[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE OHIO STATE UNIVERSITY]

Natural and Synthetic Rubber. XII. Reversible Vulcanization, by Organo-metallic Derivatives

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Oxygen compounds, sulfur derivatives, sulfur and selenium have been used to cause the change in the physical properties of rubber called vulcanization. Such vulcanization has never been reversed.

It has now been observed that under certain conditions some organo-metallic compounds produce vulcanization and that the change is reversible. Broadly speaking, these compounds can be classified as organo-metallic derivatives active toward combined oxygen. Zinc-alkyls and Grignard reagents have been used successfully. The new type of vulcanization is reversed by treating the cured sample with water or acetic acid. Even exposure to moisture is sufficient. After vulcanization has been reversed, the specimen exhibits again its original physical properties, within the experimental errors of measurement. The increase of tensile strength obtained indicates that this new and reversible vulcanization parallels customary curing with sulfur.

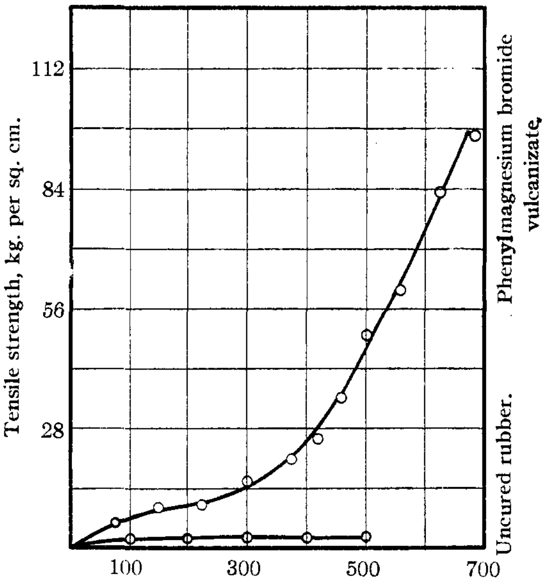

Fig. 1.

Experimental

A strip of rubber placed in a test-tube is kept in a vacuum desiccator for one day. The amount of phenylmagnesium bromide required to form the stiffest gel in a dry benzene solution of the same rubber is determined separately. The same amount dissolved in a quantity of ether equal to the weight of the rubber strip is poured into the tube. The latter is cooled to −80°, evacuated, sealed, shaken to ensure good distribution and allowed to stand for two days. After opening the tube, the ether is removed by slow evacuation in a desiccator and the tensile strength of the strip is measured as quickly as possible. Figure 1 shows typical stress–strain curves for a sample of crepe rubber milled for fifteen minutes on a laboratory mill, before and after vulcanization with phenylmagnesium bromide (0.18 g. per gram of rubber). Many samples were obtained with tensile strength ranging between 135 and 160 kilograms/sq. cm.[1]

Gelling of a benzene solution of sol rubber is an evidence of vulcanization which is particularly convenient to study. It readily occurs when a solution of "broken down" rubber in benzene is treated with a Grignard or a zinc-alkyl compound. This gelling is reversed by a subsequent treatment with water or acetic acid, the latter being especially adapted to this purpose.

A summary of the qualitative results so far obtained follows. (1) Sodium rubber prepared in the absence of oxygen does not gel; prepared in the presence of oxygen, or exposed to air, it does gel. (2) The purest sol rubber[2] obtainable by fractional precipitation gels slightly. "Broken down" rubber gels more easily and the gel is stiffer. (3) The gels are reverted to their original sol condition by the addition of water, acetic acid, or other substances capable of breaking a Grignard complex. In contradistinction to this, the gels are peptized by addition of more phenylmagnesium bromide, of ZnC_2H_5I, C_2H_5OMgBr, anhydrous $AlCl_3$, $FeCl_3$, $MgBr_2$, but not by $Zn(C_5H_{11})_2$. (4) Acetic acid added progressively to a peptized gel reforms the gel and further acid addition reverts it to its original sol rubber condition. (5) The cycle of gelling, peptizing, depeptizing and reverting, or any portion thereof, is presumably repeatable many times, but in practice accurate observation is limited to two complete cycles, as the suspensions of acetates mask the phenomena. (6) Zinc amyl does not gel rubber from a solution which does not contain

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[1] The following Grignard reagents have been used successfully: CH_3MgI, C_2H_5MgI, C_6H_5MgBr, C_6H_5MgCl, C_4H_3SMgI, $CH_3C_4H_2SMgI$, $CH_3C_2H_5C_4HMgI$, $IMgC{\vdots}CMgI$. It is convenient to use them in 1 *N* to 3 *N* solutions in ether.

[2] Midgley, Henne and Renoll, THIS JOURNAL, **53**, 2733 (1931).

hydroxyl groups, but causes gelling after exposure to air, or after the addition of water or alcohol. Grignard reagents do not gel "dry" sols containing zinc amyl, nor does zinc amyl peptize "dry" gels obtained with Grignard reagents. (7) A benzene gel of pure sol rubber incompletely vulcanized with sulfur (*i. e.*, with 0.24% combined sulfur) is peptized by the addition of phenylmagnesium bromide. Acetic acid de-peptizes it but an excess of acid does not revert the resulting gel to a sol.

Imperfect technique has prevented so far accurate quantitative data, but the following approximations have been noted. (1) The amount of C_6H_5MgBr required to complete the gel reaction (assumed to be the amount required to produce what appears to be the stiffest gel) varies from about one mole of C_6H_5MgBr per 500 isoprene units to one molecule per 6 isoprene units depending upon the degree of "break down" in the rubber, more being required for greater break down with a stiffer gel resulting. (2) Approximately an equal amount of C_6H_5MgBr is required to complete peptization as is required to produce maximum stiffness. (3) Approximately equal molecular amounts of acetic acid are required to reverse either the gelling or peptizing reactions as were originally used of the gelling or peptizing reagents.

Incomplete as the study now stands, it nevertheless justifies the following interpretations. (1) The introduction of the organo-metallic group does not produce polymerization, because carbon to carbon linkages would persist after the destruction of the organo-metallic complex and the polymerized product would differ markedly from the original material, which is not the case. (2) Since organo-metallic compounds, such as those used, do not form bridges between molecules, this new type of vulcanization results from the formation of one or several complex groups at one or more points of the rubber molecule. (3) Since the organo-metallic reagents show very slight or no action on oxygen-free rubber, it follows that the combined oxygen of the rubber molecule is the point of attack. Corollary: *combined* oxygen is present in "broken down" (degenerated) rubber. (4) Since the complex obtained with organo-metallic compounds is vulcanized rubber, since its destruction devulcanizes the rubber, and since this complex probably contains polar groups, the theory that the formation of polar groups on the rubber molecule is essential to produce vulcanization is given considerable support.

Summary

Rubber has been vulcanized with organo-metallic compounds; this vulcanization has been reversed, then repeated. An interpretation of the experiments is proposed and the bearing on sulfur vulcanization is pointed out.

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Ring Opening of Galactose Acetates[1]

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For some time it has been postulated that the reactivity of the hexoses was greatly enhanced by an equilibrium that is believed to exist in solution between the normal or pyranose (1,5) oxidic linkage; the free aldehyde (open chain) form or its hydrate; and some other oxidic linkage, usually referred to as the gamma, (*h*) or furanose (1,4).[2] It is known that the methyl furanosides of the sugars form and hydrolyze with greater ease than the methyl pyranosides. Interesting quantitative data have been given by Levene, Raymond and Dillon[3] for these rates of formation and by Haworth[4] for the relative rates of hydrolysis. The sugar galactose presents an opportunity for comparing the reactivities of these three postulated equilibrium structures by the use of certain derivatives, namely, β-galactopyranose tetraacetate (I),[5] aldehydo-galactose pentaacetate, which in aqueous solution exists as the alde-

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[1] The part of this work dealing with the phenylhydrazine reactions was presented before the Division of Organic Chemistry at the 85th Meeting of the American Chemical Society, Washington, D. C., March 28, 1933.

[2] T. M. Lowry and G. F. Smith, *J. Phys. Chem.*, **33**, 9 (1929).

[3] P. A. Levene, A. L. Raymond and R. T. Dillon, *J. Biol. Chem.*, **95**, 699 (1932).

[4] W. N. Haworth, *Ber.*, **65A**, 43 (1932).

[5] Unna, Inaugural Dissertation, Berlin, 1911.