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A CRITICAL EXAMINATION OF SOME CONCEPTS IN RUBBER CHEMISTRY[1]

By Dr. THOMAS MIDGLEY, JR.

MIDGLEY FOUNDATION, THE OHIO STATE UNIVERSITY

VULCANIZATION

It is now over one hundred years since Goodyear discovered vulcanization. Broadly speaking, vulcanization is a process whereby a semi-useless vegetal product is converted into the most amazingly versatile raw material the world of industry has ever known. Need I recite your daily contacts with it? For example, when you take a shower bath, your faucet valve is faced with rubber, the curtain is rubberized cloth, the mat that keeps you from slipping is rubber, and the imitation sponge you use is vulcanized rubber in still another form. And when you play, golf balls, tennis balls, footballs and baseballs all depend on vulcanized rubber for liveliness. Notice that I didn't mention tires. They are almost too sacred to talk about these days. And yet after a century, rubber chemists are in less agreement on the nature of the chemistry of vulcanization than Goodyear's neighbors were that he was crazy. Nor has a Hall of Fame jury yet been selected with brains enough to honor Goodyear's memory as it deserves. It is all most astounding; but also is vulcanization.

If one wished to manufacture some rubber article,

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[1] The concluding part of the address made by Dr. Midgley on the occasion of the presentation to him of the Willard Gibbs Medal of the Chicago Section of the Americal Chemical Society at Chicago on May 27. The presentation of the medal was made by Professor Harry N. Holmes, national president of the society.

the first thing is to get a priority order; after that, the crude rubber may be obtained. The crude rubber is broken down on a mill to make it plastic, sulfur and other things are added, and the rubber is shaped to the desired form and held there for some time while being heated; after that the article is finished. Comparison of the crude rubber and the finished article will show that many physical properties are remarkably alike qualitatively, although enhanced quantitatively in the vulcanizate. Naturally, this suggests that vulcanization is reversed breakdown; therefore, if breakdown is the result of molecular ruptures, it logically follows that vulcanization must be molecular building up by polymerization or condensation. This indeed is an easy conception to visualize. It gives an explanation of the part played by sulfur—simply that the sulfur atom connects two rubber molecules by joining to each of them by primary valences. The simplicity of this broad concept has won many converts, too many, for it has one grave error. There is not one single piece of sound evidence that it is true and many that it is not. In the first place, vulcanization is not breakdown in reverse, except in a very superficial way. Incipient and then progressive vulcanizates do not show the regular steps of increasing viscosity and decreasing solubility that would be expected; nor can a vulcanizate be obtained that gives quantitative properties corresponding to those of unbroken-down rubber. At first there is a slight rise in viscosity during vulcanization and a slight decrease in solubility, then a sudden conversion to a gel type rubber. During the early stages of this gel formation the gel can be peptized by various agents.[2] Who ever heard of peptizing primary valences?

Consider both breakdown and vulcanization from a different point of view. Instead of assuming that unbroken-down rubber is elastic with fair tensile strength because its molecules are long and that broken-down rubber is plastic because its molecules are short, imagine that the difference in plastic properties of unbroken and broken-down rubber is caused by a difference in the ease with which the molecules slip past one another under stress. True, this difference may be the result of different lengths of molecules or it may be that in broken-down rubber a few small molecules act as lubricants for the larger ones just as a small amount of lubricating oil in unbroken-down rubber will give a plasticizing effect. This concept does not require the rebuilding of large molecules out of small ones to account for the change that is called "vulcanization." Any procedure which results in reduced slipping will accomplish a change of this sort; witness the loading effect of carbon black or zinc oxide. But the reduction of slipping is not all there is to vulcanization. Were it all, then vulcanized rubber would disperse instead of merely swell in suitable solvents. Therefore we must assume the creation of intermolecular attractions of some sort during vulcanization. This, of course, can be accomplished by sulfur bridges between molecules. If this were the only possibility, the slipping concept would merely have been a mental detour which returned to the original starting point. But sulfur bridges are by no means the only way to stop slipping. We also have the possibility of creating groups on the molecule which will cause association. Call these polar groups or secondary valences or what you will, but in any case they differ distinctly from primary valences. The question now resolves itself into differentiating between these two concepts—namely, attraction by primary valences and attraction by association forces. The following observations are pertinent. If vulcanization is stopped at a point just beyond gel formation—that is, where the vulcanizate will swell but no longer disperse in rubber solvents—then this vulcanizate can be dispersed by peptization.[3] It is difficult to see how this could be so if this gel were held together by primary valences; on the other hand, a gel held together by association forces would be expected to behave in such a manner. Again, as the amount of combined sulfur increases, a maximum point of vulcanization properties is reached after which most of these properties decrease until, at about half saturation, the vulcanizate has decreased in physical properties corresponding almost to the condition of broken-down rubber. It is difficult to see how this can be explained on the basis of primary valence formation; whereas if the forces of association are considered to be due to the formation of some kind of polar groups, the phenomenon becomes easily explainable on the basis that, as long as the polar groups of a given molecule are far enough apart, strong external forces, capable of attracting other molecules, will be in existence. But when the number of such groups are increased and they are crowded closer together, their respective forces will be satisfied by internal attraction leaving only a small portion for attracting other molecules. This explanation admittedly is hypothetical, but it serves to demonstrate that a rational explanation of the phenomenon of over-vulcanization can be based on the concept of association forces, whereas no similar explanation is forthcoming based on the primary valency concept. Even the simple observation that the slight swelling by solvents of well-vulcanized rubber greatly reduces its tensile strength also favors the association concept. For if the mass were held together by primary valences, there would seem to be no more reason for

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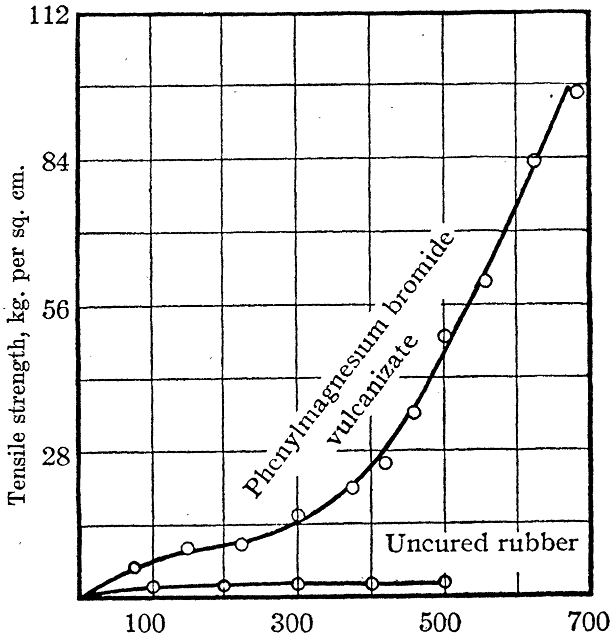
[2] Williams, *Ind. Eng. Chem.*, 26: 1190, 1934.

[3] *Ibid.*

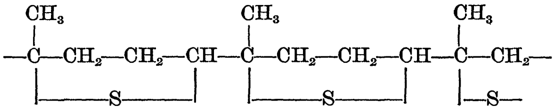
a loss of strength than occurs in a sponge when it is filled with water, while if it were held together by association forces, the adsorption of solvent would increase the distance between molecules and thus reduce the strength of the forces holding them together.



Stress-Strain Curve

Fig. 1

Several years ago we attempted to establish the existence of primary valence linkages between molecules by destructively distilling well-vulcanized rubber and examining the products in the hope of finding one which could be related to such a linkage. The resulting products differed in no significant detail from those obtained from the destructive distillation of crude rubber. We next extended this work to the destructive distillation of ebonite $(C_5H_8S)_n$, without obtaining any compound suggestive of intermolecular linkage.[4] We did obtain a group of substituted thiophenes, representing only a small part of the whole, which we interpreted[5] as demonstrating a linkage of sulfur to the rubber molecule:



$$-\underbrace{\overset{\overset{\displaystyle CH_3}{|}}{C}-CH_2-CH_2-CH}_{S}-\underbrace{\overset{\overset{\displaystyle CH_3}{|}}{C}-CH_2-CH_2-CH}_{S}-\underset{|\!-S-}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-$$

While such negative evidence can not be considered as disproving the possible existence of primary valence linkages between molecules, it does add to the total weight of evidence against their existence.

In contradistinction to the negative results obtained in our search for evidence to substantiate the primary valency concept, we were able to obtain positive evidence that association forces could be used exclusively for vulcanization. We discovered that the addition of Grignard reagents to rubber solutions would cause gelling. We extended this discovery to the vulcanization of a test sample of broken-down rubber.[6] The resulting stress-strain curve is shown in Fig. 1. This is a typical curve for a vulcanizate. The tensile strength is too great for a mere loading effect, and it is difficult to see how a small amount of methyl magnesium bromide could act as a loading agent anyway; nor is the tensile strength so very bad when it is considered that no loading agent was present. There can be no question that this result is true vulcanization. Grignard reagents do not produce intermolecular linkages; also the vulcanizate could be reverted to its original broken-down condition by counteracting the Grignard with alcohol. The recovered product could be revulcanized with Grignard and recovered again as many times as desired, a further demonstration that intermolecular primary valences were not generated in the vulcanization.

In view of the preponderance of evidence in favor of the association concept of vulcanization and the complete lack of any basis for the primary valence concepts, it is surprising that rubber chemists continue to think in terms of primary valence as an explanation of the vulcanization reaction.

Retraction

The retraction of rubber—that is, the property which causes rubber to return to its original shape and size with force after being stretched—is the outstanding characteristic that distinguishes it from chewing gum, beeswax and tar, and makes it into the useful material it is. The study of this property really falls in the field of physics rather than chemistry, but its importance justifies its inclusion in any discussion of rubber or rubber chemistry. Indeed, this property is so important that any material which possesses it can be called a rubber, no matter what its chemical constitution.[7]

The early students of this property took the viewpoint that rubber was analogous to gelatin in some way, that it was some sort of two-phase system,[8] that it was a colloidal suspension,[9] that it was corpuscular in structure,[10] that its molecules were gathered together in miscelles,[11] etc. None of these conceptions

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[4] Midgley, Henne and Shepard, *Jour. Am. Chem. Soc.*, 54: 2953, 1932.

[5] *Ibid.*, 56: 1326, 1934.

[6] *Ibid.*, 56: 1156, 1934.

[7] Midgley, in Davis and Blake's "Chemistry and Technology of Rubber," A. C. S. Monograph 74, p. 679, 1937.

[8] Freundlich and Hauser, *Kolloid-Z.*, Spec. No. 36, 15, 1925.

[9] Pummerer, Nielson and Gündel, *Ber.*, 61: 1583, 1928.

[10] Freundlich and Hauser, *loc. cit.*

ever yielded constructive results or advanced rubber technology.

Some twenty-odd years ago, after Staudinger announced the long-chain structural formula, opinion began taking shape that the extension and retraction of rubber were simply an integration of the behavior of the component molecules.[12] In other words, it was assumed that the rubber molecule itself is subject to extension and exhibits forceful retraction thereafter. This concept has steadily gained ground. It is true that no direct evidence exists to confirm this concept, and by its very nature perhaps there never will be; on the other hand, no contradictory evidence exists, which very well could if this concept were in great error. Therefore, until some such evidence is obtained or a concept is developed which fits the facts more accurately, this theory should be accepted as the nearest available approach to the truth.

Under this concept a generalized theory of molecular behavior has been developed. For example, refer to Staudinger's long-chain formula above. It is obvious that this is not a true space configuration since the tetrahedral characteristics of carbon atoms are disregarded. Imagine such a space model and take into account that parts of this molecule can rotate about any single bond. Now fold the molecule back on itself many times about single bonds and a much more compact model is obtained than would appear from looking at the long-chain formula. This is a good picture of how a rubber molecule may retract, but it gives no insight into why it does so. Long paraffin molecules, such as hydrogenated rubber, could do the same thing as far as structure goes, but they do not. Rubber molecules do. Why?

Two explanations have been offered; one is by Shecklock[13] with later variations by others, based on thermal and thermodynamic considerations, and one is by Mack,[14] who makes use of van der Waals forces, applied to scale models. I am incompetent to differentiate critically between these two. Each of them fits certain observed data better than the other, but Mack's concept appeals more strongly to me, as it is based more closely in the fields of rubber chemistry with which I am familiar, and it predicts quite well the behavior of rubberlike and related substances of known composition, structure and isomerism. Its extension might be useful in predicting new molecular forms which could lead to better and less expensive synthetic rubbers than we now have.

As just stated before, I am not qualified to criticize either of the above theories, but I do feel qualified to criticize both rubber chemistry and chemists for not having mastered either of them more thoroughly. That they are difficult to master is no excuse, for the rubber chemist who expects to serve humanity well must be prepared to master many things more difficult than either of these theories.

In closing I should like to make myself clear on one point. I have not hesitated to criticize, severely, those concepts which are in disagreement with the results that I and my colleagues have obtained. I have done this in the full knowledge that I can be just as wrong as any one else, and I shall feel grateful to any one who proves that I have been, for then I shall profit by such proof in increasing my own understanding of these problems. Likewise I shall feel pleased if our results are confirmed, for then I shall have the satisfaction of feeling that I have aided in advancing rubber chemistry. I can be disappointed in only one way, to have our results ignored.

THE AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE

THE TWENTY-SIXTH ANNUAL MEETING OF THE PACIFIC DIVISION. II

Edited by Professor J. MURRAY LUCK

SECRETARY

AMERICAN SOCIETY OF PLANT PHYSIOLOGISTS, WESTERN SECTION

(*Report by D. I. Arnon*)

The annual meeting of the Western Section of the American Society of Plant Physiologists was held at Salt Lake City, Utah, from June 17 to June 19.

The effect of war conditions was reflected in a number of last-minute cancellations of papers by prospective participants, but the cooperation of societies in arranging joint sessions for topics and papers of mutual interest contributed to the success of the meeting by favorably influencing both program and attendance. The program consisted of a symposium on "Organic Matter in Relation to Plant Growth," sponsored jointly with the Western Society of Soil Science and the Western Section of the American Society for Horticultural Science; a symposium on "Present Concepts of Water Relations of Plants,"

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[11] Meyer and Mark, *Ber.*, 61: 1939, 1928.

[12] Astbury, *Ann. Repts. Chem. Soc.*, 1931, 322.

[13] Shecklock, *Trans. Inst. Rubber Ind.*, 8: 568, 580, 1933; 9: 94, 1933.

[14] Mack, *Jour. Am. Chem. Soc.*, 56: 2757, 1934.