly-vinyl acetate have been most closely investigated.

Polystyrene at ordinary temperatures is a hard solid; clear, when in massive pieces or fibers; white, when precipitated. At ordinary temperature it is not elastic, the films being brittle and the powder friable, but, as was first observed by the writer,[27] when warmed or swollen, it shows elastic properties. The

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* In this connection it may be mentioned that the viscosity of such sols of vulcanized rubber is very much less than that of sols of raw of the same concentration in the same liquids. The former sols are now being studied more fully. It may also be mentioned that crystals obtained from some of the sols apparently represent vulcanized rubber in a crystalline condition. They are being made the subject of closer investigation.

elastic properties are essentially similar in kind to those of raw rubber. The following observations made by Whitby and McNally[28] will serve to indicate the nature of the elastic phenomena displayed by autopolymerized styrene and to show their general similarity to those of raw rubber.

(a) Both polystyrene and rubber have an "elasticity temperature" below which the material becomes inextensible or "frozen." For rubber, however, this temperature is somewhat below ordinary room temperature.

(b) Polystyrene shows the effect known in rubber as "racking"; that is to say, if stretched while above its elasticity temperature and then, while extended, cooled below that temperature, it retains the extension, and, if then heated above its elasticity temperature, retracts. (This phenomenon can readily be observed in raw rubber by stretching a strip of smoked sheet and then, while maintaining the extension, cooling it in a stream of cold water. The rubber will be found to retain its extension if now released, but when warmed slightly, as, for instance, by holding it in the palm of the hand, will undergo retraction. It should be mentioned that the term "racking" is not very clearly defined and has sometimes been used to denote particularly the extension of rubber at elevated temperatures to lengths greatly exceeding those to which it can be extended without rupture at ordinary temperature. In this usage of the term too, polystyrene can be "racked," i.e. at temperatures well above the elasticity temperature it can be extended to lengths much beyond those at which near the elasticity temperature it suffers rupture.)

(c) Like rubber, polystyrene shows elastic after-effect, i.e. on releasing a specimen which has been stretched, a slow retraction follows on the initial rapid retraction. This is shown by the following experiment. A strip 6 cms. long was placed in water at 95°, stretched to a length of 22.5 cms., and then released under no-load. Table II gives the length of the strip at intervals after its release.

TABLE II

Retraction of Polystyrene

Time after release (secs.)	0	1	7	102	310	900
Length (cms.)	22.5	10	9	8	7.5	7

(d) When the material is stretched and then released, the amount of set left after any time is profoundly influenced by the length of time for which the material has been maintained in a stretched condition. In an experiment, strips of polystyrene were stretched 450 per cent at 95°, and, after being held at this extension for various periods of time, were released. The retraction over a period of time was followed. The data in Table III indicate the character of the results obtained.

TABLE III

Influence of Period of Stretching on Retraction of Polystyrene

Time kept at 450% (mins.)	0	5	10	90
Extension immediately after release (%)	50	150	175	300
Extension 200 secs. after release (%)	0	55	75	150

The following experiment carried out with strips of raw rubber (smoked sheet) shows that the set in rubber is similarly influenced by the length of the period of time for which the material is maintained in a stretched condition. Strips were held at an elongation of 200 per cent at 48° for various periods of time, and, after being released, they were allowed to stand at room temperature for ten days, when no further retraction could be observed. The set remaining is tabulated as E_1. The strips were then heated for one hour at 100°, and, after they had been allowed to cool to room temperature, the set (E_2) was again measured. The results are given in Table IV.

TABLE IV

Set in Raw Rubber after Extension for Various Times

Time kept at 200% at 48° (mins.)	Set at room temperature (%) E_1	Set at 100° (%) E_2
5	22.5	17.5
10	27.5	17.5
15	37.5	20
30	40	27.5
60	52.5	35
120	62.5	42.5
240	67.5	47.5

(e) The higher the temperature at which either rubber or polystyrene is stretched to a given extent, the greater is the set remaining on release. This was observed qualitatively for polystyrene. For raw rubber more exact data were secured. Strips of smoked sheet were held at different temperatures for 30 minutes at an extension of 200 per cent, and were then allowed to retract at room temperature for 10 days (set: E_1) and subsequently were heated to 100° and the set (E_2) again measured. Table V gives the results.

TABLE V

Influence of Temperature of Stretching on Set in Raw Rubber

Temperature during extension	Set at room temperature (%) E_1	Set at 100° (%) E_2
20°	17.5	15
25	22.5	15
35	30	20
40	47.5	22.5
60	55	45
70	70	55
83	90	75

(f) Both with polystyrene and with rubber, the greater the length to which a specimen is extended, the greater the set present under given conditions. This was determined only qualitatively for polystyrene. For rubber (smoked sheet) the following more exact data were secured.

TABLE VI

Effect of Original Elongation on Set in Raw Rubber

Elongation maintained for 30 minutes at 48° (%)	Set after 10 days at room temperature (%) E_1	Set at 100° (%) E_2
50	7.5	7.5
100	20	17.5
150	27.5	20
200	40	27.5
250	· 55	30
350	125	52.5
400	142.5	—

(g)   The following experiment was carried out on a strip of polystyrene of cross section 2.05 sq. mm. A constant load of 75 grms. was maintained throughout; the temperature was first raised at a definite rate; then lowered; again raised, and so on. The elongation at the end of each period of heating and cooling and at certain intermediate points is shown in the following Table.

TABLE VII

Heating and Cooling Polystyrene under Fixed Load

Temperature Rising	Falling		Elongation (%).
1. 55°			0
65			10.8
75			35.2
80			457
	1 a.	70°	473
		64	481
		40	481
2. 67			481
70			495
79			523
	2 a.	74	528
		70	528
3. 79			560
	3 a.	25	560
4. 79			590

These results indicate a behavior analogous to that of rubber in two respects. (a) During the first period of cooling, it will be noticed, "creep" takes place until the temperature has fallen below the elasticity temperature. (b) During the periods, 1, 2, 3, 4, the final extension increases in each succeeding period, but the difference between the extension at the end of the first and of the second period is greater than the difference between that at the end of any other two successive periods. This clearly recalls the behavior of rubber when sub-

jected to successive cycles of extension and retraction. With rubber, the difference between the first and the second cycles is greater than that between any other two successive cycles (see Whitby, Plantation Rubber and the Testing of Rubber, 1920, Chap. XVIII).

(h) It has been shown by Rosbaud and Schmid (Z. tech. Physik, **9**, 28 (1928)) that even extremely small loads will cause raw rubber to extend and will even rupture it if allowed to act for sufficiently long periods. A similar behaviour was observed with polystyrene. For example, while a load of 45 grms. applied at 95° to a strip 2.13 sq. mm. in cross section caused relatively rapid stretching and produced an elongation of 122 per cent in 5 seconds, even a load of 5 grms. would produce the same elongation if allowed to act for 225 seconds.

(i) Sols of autopolymerised styrene show many similarities to sols of rubber. At the same temperature and in the same solvent sols of rubber and of polystyrene have similar viscosities. The nature of the solvent affects the viscosity of sols of the two materials in, broadly, a similar way. The lowest viscosities in both cases were observed in the same solvent, viz. acetal.

Poly-vinyl acetate has also been shown to possess elastic properties similar to those of polystyrene.[29]

The high degree of heterogeneity which has been shown to be characteristic of high polymers in general[30] has also been found to exist in elastic polymers. Data showing the heterogeneity of poly-vinyl acetate have already been put on record.[29] The following data show that polystyrene is heterogeneous. A sample of polymer prepared by heating styrene for four days at 245° was separated by fractional precipitation with alcohol from solution in benzene into six fractions. The fractions had molecular weights as follows:[31]

TABLE VIII

Fractionation of Thermo-Polymerized Styrene

Fraction No.	1	2	3	4	5	6
Mol. wt.	4405	2914	2632	1979	1274	977

The heterogeneity of autopolymerized styrene was demonstrated by determining the viscosity of sols prepared from fractions secured by means of fractional precipitation and by means of fractional solution.

A sample of synthetic methyl caoutchouc, prepared by the thermo-polymerization of 2:3-dimethylbutadiene-1:3, was found to be resolvable into fractions having different properties, as the following data will show:

TABLE IX

Fractionation of Methyl Caoutchouc

Fraction No.	1	2	3
Time of flow of sol (0.854 gm. in 20 ccs. benzene) (secs.)	55.4	67.8	81.3

Direct experimental evidence has also been secured of the fact that natural rubber shows a degree of heterogeneity similar to that of the artificial elastic colloids mentioned above. The diffusion of swollen rubber into the swelling agent was carried out fractionally, fractions being poured off and fresh liquid added from time to time. The sols thus obtained were found, after being adjusted to the same caoutchouc content, to differ widely in viscosity. Diffused rubber was also separated by fractional precipitation into fractions having different properties. The data obtained in this connection will be published elsewhere. They afford conclusive evidence that raw rubber considered as a whole and also diffusion-caoutchouc ("sol" rubber) are far from homogeneous.

In the case of solid polymers obtained from styrene by means of heat, heterogeneity is easily recognizable when the materials are treated with ether, acetone or ethyl oxalate. When the much more highly polymerized product obtained by allowing styrene to undergo autopolymerization is treated with ether or acetone, no solution or apparent swelling takes place, and when treated with diethyl oxalate, only a very slight swelling. When, however, styrene polymerized by heating at 140° or 180° is treated with these liquids, the major part rapidly goes into solution, but there remains a portion which fails to disperse and which on standing settles out as a white powder. This is clearly a fraction of the material more high polymerized than the rest. If it is separated and treated with benzene (a solvent for highly-polymerized styrene), it readily goes into solution.[28]

The ease of dispersion of colloidal polymers derived from a given monomer depends on the degree of polymerization. Thus the product obtained by the spontaneous polymerization of styrene disperses far less than the much less highly polymerized product obtained by heating styrene. The fact that rubber, like other elastic colloids, consists of a mixture of polymers covering a rather wide range of molecular sizes is in full accord with observations outlined earlier on its behaviour to a variety of swelling agents. In a homologous series of polymers the extent to which swelling agents are imbibed rises and the ease with which dispersion takes place falls, as the series is ascended. Futher, imbibition by and dispersion of a given polymer is different in different liquids. Hence, the proportion of a given sample of raw rubber which will pass readily into the solvent, *i.e.* the proportion of "sol" rubber obtained, differs in different liquids.

As the higher polymers disperse more slowly than the lower, the rate at which a sample of rubber disperses falls as the proportion which has undergone dispersion increases. Even the highest polymers present will, however, if given time, disperse in many solvents, and hence, as already stated, the whole of the rubber disperses in many cases if left to stand for a long time. The protein network present in rubber may possibly retard the dispersion of the caoutchouc somewhat, but can hardly be regarded as the main cause of the slowness with which the higher fractions of rubber disperse. In this connection it may be noted that diffused rubber (obtained by means of petrolic ether), although free from protein, was found after being vulcanized to behave in solvents essentially similarly to ordinary vulcanized rubber. Vulcanized

fatty oils, in which too a protein network is lacking, were observed to disperse more and more slowly, as the period of vulcanization and, as it may be assumed, the degree of polymerization, increased. After the polymerization of a sulphurized oil (containing no free sulphur) had proceeded just to the point at which the material had set solid, the product dispersed readily in benzene, but, as the polymerization was carried further by continued heating, dispersion became slower and slower, and finally a product was obtained, which, like vulcanized rubber, dispersed in benzene only after standing for several years.

A striking case of the difficulty of dispersion due apparently to a high degree of polymerization is presented by poly-methyl acrylate. This material, which was prepared by heating methyl acrylate for half an hour on the water-bath with o.1 per cent benzoyl peroxide, has a molecular weight so high that it produces no appreciable depression of the freezing point of benzene. It shows greater swelling than any other polymeric product which has been examined by the writer, taking up, *e.g.*, 88.8 times it weight of methyl acetate; yet it failed to disperse in any reasonable time even in good swelling agents.

Not only the ease of dispersion in solvents, but many other properties of organic colloids are influenced by the degree of polymerization. This has been shown to hold for the melting point of a series of polymers such as the poly-indenes;[32] for the softening point of elastic colloids such as fractions of polystyrene and poly-vinyl acetate; for the ease of cracking on pyrolytic decomposition in the case of polyindenes[33] and polystyrenes, and for the viscosity of sols of a given concentration.[29] It also holds for the elastic properties, as may be well illustrated by reference to polystyrene.

As obtained by allowing styrene to undergo spontaneous polymerization at room temperature, polystyrene has a molecular weight of the order of 100,000 or more; it produces an almost inappreciable depression of the freezing point of benzene. The data quoted earlier in regard to the physical properties of polystyrene all refer to such material. As obtained by heating styrene, however, polystyrene has a lower and measurable molecular weight and correspondingly possesses a lower elasticity temperature and poorer elastic properties. A sample prepared by heating styrene for 48 hours under reflux at 140° had a molecular weight, determined cryoscopically, of 1920; and one prepared by heating styrene for 24 hours in a closed vessel at 180°, a molecular weight of 2180. These samples became soft at 40° and readily extensible at 47°, whereas the corresponding figures for autopolymerized styrene were 65° and 75°. While they could be extended readily, their power of retracting was poor and they showed a vast amount of set when the extending stress was removed. At 72° a specimen stretched 800 per cent and then released, retracted to 600 per cent and remained there. A specimen extended to 1400 per cent at 89° and then released, retracted only to 1100 per cent and remained there.[28] Compare the data for autopolymerized styrene in Tables II and III. Synthetic rubber also illustrates the influence of the degree of polymerization on the elastic properties. A sample of synthetic rubber made by heating isoprene at 85°, found to have a molecular weight of about 4000—far lower than that of natural rubber—and to give sols of much lower viscosity

than those from natural rubber, had, correspondingly, elastic properties much inferior to those of raw rubber.

Since the properties of elastic polymers derivable from a given monomer are clearly dependent on the degree of polymerization, the properties of a given sample of materials such as those under discussion in the present paper will be determined both by the mean molecular weight of the material and the range of molecular sizes in the mixture of which the material is composed. For the polymeric products obtainable from a given monomer there is probably a certain degree of polymerization which is optimal for the possession of good elastic properties. If the degree of polymerization is too low, the material, while readily deformable, shows poor recovery from deformation, *i.e.*, it shows a large amount of set when allowed to retract after deformation; if the degree of polymerization is too high, the deformability is small and the material is tough, or, in the highest states of polymerization, brittle or "short." In a certain intermediate state of polymerization, the material is both deformable and retractable.

A consideration of data such as those given to illustrate the elastic behaviour of polystyrene and raw rubber shows that the materials are not perfectly elastic; that on allowing them to recover after deformation, recovery is not immediate and complete, but that there is a certain amount of set. The amount of set is dependent not only on the degree of polymerization, but is also greatly influenced by other factors. The longer the period of time for which the material is kept stretched the higher the temperature at which it is stretched and the greater the extent to which it is stretched, the greater is the set.

Further there are three kinds of set, viz. (a) that which disappears in time at ordinary temperature, (b) that which remains permanently at ordinary temperature but disappears on raising the temperature $(E_1 - E_2)$, (c) that which remains permanently even on raising the temperature (E_2). Set of the first and of the last types, *i.e.* sub-permanent and permanent set, are due chiefly to the lower polymers present. Set of the second kind, which is permanent at ordinary temperature, but sub-permanent at an elevated temperature, may for convenience be referred to as apparent set and is of special interest. It is due to the fact that, although retractive forces are still present in the material, they become apparent only when the internal viscosity of the material is reduced by increasing the temperature.

What has just been referred to as the viscosity might perhaps more correctly be termed the "elastic yield value." The potential retractive forces in the material are unable to effect refraction because the yield value is too high, unless the temperature is raised. As the unqualified term "yield value" has been assigned to the deformation and flow of plastic materials, it would seem desirable in the case of elastic materials to refer to "elastic" yield value. This yield value is significant in connection with other phenomena presented by elastic colloids as well as in connection with apparent set under that aspect of it just discussed. If a strip of polystyrene is stretched and then, while stretched, cooled below its elasticity temperature, it sets hard and retains its

extension indefinitely at room temperature. The material now presents an extreme case of apparent set. If it is warmed to above its elasticity temperature (the temperature at which the elastic yield value is less than the ultimate breaking stress), the elastic yield value becomes reduced sufficiently to permit the potential retractive forces to become effective, and consequently the material retracts. Polystyrene can also be rendered deformable at ordinary temperature if the elastic yield value is reduced by causing it to imbibe a swelling agent. Another phenomenon which is probably due to reduction in the elastic yield value as a result of increase of temperature is the retraction which follows the application of warmth to a strip of rubber under load. This phenomenon is one aspect of what is known as the Joule Effect.[34] Similarly the removal of "grain" from milled rubber by means of a hot table depends on the reduction of the elastic yield value. The same effect, viz. the release of internal strains in calendared rubber sheet, may be brought about, as Weigand showed,[35] by applying a swelling agent.

The effect of swelling agents in reducing the elastic yield value, and thus rendering elastic colloids which are not normally so, is not confined to the cases, such as polystyrene and poly-vinyl acetate, which have already been mentioned. It is also observable with hydrophilic colloids such as the proteins, silk fibroin and wool keratin. Von Weimarn[36] records that when silk fibroin is dissolved in certain concentrated aqueous salt solutions and then precipitated by the addition of alcohol, it shows elastic properties when the degree of hydration is suitable. "As the degree of dehydration increases," he says, "we may witness the realisation of every possible transition stage marking the gradual conversion from the condition of an extremely viscous syrup through a gluey mass to that of an elastic caoutchouc-like jelly (in which condition an *elastic* extension to twice or even four times the former length is possible) and thence to that of masses possessing the consistency of an animal tendon, till it finally reaches the state of an altogether solid mass, so solid that when in thin sheets it may be broken."

Similarly, the elastic properties of wool are greatly influenced by the extent to which the protein is swollen by moisture in the fibre.[37] If a wool fibre containing the normal water-content is stretched and then, while stretched, is dried, it will be found to retain its extension on release, but will then re-' tract if again allowed to absorb moisture, i.e. if the elastic yield value of the protein is reduced by allowing it to swell somewhat. Advantage is taken of this phenomenon in the treatment of wool known as "crabbing."

Although wool is much less extensible than rubber, there is broadly an analogy, not only in this respect, but also in other respects between the elastic behaviour of wool and of raw rubber. In both cases time plays an important part in the result of any series of mechanical manipulations through which the material may be made to pass. Strictly speaking, there is no such thing in either case as a stress-strain diagram, but only a stress-strain-time diagram. This is perhaps more obvious with wool than with rubber. On loading a wool fibre, there occurs first a rapid extension, which is reversible, and this is

followed by a further, slow extension, which is only partly reversible and is greatly influenced by the length of time over which the load acts, owing to plastic flow of material.

The ultimate explanation of the fact of elasticity in elastic organic colloids cannot yet be given with any sufficient degree of definiteness. It seems desirable to bear clearly in mind that what distinguishes elastic materials from other deformable materials, such as plastic solids or viscous liquids, is, not their ability to undergo deformation, but their power to recover from deformation. The important feature which calls for explanation is not their deformability but their retractability. It has recently been suggested that the explanation of the elasticity of rubber is to be found in the shape of the molecules themselves. The molecules are regarded as helical in shape. It is supposed that on stretching rubber the spirals straighten out and that "the force which causes the extended chains to coil again into spirals when the stress is released is the residual valencies of the double bonds."[38] On this view the retraction is due to the attraction of the double bonds in the caoutchouc molecule for each other. But the molecules of many other elastic colloids are saturated or substantially so. Polymers of styrene, vinyl acetate and methyl acrylate, for example, are capable of retracting after extension despite the absence of double bonds. In support of their view that the retractibility of rubber is due to its double bonds Fikenscher and Mark quote the fact that if the double bonds are saturated with hydrogen chloride the product is inelastic. It may, however, be pointed out that caoutchouc hydrochloride is only apparently inelastic, since, although inelastic at ordinary temperature, it shows elastic properties when warmed.[27]

Further, according to the view of Fikentscher and Mark, mere unfolding of the spiral molecules will permit of rubber being stretched sixfold. Only beyond that extension is the lattice actually stretched, and, they imply, will permanent set appear. The data given on pages 208-209 of the present paper show, however, that permanent set can be produced in rubber at much lower extensions than 600 per cent.

It may well be supposed that the forces which bring about the retraction of elastic colloids after deformation are essentially the same as those which produce cohesion in the unstrained material. Elastic solids stand between brittle solids on the one hand and liquids on the other in regard to the strength of the cohesional forces involved. In a brittle solid cohesion is such that, on applying stress, rupture takes place before change of shape. In a liquid, change of shape occurs with great readiness and the cohesional forces are insufficient to restore the shape. In an elastic solid, subjected to stresses below the breaking stress, the cohesional forces are insufficient to prevent change of shape but sufficient to restore the shape when the stress is removed.

In imperfectly elastic materials, such as are under discussion in the present paper, the phenomena are complicated by the fact that the materials are mixtures of polymers which differ in regard to the strength of the cohesional forces associated with them. It seems probable that the forces involved in the elastic behaviour of these materials are not only, and perhaps not chiefly,

the primary valencies or lattice forces, but secondary forces such as the force of association responsible for the abnormal viscosity of all but the most dilute sols of these colloids.

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