

Reinforcement of Natural Rubbers by Fillers¹

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The importance of fillers in the field of rubber compounding is well known. Fillers can be reinforcing (as carbon black in tires), they can be inert (as CaCO₃) and silica has been reported as elasticizing.

The process by which fillers modify the mechanical behavior of natural rubber is not thoroughly understood. Considerable progress has been made by the use of the electron microscope in the study of the size and shape of the particles of fillers and of the interaction between these particles and the rubber molecules.

Some factors have been determined: carbon black adsorbs the "sol" fraction of rubber preferentially (5), the size of the particles of filler must remain between rather narrow limits (9b) (25 to 35 m μ for carbon black) otherwise the contact is poor or the rubber is degraded by the heat generated by too small particles, a too acidic or too basic filler slows the vulcanization down considerably (6) which justifies the coating of basic fillers (such as calcium carbonate) with fatty acids and of acidic fillers (such as kaolin) with basic organic compounds. In either case, the organic "tail" is in contact with the rubber and the adsorption upon the filler is favored.

Testing Conditions

In final resort, the testing of the influence of the filler must be made by measuring the mechanical properties of the vulcanized mixtures. The testing itself can involve one or more of the following: tension testing (ultimate tensile strength, elongation at break and elastic moduli), tear resistance, abrasion, etc. We used "dumbbell"-shaped samples with a straight-away part of dimensions 25 x 2 x 2 mm. as adopted by the French Rubber Institute (7). The other conditions (speed of testing, etc.) were as close as possible to the recommendations of the A.S.T.M. (7). The machine used was a modified textile machine equipped with specially designed jaws.

In testing the fillers, the following proportions were respected in compounding the mixtures:

natural rubber	:	100 parts (30 gm.)
zinc oxide	:	5 parts (activating agent)
stearic acid	:	2 parts (dispersing agent)
Captax	:	1 part (mercaptobenzothiazole, accelerator)
sulfur	:	3 parts (vulcanizing agent)
filler	:	0 to 60 parts/100 parts of natural rubber.

No anti-oxidant was added since the samples were tested 48 hours after mixing. The mixtures were all cured at 141°C. for 10, 20 and 30 minutes and, in each case, the optimum results are reported. The composition,

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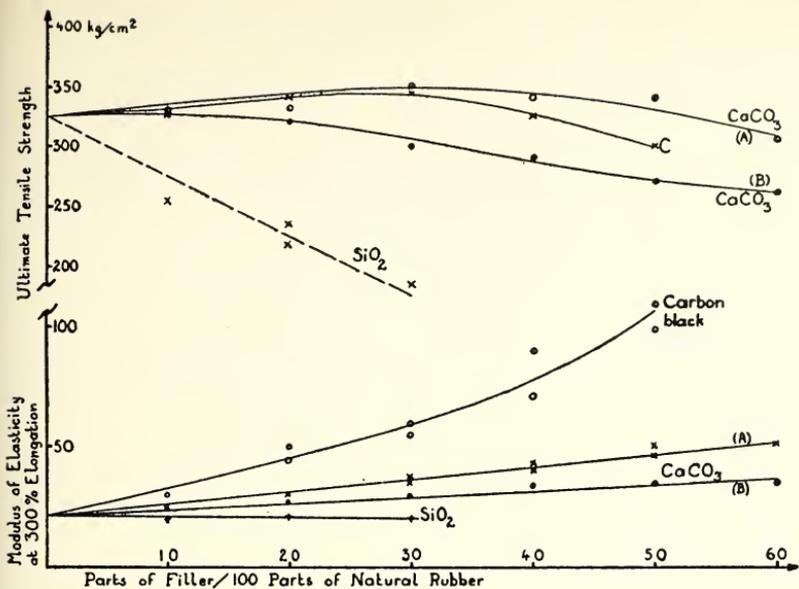


Fig. 1. The influence of different fillers upon the elastic modulus and ultimate tensile strength of natural rubber mixtures vulcanized at 141°C.

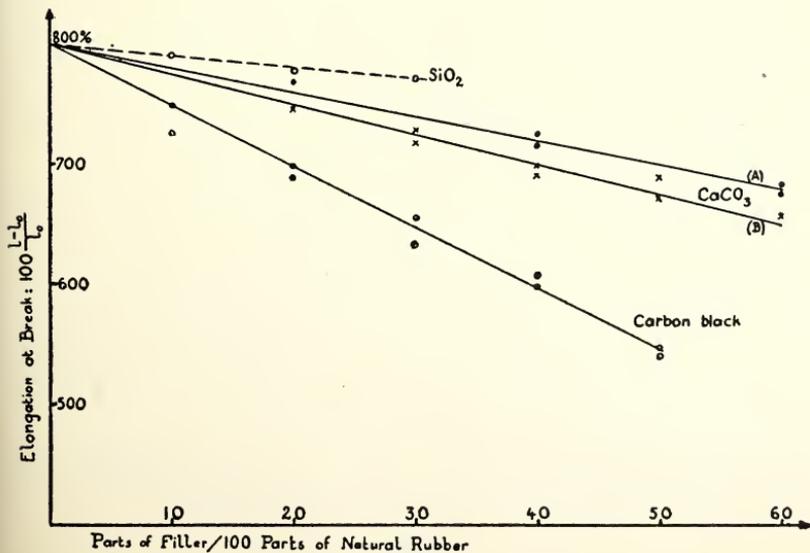


Fig. 2. The influence of different fillers upon the elongation at break of natural rubber mixtures.

time and temperature of cure of the mixtures are those usually selected and permit comparison with published results (10).

Preliminary Measurements: Sulfur and Carbon Black

To test the value of the testing method, a first group of mixtures containing 40 parts of carbon black and from 1 to 5 parts of total sulfur was tested. Linear relations were obtained between the total sulfur content and the elastic moduli and ultimate tensile strength. These results are similar to those reported by Barton and Hart (11).

A second group of mixtures, containing 3 parts of total sulfur as all the following ones, was then prepared with 0 to 50 parts of carbon black Micronex (average particle diameter: 28 μ).

The results are shown in Fig. 1 & 2: the ultimate tensile strength remains essentially constant, the elongation at break decreases rapidly with an increase in carbon black while the elastic modulus increases rapidly. The optimum vulcanization time was about 22 minutes. It is worth pointing out that the stress is calculated by dividing the load by the original cross-section whereas some authors calculate the actual stress by considering that the reduction in cross-section is directly proportional to the elongation. The results are in good agreement with those of Wildschut (10).

Calcium Carbonates

As pointed out before, ordinary calcium carbonate delays the vulcanization because of its basicity and the contact with the rubber is poor. By coating it with stearic acid, one obtains a product which is no longer wetted by water but which comes in good contact with the rubber through the organic tail of the acid.

The purpose of this investigation was to find a suitable substitute for the Japanese product available before the war (Hakuenka). The calcium carbonate designated as A was a commercial product while product B had been made in the laboratory. By inspection of Fig. 1 & 2, it is seen that the product A was somewhat superior to B as far as the mechanical properties were concerned. The optimum time of cure was about 8 minutes for A, 12 minutes for B and 17 minutes for an even rougher product C.

The correlation between good mechanical properties and low optimum time of cure lead us to conclude that the quality of the coating was involved since a poor coating would delay the vulcanization or cross-linking and give a poor contact between the filler and the rubber. However, other factors had not been considered at this point such as the size and shape of the particles. It is possible that calcium carbonate would be a better filler if obtained as aragonite needles rather than as calcite. Studies of the conditions of precipitation and studies of the crystalline structure by electron microscopy have since been published (2, 4).

The inert-filler behavior of calcium carbonate is shown by the above results: little variation in ultimate tensile strength, small increase in elastic modulus and small decrease in elongation at break.

Silica

Attempts were made, in Germany, during the war, to use colloidal silica as an elasticizing filler. The results that we obtained, using silica

prepared by Mr. Pottier, seem to verify this possibility. In Fig. 1 & 2, one can see that silica hardly decreases the elongation at break (but an increase in elongation at break was sought), the elastic modulus decreases very slightly but the ultimate tensile strength decreases very rapidly.

However, in this case, the mechanical properties were found to increase nearly linearly with the time of cure. The optimum time of cure was not reached and must be 45 minutes or more. This bears out the fact that an uncoated acidic filler slows the cross-linking down and would justify an attempt to coat silica with a basic organic compound.

Stress-Strain Curves

Many expressions have been proposed for the mathematical representation of the stress-strain curves of rubber mixtures. Wildschut (10) proposes an empirical hyperbolic equation. Alfrey (1) takes crystallization into account. James, Guth & Mark established the expression:

$$\text{stress} = KT \left(\alpha - \frac{1}{\alpha^2} \right) \quad \text{where } \alpha = \frac{1}{l_0}$$

This expression is very satisfactory for soft rubber mixtures up to 350% elongation.

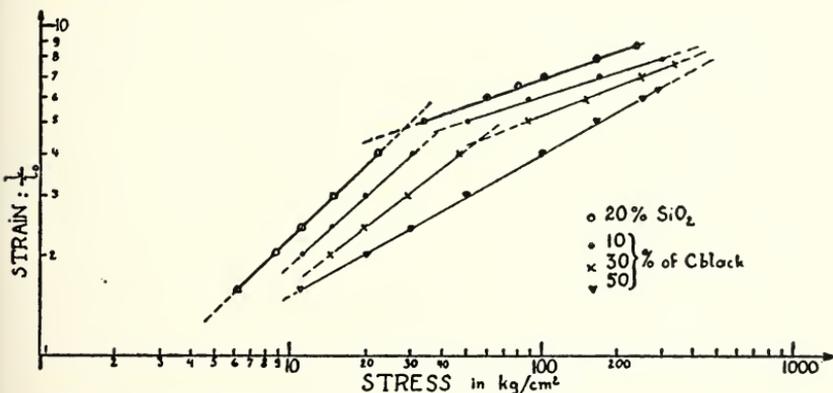


Fig. 3. Log-log plots of the stress-strain curve of rubber mixtures with different amounts of SiO_2 and carbon black.

By plotting all of our stress-strain curves in log-log scale, we found that they all presented the same appearance: i.e., two straight lines intersecting at sharp angle. In the case of mixtures with a high carbon black content, the angle was very small and one single straight line could be drawn. Four of these curves are plotted in Fig. 3, and it can be seen that the break between the two lines occurs in the range of 300 to 400% elongation ($\alpha = 4$ to 5).

This range has been reported by Hauser and Mark (1, 8, 9c), Goppel and Wildschut (10) to be the one in which crystallization takes place. Crystallization also occurs earlier in the case of mixtures containing carbon black. This can be shown by X-rays and by thermodynamical calculations.

It has also been reported (3, 6) that the tear resistance of rubber mixtures goes through a rather sharp minimum in the range of 250 to

350% elongation. We have verified those results for a mixture containing 40 parts of carbon black.

It appears thus likely that the crystallization of a large part of the rubber would account satisfactorily for the break in the stress-strain curve. The log-log plot has the advantage of putting this break sharply in evidence. Above this range, rubber mixtures will stretch up to 300% more (60% more than the elongation reached at the end of the crystallization).

We deal thus now with a crystalline phase with some amorphous material dispersed around the crystallites, it is thus normal for the crystallized rubber to behave as a fiber-like material of high elastic modulus and low extensibility which would be represented by the second straight line in the log-log plot.

Summary

A study of the reinforcing properties of carbon black Micronex, silica and two coated calcium carbonates in natural rubber mixtures was based on the mechanical properties of the compounded and vulcanized mixtures. The ultimate strengths, elastic moduli and elongations at break are reported.

Carbon black was found to be strongly reinforcing, causing a considerable increase in the elastic modulus and reducing the elongation at break. Calcium carbonate, coated with stearic acid, was found to be a satisfactory inert filler causing little variation in the mechanical properties. A commercial product (type A) was found to be superior to a laboratory product (type B): the poorer mechanical properties of the type B were accompanied by an increase in the optimum vulcanization time. This could have been caused by a less satisfactory coating but possibly also by different crystalline forms of the calcium carbonate.

Silica proved to slow down the vulcanization considerably. This is probably due to its acidity and would justify an attempt to coat silica in a manner similar to calcium carbonate. The results obtained with under-vulcanized mixtures show that silica is somewhat of an elasticizing filler: decreasing the elastic modulus and the ultimate tensile strength without appreciable reduction of the elongation at break.

Finally, a log-log plot of the stress-strain curve shows a definite break corresponding to the range in which crystallization upon extension occurs. Rubber mixtures could thus possibly be considered as fibers of high modulus and low extensibility between 500% and 800% elongation.

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