

The Filler–Elastomer Chemical Link and the Reinforcement of Rubber

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Synopsis

Reinforcement, the improvement of the service life of rubber goods, is dependent on the behavior of the carbon black–elastomer interface. It is generally believed that the interaction between the filler and the matrix involves physical and chemical forces. The aim of this work is to demonstrate the significance of the chemical interaction. In order to demonstrate the influence of the chemical bond without interference of physical forces, the problem is approached in a different way. The chemical bond is first realized by grafting the polymer onto the carbon surface. Then, two mixes are prepared by avoiding milling: one with the grafted black and the other with regular black. The comparison of the static and dynamic mechanical properties highlights the influence of the chemical bonding of the elastomer onto the black: the grafted black bestows much higher performance to the corresponding vulcanizate than does the regular black. However, the degree of reinforcement observed is somewhat lower than the one obtained by dry milling.

INTRODUCTION

The improvement of the mechanical properties of vulcanizates, and hence of their service life, is achieved with active fillers such as carbon blacks. This phenomenon, called reinforcement, was early recognized but has not yet been entirely explained despite a tremendous amount of work. The situation stems from the intricacy of the problem to which both physical and chemical properties of elastomers and active fillers contribute.

All theories of the reinforcement of elastomers by pigments postulate the existence of physical or chemical interactions at the polymer–solid surface interface.¹ We shall be concerned here only with chemical interaction. As a matter of fact, numerous observations are in favor of the formation of such interactions through the medium of either surface groups² of the carboxylic, phenolic, quinone, or lactone types, or reactive hydrogen from the polyaromatic structures³ which exist on the carbon black surface. During milling, shear forces cause the breakdown of carbon aggregates, creating active sites capable of combining with the free radicals formed by the scissions of macromolecular chains, according to which insoluble bound rubber is formed.^{4,5} The formation of chemical bonds results also from the use of chemical promoters⁶ or coupling agents which have been more precisely designed to improve the silica–rubber reinforcement.^{7,8}

Nevertheless, even though the preceding facts act in favor of the actual creation of chemical bonds, however it is extremely difficult to demonstrate their existence. Therefore, we used grafted carbon blacks⁹ in order to avoid the milling and, hence, all the corresponding difficulties which render hazardous the interpretation of the results.

PREPARATION OF MIXES AND VULCANIZATES

Grafted carbon black, as it is recovered after centrifuging, disperses remarkably well in a toluene solution of polyisoprene (natural rubber) containing 20 g polymer per 1000 cm³ solvent. The total volume of the polymer solution is adjusted so as to realize the filler/polymer ratio necessary for the preparation of the vulcanizates. The other compounding ingredients are next added to this dispersion in the following proportions: rubber (total), 100; stearic acid, 2; zinc oxide, 5; sulfur, 2.5; accelerator (Santocure CBS), 0.8; phenyl- β -naphthylamine, 1; carbon black, 33.

A fair dispersion of the ingredients is achieved by pressurizing the suspension through the screw threads of a homogenizer; this operation is essential since the nongrafted carbon black, used as a reference, is in pellet form.

As soon as a fair dispersion has been obtained, the suspension is precipitated into an excess of methanol and kept at -60°C with Dry Ice. The whole is recovered by a quick filtration, vacuum dried at room temperature, and kept away from light at a low temperature (-20°C) up to the vulcanization step.

In order to estimate the effect of milling, the mix prepared as described above is divided into two equal parts, one of them to be milled. Before introducing the mix into the mold, it is necessary to transform the mix into sheets by passing it between the cylinders turning at equal speeds of an open mill. Moreover, in order to avoid a chemical fixation of the polymer onto the carbon black which may follow the slight mechanical breakdown of the polymeric chains, especially with the mix containing the ungrafted black used as a reference, the operation should take only a few moments and the temperature of the rolls should reach only 50°C . The sheet prepared in this manner, containing either the grafted or the ungrafted black, is called unmilled mix.

The second part of the raw mix is placed in a Brabender mixer and milled at 80°C before preparing a sheet under the same conditions as those described above, ready for vulcanization; it is named milled mix. Of course, we also prepared a blank with the initial ungrafted carbon black by dry milling in the Brabender. The milling time was 10 min.

The vulcanization was carried out in all cases in a press at 145°C for 20 min. In this manner, a vulcanized sheet 15 cm long and 1 mm thick is obtained. Test pieces are cut out of this sheet for the determination of the static mechanical properties with the Instron dynamometer and the dynamic properties, with a viscoelastometer of the Rheovibron type. Table I gives the characteristics of the mixes and their numbering.

TABLE I
Characteristics and Numbering of the Studied Samples

Sample no.	Characteristics
1	Mix with grafted black, prepared by solution mixing, nonmilled
2	Mix with grafted black, prepared by solution mixing, milled
3	Mix with ungrafted black, prepared by solution mixing, nonmilled
4	Mix with ungrafted black, prepared by solution mixing, milled
5	Mix with ungrafted black, prepared by dry milling

EXPERIMENTAL RESULTS

Comparison of samples 1 and 3 will demonstrate the reinforcement given by the previous grafting of part of the elastomer onto carbon black versus the one given by the ungrafted black in the same conditions of preparation in solution.

Comparison of samples 1 and 2 on the one hand and samples 3 and 4 on the other hand will show the influence of an additional mixing on the properties of the vulcanizates containing respectively the grafted and the ungrafted blacks (mixes prepared in the same conditions in solution). Finally, the comparison of sample 5 with the other four will focus on the reinforcement observed with these samples in relation to the reinforcement obtained after classical dry milling.

Stress-strain curves were determined on the vulcanizates containing 33 phr carbon black (Fig. 1). The examination of the results leads to the following observations:

Sample 1 (with grafted black, nonmilled) has a tensile strength at break equivalent to that of sample 5 (dry milled), a slightly higher elongation at break, and a lower modulus. Its properties are much higher than those of sample 3, which was prepared in solution with an ungrafted black and nonmilled.

The milling of sample 1, giving vulcanizate 2, decreases the properties, whereas the milling of sample 3, giving vulcanizate 4, improves the properties (however, in a relatively small proportion). This can be explained by the fact that the grafting of elastomer onto carbon black deactivates the carbon surface; it follows that during milling no supplementary bonds between the elastomer and the carbon can be formed*; with the ungrafted black, the formation of such bonds obviously remains possible.

The reinforcements observed with the five samples are in the following decreasing order: $5 > 1 > 2 > 4 > 3$.

The most significant observation is, without any doubt, that the vulcanizate containing the carbon black modified by grafting of elastomer has stress-strain properties far better than those of vulcanizate 3, which is the blank with ungrafted black, and that these properties correspond to a significant degree of reinforcement. These two vulcanizates have been prepared exactly in the same conditions, the only difference being that the black was grafted in one case and not in the other.

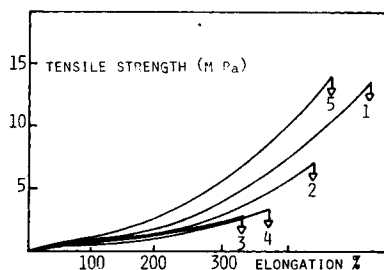


Fig. 1. Stress-strain curves for vulcanizates containing 33 phr carbon black. The numbers describing the curves are the same as in Table I.

* This result is in line with the decrease in tensile strength, modulus, and bound rubber observed previously¹⁰ when vulcanizates prepared in the classical way and containing a grafted black are compared with vulcanizates containing an ungrafted carbon black.

Yet in practice, filled rubbers such as those used in tires are subjected to stresses far inferior to the high values required for rupture. In most applications, filled rubbers are subjected to rapid dynamic deformations with a low amplitude. For this reason, the measurement of dynamic properties is of great interest. Measurements were made with the Rheovibron viscoelastometer. Voet and Morawski¹¹ made some modifications to this apparatus to improve its performance. One of the main advantages of this apparatus consists in the possibility of measuring elastic and viscous moduli corresponding to extremely small elongations of the sample.

Figure 2 shows the evolution of the elastic modulus E' as a function of the double dynamic strain amplitude for a zero static deformation of the sample. The measurements were carried out at 30°C, the frequency of the sinusoidal deformation being equal to 35 Hz. For a given amplitude, an abrupt fall of elastic modulus is observed. This well-established fact¹² is assigned to the gradual destruction of the "secondary structure" originating from the reversible agglomeration of carbon black particles.

This figure shows significant differences among the five vulcanizates. Sample 5, prepared by dry milling, has the highest E' value; the four others are ranked exactly in the classification given by the static measurements. Again, vulcanizate 1 performs much better than vulcanizate 3, and the supplementary milling imparts the same inverse effects on the pairs of samples 1 and 2 and 3 and 4.

The determination of the variations of the elastic moduli as a function of sample elongation (Fig. 3) leads to similar results. The measurements were made at 30°C, with a vibration frequency of 35 Hz and a double-strain amplitude equal to 0.00316 cm, for elongations situated between 0 and 100%. The classification of the five vulcanizates is again the same with however one difference: beyond an elongation of 50%, the curve showing the evolution of the modulus of sample 4 (prepared in solution, with an ungrafted black and thereafter milled), which was initially inferior to the corresponding modulus of sample 2 (prepared with grafted black and milled), is the same as the one of sample 2. The influence of

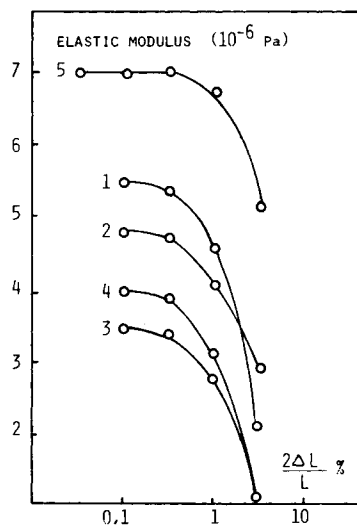


Fig. 2. Variations of elastic modulus as a function of the double-strain amplitude. The numbers describing the curves are the same as in Table I.

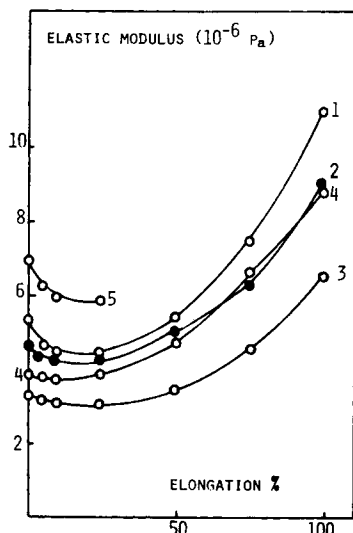


Fig. 3. Variations of elastic modulus as a function of the elongation. The numbers describing the curves are the same as in Table I.

the supplementary milling is then more clearly shown. The shape of the curves, with an initial decrease in modulus followed by an increase, can be explained¹² as follows: at small deformations, the elimination of the secondary structure of the black causes a fall in modulus; when the strain increases, the modulus begins again to increase, manifesting the extension limits of the chains and consequently a stiffening of the material.

CONCLUSIONS

The results confirm the rationale which guided the experiments. The mechanical properties of the vulcanizate prepared *without any milling* and which contains a carbon black having chemically grafted on it part of the elastomer are definitely superior to those of the blank, prepared under the same conditions but with an ungrafted black. This indeed proves that merely creation of a chemical bond between the carbon black and the rubber brings about reinforcement and that therefore the reinforcement mechanism cannot be solely accounted for by physical interactions. Of course, optimum reinforcement as would be observed by classical mixing is not attained, since in this case complementary effects intervene.

We believe that, for the first time, we have given absolute proof that the establishment of a chemical link between the carbon black and the elastomer induces reinforcement. New experiments are in progress with SBR; they should accentuate the differences in mechanical properties taking into account the very low values for nonreinforced vulcanizates.

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