

The Effect of Pressure on Carbon Black/Elastomer Powders. IV. Comparison of Press-Cured Powders Containing Vulcanizing Agents with Mill-Mixed Compounds*

G. ANGERER and H. SCHILLING, *Dunlop Forschung, Hanau/Main, Germany*

Synopsis

SBR latex was compounded with six different types of carbon black (SRF, FEF, HAF, SAF, HEB, and HCC-I) and vulcanization ingredients in aqueous dispersion by means of a dispersing agent. The particle size of the carbon black agglomerates in aqueous dispersion was estimated from turbidity and light scattering measurements. It was found that the size of the aggregates is by far larger than the average particle size of the SBR-latex used. The latex mixture containing carbon black and vulcanization ingredients was spray-dried to a fine-sized powder of an average particle size of 0.25 μm ; this powder was subsequently vulcanized without the action of shear forces at a pressure of 200 bar. It was the aim of this study to answer the question whether latex-stage compounded vulcanizates can be reinforced without applying shear forces, if only the distribution of the carbon black in the compound is sufficiently good. The tensile strength was used for judging reinforcement; the quality of the carbon black dispersion was estimated by means of the Cabot rating method. The carbon black dispersion in the compounded powders proved to be excellent with fine-sized carbon blacks and was in the order of A 1 and B 2 of the Cabot scale. Scanning electron micrographs of the fracture zones and transmission electron micrographs on ultrathin cuts showed, however, differences in the microdispersion of the carbon blacks between powder- and mill-mixed compounds. A comparison of the mechanical properties of powder- and mill-mixed compounds yielded partially comparable tensile values for the powder compounds up to 20 MN/m^2 , but strikingly high hardness, elongation set and a pronounced stress-softening after repeated deformation (Mullins-effect).

INTRODUCTION

Parts I-III of this series^{1,2,3} deal with pure carbon black/elastomer powders which were compacted by high pressure to moldings with vulcanizate-like properties.

In this part, carbon black/elastomer powders containing curing agents are simply press-cured under a medium pressure of 200 bar without the deliberate application of shearing forces to the polymer powder prior to molding. The properties of such press-cured powders are compared with those from conventionally mill-mixed compounds of equal composition.

Powders can neither be considered as liquids nor as fluids; nevertheless,

* Full version of paper "Preparation and Properties of Vulcanizates from Powder-like Rubbers," presented at the International Rubber Conference, September 5, 1974, Munich.

fluidized powders behave nearly like Newtonian liquids, and compacted powders exhibit the elastic properties of the corresponding solid.⁴ Free-flowing powders are easy to transport and to meter; in the fluidized state, they can be mixed easily with other powders or with liquids.

If, however, the attempt is made to extend powder technology to rubbers, surface tackiness is a serious obstacle. Recently, the development of free-flowing nontacky powders from masterbatches of general purpose rubbers and carbon black was reported.⁵ If such powders are available, compounds from powdered rubber can be obtained in a simple way by mixing the masterbatch powders with powdered compounding ingredients to a coarse dispersed powder compound which has to be further processed in an internal mixer or mixing extruder. The shear forces consolidate the powder into a coherent mass and give a fine dispersion of the compounding ingredients. It is generally agreed that such shear forces are necessary for carbon black-loaded compounds in order to develop reinforcement completely. In the case of powders from nitrile rubber, Goshorn and Wolf⁶ have described such a type of process which has since found practical application. If, however, rather than a coarse powder a much finer dispersion is used for compound preparation, in which the polymer is employed as latex or as solution, a significantly different method for compound preparation results.

The compounding ingredients are added in dispersion or solution and the powder compound is obtained by precipitation, spray-drying, or other suitable means. In general, a finely dispersed compound will thus be obtained on which hardly any work of mixing and dispersion has to be done; only work for compacting is necessary in order to convert powder into a coherent material. Elements of this compounding technique are practised by the manufacturers of carbon black/rubber masterbatches.

Dogadkin and co-workers⁷ have studied the reinforcement of latex-mixed carbon black-loaded SBR compounds in more detail; three factors are mainly responsible for an insufficient reinforcing effect: agglomerate formation of fine-sized compounding ingredients, insufficient dispersion of them, and the presence of protective surface coating. The reinforcing effect was improved by the addition of protective colloids. Drogin⁸ discussed potential advantages and disadvantages of carbon black-loaded, latex-stage compounded rubber mixes. Mikhant'ev and co-workers⁹ compared latex-stage compounded SBR/HAF vulcanizates with those compounded on the mill. Zeppernick¹⁰ studied powders coprecipitated from SBR and highly active silica, which were dry blended with powdery or liquid compounding ingredients.

Carbon black-loaded powder vulcanizates, which were compounded in the latex stage, to our knowledge have not yet been described in detail and such systems are mainly the subject of this study. Alliger¹¹ gave a pessimistic judgement of such systems by pointing out to insufficient reinforcement of latex-stage compounded rubber/carbon black vulcanizates. Particular attention is given to the problem of reinforcement in such vulcanizates, and an answer to the following central question will be sought: is it possible to obtain reinforced vulcanizates even without applying shear forces, if one succeeds in dispersing reinforcing fillers and other compounding ingredients as well as in conventionally mixed compounds?

This could be checked by applying work for compacting the powders com-

pounded in the latex stage rather than allowing shear forces as exerted by Banbury mixers, mills or extruders to attack the powder compounds.

Among the three criteria for reinforcement¹² which are important for the pneumatic tire industry, namely, tensile strength, tear strength, and abrasion resistance, only tensile strength will be considered as a measure of the degree of reinforcement achieved.

EXPERIMENTAL

Raw Materials

Styrene-butadiene latex, seven carbon blacks of graded activity, and corresponding vulcanization agents were used as raw materials. Table I lists some properties of the SBR latex used; it is of high molecular weight and of a fine particle size and is neither concentrated nor agglomerated. Its average particle diameter was determined from turbidity measurements to be 44 nm.

In Table II are shown the carbon blacks used, their specific surface, and average particle diameter. HEB black represents a new type of carbon black obtained by a new process. The blacks listed were used as "fluffy" as far as available. For compound preparation the carbon blacks are dispersed in water together with vulcanization and dispersing agents by means of a ball mill and are then poured into the latex under agitation. The powder is obtained from the fully compounded latex mixture by spray-drying. With respect to the central question initially mentioned, it was of minor importance whether the powders obtained were completely nontacky and free-flowing or not; in any case, no efforts were made to improve those properties, e.g., by appropriate additives.

TABLE I
Properties of the SBR Latex Used

Trade name	INTEX F-28 (ISR)
Dry solids content	32% (w/v)
Mooney viscosity	100 MS 4 (100°C)
Molecular weight \bar{M}_n	670,000
Particle size	44 nm

TABLE II
Properties of the Carbon Blacks Used

Type	Trade name	BET surface, m ² /g	EM particle size, nm
SRF	Durex O ^a	22	115
FEF	Corax A ^a	42	40
HAF, N-347	Corax 3 fluffy ^a	75	27
HAF, N-326	Printex 300 ^a	78	27
SAF, N-110	Corax 9 fluffy ^a	150	17
HEB	CRX 2002 ^b	328	<24
HCC-I	Regent ^a	420	10

^a Producer: Degussa.

^b Producer: Cabot Corp.

Carbon Black Particle Size

It is obvious that the quality of the dispersion of the carbon black in rubber must depend on the particle fineness of the latex and of the carbon black dispersion. An optimal dispersion will preferably be obtained if the average particle size of the latex and of the carbon black dispersion are of the same order; in this case, if we assume a ratio of 1:1 by volume of latex to carbon black and if no processes of demixing take place, according to the laws of statistics on average one latex particle will meet one carbon black particle each, so that the degree of dispersion performed in the latex stage will be preserved also in the solid rubber/carbon black batch after spray drying.

Adams and Howland¹³ have calculated that the size of a carbon black particle is comparable with the size of a latex particle of a standard SBR latex, if the carbon black dispersion is correctly stabilized. Janssen and Weinstock¹⁴ give an average diameter of 60 to 70 nm for latex particles and of 15 to 30 nm for reinforcing carbon blacks. Thus, the ratio of particle size latex particle to carbon black would be between 2 and 4.7, i.e., the latex particle would be much larger than the carbon black particle on average. However, a carbon black particle consists of stable aggregates which were formed during its preparation by sintering together elementary carbon black particles. The particle size given by the authors mentioned refers obviously to elementary carbon black particles, and not to aggregates which are many times larger. This can be shown by optical methods as well as by sedimentation analysis. Thus, Ravey, Premilat, and Horn¹⁵ carried out light scattering measurements on highly diluted aqueous dispersions of HAF blacks which were ozonized in order to improve their dispersibility. The authors found that the diameter of the primary aggregate was in the region of 200 nm; the aggregates proved to be stable and exhibited a relatively narrow particle size distribution. This is on the whole confirmed by recent measurements by Medalia, Dannenberg, Heckman, and Cotten,¹⁶ who estimated distribution curves of the Stoke's diameter of ISAF black dispersions in water by sedimentation analysis, where for a typical ISAF black an average Stoke's diameter of 142 nm resulted.

The aggregate size of the reinforcing carbon blacks in aqueous dispersion appeared important for the quality of the carbon black dispersion; therefore, light scattering and turbidity measurements on aqueous carbon black dispersions were carried out in order to estimate this parameter.¹⁷

Table III shows the result of such measurements; although there is a not

TABLE III
Average Particle Diameter of Carbon Blacks in Aqueous Dispersion
from Light Scattering and Turbidity Measurements

Type of carbon black	Average particle diameter, nm	
	Light scattering	Turbidity
SRF		358
FEF	113-250	240
HAF, N-347	118-255	170
SAF, N-110	131-230	144
HEB		133
HCC-I		122

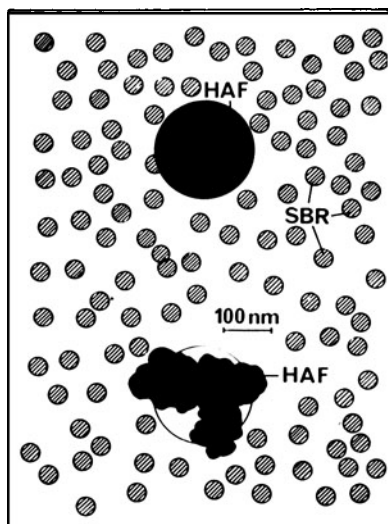


Fig. 1. Size ratio of HAF black and SBR latex particles in aqueous dispersion.

very sharp average value for the particle size when evaluating the measurements from the Guinier plot,¹⁸ there can be no doubt that the carbon black particles in aqueous dispersion are aggregates of at least 100 nm, which is more than the particle size of the latex used. Contrary to earlier expressed views, we must, therefore, when mixing a carbon black dispersion into non-agglomerated latex, start with the assumption that the primary carbon black aggregates are much larger than the SBR latex particles.

If we assume a value of 200 nm for HAF, the fine-sized SBR latex with 44 nm, as used by us, will result in a particle size ratio of ca. 1 to 5, which is illustrated in Fig 1. The upper large sphere symbolizes a carbon black particle whose entire mass is compressed in a sphere of 200 nm diameter. The lower diagram tries schematically to illustrate the real fissured form of a primary aggregate differing from the spherical form. For simplicity's sake, the hatched circles show the SBR latex as a monodisperse latex.

With this example of a size ratio of black to latex particles of 5:1, this would mean that in a latex mixture with a volume ratio of carbon black to rubber of 1:4 at even distribution there would be 2500 latex particles per 1 carbon black particle in form of a primary aggregate. This would be the optimal fine dispersion of carbon black in rubber, therefore, that could be expected with this mixing mode.

TABLE IV
Effect of Dry Ball Milling and of Different Modes of Dispersing
on the Particle Diameter of HAF Black from Turbidity Measurements

Dispersion of HAF black (0.2%) + Vultamol (0.2%) in water by means of	Average particle diameter, nm	
	Without pretreatment	After 30 min dry ball milling
Ultraturrax, 5 min	184	186
Ball mill, 48 h	168	186
Ultrasonics, 3 min	170	170

TABLE V
Effect of Dry Ball Milling and of Different Modes of Dispersing
on the Particle Diameter of HAF Black from Light Scattering Measurements

Dispersion of HAF black (20%) + Vultamol (1.4%) in water by means of	Average particle diameter, nm	
	Without pretreatment	After 30 min dry ball milling
Ultraturrax, 5 min	121-272	127-284
Ball mill, 10 h	105-252	129-254
Ultrasonics, 3 min	118-255	125-244

One might consider reducing the primary aggregate by comminution in order to reach a more appropriate range of particle sizes. It becomes apparent, however, that neither dry milling nor wet milling, neither high speed stirring nor ultrasonic treatment have a definite effect on the average particle size of HAF carbon blacks, as is shown in Table IV. On the contrary, turbidity measurements indicate that in wet milling of previously dry milled carbon black in comparison to the untreated sample aggregation occurs rather than comminution. A similar picture is obtained from light scattering measurements, which are shown in Table V. Due to the nonlinearity of the already mentioned Guinier plots which were chosen for the light scattering measurements, there are here indeed fairly wide margins with regard to the average particle size; nevertheless, here, too, a particle size reduction should become apparent if it had taken place.

Since particle degradation has not proved a promising way toward finer-sized carbon black dispersions, fine-sized carbon blacks like HEB or HCC-I may be taken into consideration. These, however, are not commonly used in rubber technology, but even so will not bring us below 120 nm particle diameter.

Compounding

For the production of the compound carbon black was dispersed in water in the ball mill, together with zinc oxide, stearic acid, accelerator, and sulfur. Vultamol, the sodium salt of an alkylated naphthalene sulfonic acid, served as dispersing agent. Other than for the fine-sized blacks SAF, HEB, and HCC-I, 7% proved sufficient while for the former, 10% Vultamol was necessary.

The dispersion of carbon black and vulcanizing ingredients (30% to 35% w/v) was added over 15 min (at 100 g scale) under vigorous stirring into the SBR latex diluted to 25% w/v, and after completion it was treated with a high-speed Ultraturrax stirrer for a few minutes. Following this, the completely compounded latex mixture was dried in a commercial laboratory spray dryer at a column-entry temperature of 155°C to a more or less free-flowing powder with an average particle size of 0.25 mm. Figure 2 shows the spray dryer used. The yields are at best 90-95%.

Figure 3 shows scanning electron microscope (SEM) photographs of an SBR carbon black powder, containing vulcanizing agent, and 50 parts HAF in three different magnifications. On the powder particle of the middle SEM photograph some fine structures become visible which, when magnified

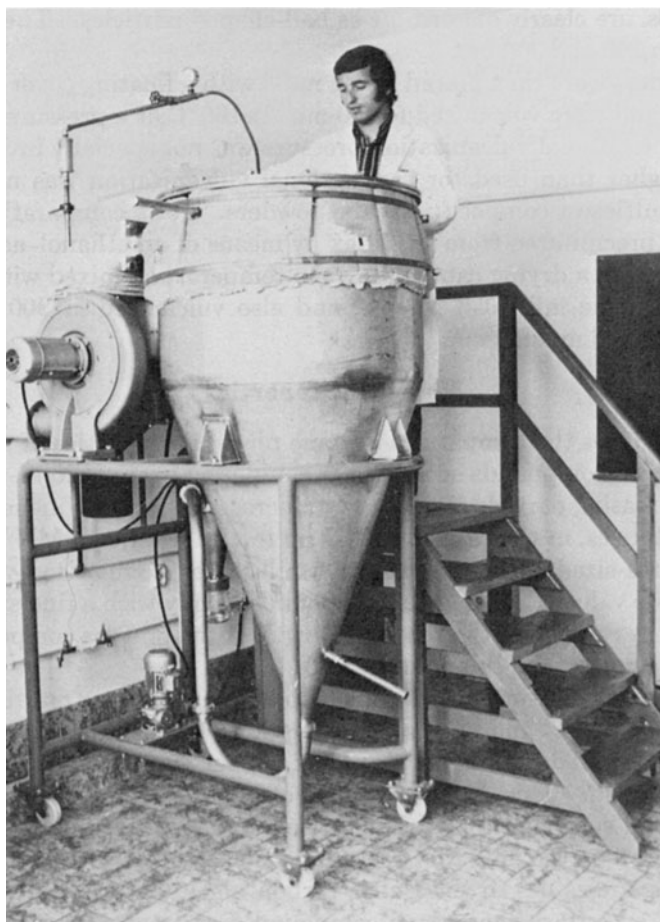


Fig. 2. View of the Nubilosa spray dryer used.

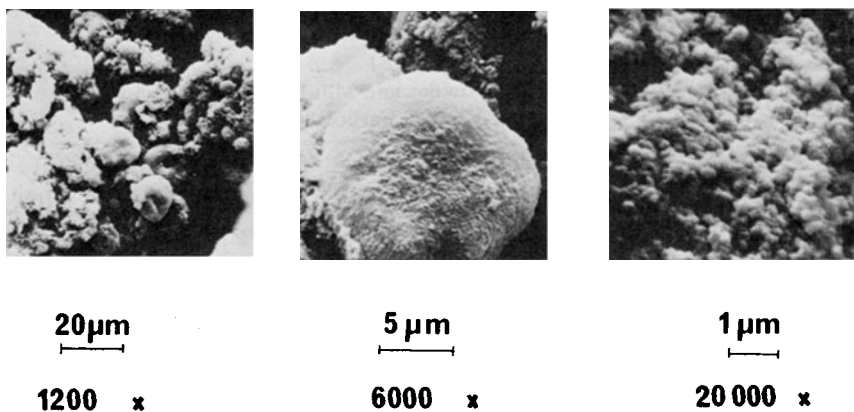


Fig. 3. SEM photographs of compounded SBR/HAF powder at different magnification.

20,000 times, are clearly discernible as ball-shaped particles. Their diameter lies between 100 and 300 nm.

The powders were then placed into a mold with a floating cover of 20 × 150 mm in size and were vulcanized for 40 min at 160°C at a pressure of 200 bar. Although the optimal vulcanization pressure was not specially investigated, a pressure higher than used for conventional vulcanization was necessary to guarantee sufficient compacting of the powders. For a comparative test, the rubber was precipitated from the latex by means of an ethanol-acetone mixture 1:1, dried in a drying cabinet at room temperature, mixed with vulcanizing agents on the mill (6–8 passes), and also vulcanized at 200 bar in the above-mentioned mold.

Physical Properties

Table VI shows the comparison of some physical properties of the powder- and mill-mixed compounds according to compound formulation I.

With decreasing particle size, i.e., with increasing particle fineness, the tensile strength rises, in the case of HCC-I up to a value of 20.4 MN/m². In the case of coarse-sized carbon blacks, the mill-mixed comparison values show higher tensile values than powder compounds. Only with a fine-sized carbon black, such as SAF, does the tensile strength of the powder compound correspond to the mill-mixed compound.

These findings call for an additional explanation; to carry out the comparison between powder- and mill-mixed compound in as similar a way as possible, the precipitated high-molecular latex rubber was also used for the mill-mixed compound. This, however, does not behave favorably on the mill, so that there is a suspicion that the fine-sized carbon blacks have not been incorporated well on the mill; this was confirmed by the determination of correspondingly poor values in the Cabot carbon black distribution rating. For this reason, a further comparison compound was prepared from a standard SBR-1500 and HCC-I carbon black; Table VII shows the result. The mill-mixed compound SBR-1500 attains the same tensile strength as the latex compound. The only distinct difference is the high hardness value of 90 Shore A for the powder compound compared to 74 for the mill-mixed compound.

TABLE VI
Mechanical Properties of Powder and Mill-Mixed Compounds^a
Containing Various Carbon Blacks

Carbon black	Hardness Shore A		Tensile strength, MN/m ²		Elongation at break, %		Modulus at 50% elongation	
	Powder	Mill	Powder	Mill	Powder	Mill	Powder	Mill
SRF	77	68	5.2	11.4	230	200	2,6	3,3
FEF	83	77	8.1	15.0	215	155	3,6	4,2
HAF,N-347	85	72	13.4	16.5	220	185	4,2	4,8
SAF	80	77	16.8	16.3	490	200	2,2	4,0
HEB	82	72	16.5	12.4	590	230		
HCC-I	90	79	20.4	8.7	448	180	4,0	3,4

^a Compound formulation I: SBR, 100; carbon black, 50; ZnO, 5; stearic acid, 1; CBS, 1; S, 3; (Vultamol 4,4).

TABLE VII
Comparison of a Latex-Stage Mixed Powder Compound with a
Mill-Mixed Compound Containing SBR-1500

	Powder ^a	Mill ^a
	INTEX F-28/HCC-I	SBR 1500/HCC-I
Hardness Shore A	90	74
Tensile strength, MN/m ²	20.4	20.9
Elongation at break, %	448	400

^a Compound I, formulation cf. Table VI.

In order to check the fairly satisfactory results obtained with consolidated powder compounds containing fine-sized carbon blacks, a further series with another compound formulation II was prepared and tested.

Table VIII shows, in addition to hardness, tensile strength and elongation at break, the quality of the carbon black distribution according to the Cabot scale. The high tensile strengths of 20 MN/m² in the case of HCC-I carbon black were not obtained any more, even though the value of 12.4 MN/m² lies considerably above the mill-mixed comparison compound with 8.5 MN/m². It can clearly be seen that the tensile values of the powder compound despite excellent carbon black distributions generally lie considerably below those of the mill-mixed compound, although in the latter carbon black distribution can by no means be regarded as optimal because of the reasons already mentioned.

If in the mill-mixed comparison compound, an optimal carbon black distribution is obtained by using standard SBR-1500 the comparison turns out still less favorable for the powder compound, as can be seen in Table IX. Here, a tensile strength of almost 40 MN/m² is obtained from the mill-mixed compound with colour black HCC-I compared to the powder compound with only 12 MN/m², even though its carbon black distribution C 3 compares with A 1 for the powder compound.

The tensile values of powder vulcanizates, which contain colloidal sulfur and fine-sized zinc oxide Weissiegel (Table X), show that not only the compound formulation but also the particle fineness of the compound constituents are of importance with a latex compounding process: When both com-

TABLE VIII
Mechanical Properties of Powder Compounds^a and of
Mill-Mixed Compounds^a with F-28

Carbon black	Cabot rating ^b		Hardness Shore A		Tensile strength, MN/m ²		Elongation at break, %	
	Powder	Mill	Powder	Mill	Powder	Mill	Powder	Mill
SRF	C 2	H 4	71	78	3.9	14.7	650	290
FEF	A 1	H 3	82	78	6.4	18.2	400	160
HAF, N-326	B 1	H 5	82	78	10.6	13.4	380	190
SAF	A 2	H 3	84	84	10.5	16.7	280	160
HCC-I	A 1	H 4	90	85	12.4	8.5	280	180

^a Compound formulation II: SBR, 100; carbon black, 50; ZnO, 4; stearic acid, 2; PBN, 1; 4010 NA, 1.5; CBS, 1.25; S, 1.75; (Vultamol 4.6).

^b Carbon black dispersion according to the Cabot classification chart.

TABLE IX
Mechanical Properties of Powder Compounds^a and
of Mill-Mixed Compounds^a with SBR-1500

Carbon black	Cabot rating ^b		Hardness Shore A		Tensile strength, MN/m ²		Elongation at break, %	
	Powder	Mill	Powder	Mill	Powder	Mill	Powder	Mill
SRF	C 2	B 2	71	60	3.9	16.6	650	700
FEF	A 1	A 2	82	64	6.4	20.8	400	500
HAF, N-326	B 1	A 3	82	58	10.6	27.4	380	600
SAF	A 2	A 2	84	70	10.5	33.	280	480
HCC-I	A 1	C 3	90	68	12.4	39.8	280	610

^a Compound II, formulation cf. Table VIII.

^b Carbon black dispersion according to the Cabot classification chart.

pounding ingredients are of fine size, the tensile strength increases almost to 20 MN/m², which is the maximum value for rubber powder vulcanizates obtained so far.

At this point, some remarks should be made about the potential reduction of reinforcing properties due to the presence of dispersing agents on the carbon black surface. In the case of SBR carbon black masterbatches containing lignin sulfonate, a loss of 5–10% of the abrasion resistance compared to systems free of dispersion agents¹⁹ was claimed although these findings were questioned.²⁰ We did not study systematically the effect of dispersion agents, like Vultamol, on the vulcanizate properties. In one case, we dispersed FEF carbon black in water with Vultamol, then spray-dried it and mixed it with standard SBR-1500 according to compounding formulation II. The tensile value of 20.8 given in Table IX dropped by about 15% to 17.7 MN/m². But as the table shows, the differences between powder- and mill-mixed compound are much more pronounced. Hence the dispersing agent seems to be responsible for reduced tensile values to a minor degree only.

If the powder compounds are subjected to a mill treatment, usually an improvement of the tensile values can be noticed; thus, the tensile strength of an FEF carbon black-containing powder compound increases from 6.4 to 10.4 MN/m² after 2 passes on the mill. However, in the case of powder com-

TABLE X
Effect of Fine-Sized S and ZnO on the Ultimate Properties
of SBR/HCC-I Powder Vulcanizates^a

Ultimate properties	Standard		Fine-sized compounding ingredients		
	S ZnO	Ground 3000	Colloidal 3000	Ground Weissiegel	Colloidal Weissiegel
Tensile strength, MN/m ²		12.4	12.2	17.5	18.9
Elongation at break, %		280	310	360	380

^a Compound II, formulation cf. Table VIII.

TABLE XI
Effect of Mill Treatment of an SBR/HCC-I Powder, 2:1, With and Without
Vulcanizing Agent (Press Curing 40 min at 160°C)

Properties	Powder with vulc. agent ^a		Powder Without vulc. agent	
	Mill treatment		Mill treatment	
	Without	With	Without	With
Hardness Shore A	90	76	85	77
Tensile strength, MN/m ²	21	13	15	11
Elongation at break, %	400	180	410	180

^a Compound I, formulation cf. Table VI.

pounds with highly active carbon blacks, especially with the fine-sized color black, a stiffening occurs on the mill, suggesting scorching of the compound. However, an SBR/carbon black powder in the weight ratio 2:1 was prepared completely without vulcanization agents and also treated on the mill when almost the same scorching phenomena occurred here as with the compound containing vulcanization agents. Obviously, this is due to strong carbon black/rubber interactions which result from the influence of the shear forces of the mill and lead to vulcanizate-like behavior; similar effects were observed on carbon black/rubber powders without vulcanization agents after the influence of high pressure as described earlier.^{1,2,3}

For comparison, the powder compound without vulcanization agent was also immediately as well as after milling subjected to a "vulcanization", i.e., a temperature-pressure treatment at 160°C and 200 bar for 40 min.

Table XI gives the physical properties. For a powder compound containing color black, mill treatment leads to a deterioration of tensile values due to carbon black/rubber interaction, which apparently results in scorching of the compound during mill treatment.

Especially surprising is the relatively high tensile strength of the powder molded without vulcanization agents which shows that by means of pressure and temperature only, vulcanizate-like characteristics can be obtained.

TABLE XII
Elongation Set of Powder Compounds^a and Mill-Mixed Compounds^a

Carbon black	Elongation set, % ^b (100% preelongation for 1 h)					
	After 15 s			After 1 h		
	Powder	Mill		Powder	Mill	
		F-28	SBR-1500		F-28	SBR-1500
SRF	18	4	9	7	1	2
FEF	18	8	9	10	7	3
HAF, N-326	14	7	8	7	4	2
SAF	24	4	10	14	3	3
HCC-I	24		20	18		10

^a Compound II, formulation cf. Table VIII.

^b According to DIN 53 518.

TABLE XIII
Electrical Resistivity of Powder Compounds^a and Mill-Mixed Compounds^a

Carbon black	Resistivity, $\Omega\cdot\text{m}$		
	Powder	Mill	
		F-28	SBR-1500
SRF	4.7	2.6×10^2	5.0×10^9
FEF	0.24	7.0	4.9×10^3
HAF	7.9	5.5×10^2	7.1
SAF	0.30	1.5	1.4
HCC-I	0.15	3.5×10^2	0.44

^a Compound II, formulation cf. Table VIII.

Table XII shows the elongation set after 15 sec and 1 hr, respectively, for powder and mill-mixed compounds on the basis of F-28 and SBR-1500. As can be seen, powder vulcanizates generally exhibit very high elongation set values; the mill-mixed compound containing color black does show a similar behavior.

The electrical behavior of the powder vulcanizates in comparison to the mill-mixed vulcanizates was also studied. Table XIII gives the electrical resistivities of the compounds with different carbon blacks. It is remarkable that on the whole the powder vulcanizates exhibit lower resistivity values than the mill-mixed vulcanizates.

Stress Softening

Since high elongation set and high hardness seem to be typical for powder vulcanizates which were vulcanized without application of shear forces under pressure, the stress-strain behavior of such vulcanizates has been considered in more detail for the Mullins effect.²¹

Figure 4 shows the stress-strain behavior of a powder compound containing color black, vulcanized according to formulation I, in comparison to the mill-mixed compound with repeated elongation to 100%. In each case only the ascending parts of the stress-strain cycles are shown. The upper family of curves relates to the powder compound which showed an extremely high permanent deformation of 25% after the first stress-strain cycle. The sample was then newly clamped and, related to the new length, again stretched to 100%. From this, a permanent deformation of 7% resulted; the third cycle was also carried out again on the newly clamped sample. It turned out that from the first up to the fifth cycle a considerable stress softening takes place and softening does not cease before the sixth cycle. The lower family of curves relates to the mill-mixed compound which, in a strongly diminished way, also shows stress softening. It is interesting that the medium curve, which results from the powder compound already measured and then annealed at 100°C for 1 hr, has strongly approached the mill-mixed compound in its final shape without losing the strong stress increase at low elongations.

In Figure 5, three families of curves are plotted, the stress-strain cycles of color black containing powder vulcanizates, mill-mixed vulcanizates, and finally SBR F-28 without carbon black. The samples were left at their respec-

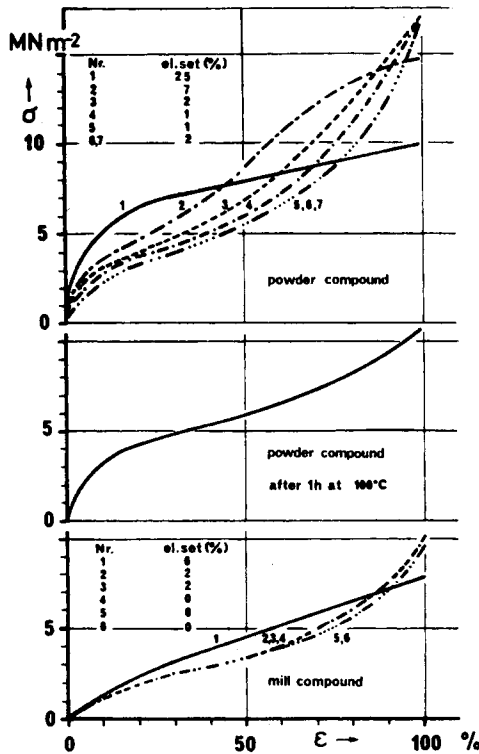


Fig. 4. Effect of repeated tensile loading on the stress-strain curves of powder compounds and mill-mixed compounds containing color black (compound I).

tive elongation set after each cycle; the following elongation cycle started at the elongation of the permanent set as a new zero point. In each elongation range of 10%, 50%, 100%, 150%, 200%, and 300%, four to six cycles were run until the hysteresis curve became constant in each case. For clarity, only the

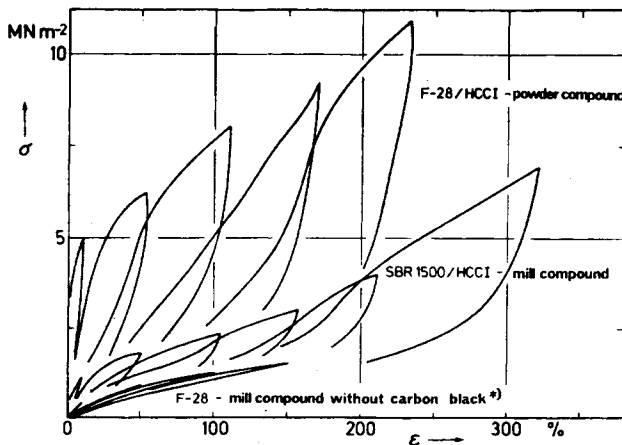


Fig. 5. Stress-strain behavior of powder compounds and mill-mixed compounds (compound II). (*) SBR, 100; ZnO, 5; stearic acid, 1; PBN, 1; CBS, 1; S, 3; Vultamol, 0.7.

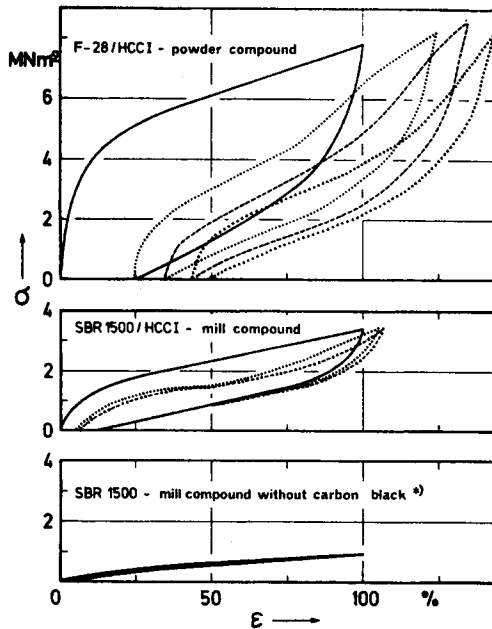


Fig. 6. Effect of subsequent tensile loading up to 100% elongation on the stress-strain behavior of powder compounds and mill-mixed compounds (compound I). (*) SBR, 100; ZnO, 2.5; stearic acid, 0.5; PBN, 0.5; CBS, 0.5; S, 1.5.

first stress-strain cycles of the respective deformation ranges are recorded in the figure.

Clearly, the powder compound is characterized by extremely high stress values at lower elongations and by high hysteresis phenomena. However, the latter applies also to the mill-mixed comparison compound based on SBR-1500. Compared with this the SBR vulcanizate without carbon black shows practically no hysteresis, as would be expected.

Figure 6 shows successive stress-strain cycles for the powder vulcanizate containing color black, a mill-mixed vulcanizate, and SBR without carbon black, with a deformation of 100%. The hysteresis curves of the powder com-

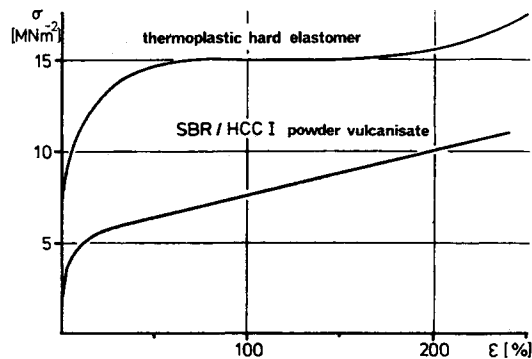


Fig. 7. Stress-strain curves of thermoplastic hard elastomer and of SBR/HCC-I powder vulcanizate.

pound change with the number of tensile stresses and become smaller and smaller, and this applies to some extent also to the mill-mixed comparison compound. The carbon black-free SBR vulcanizate shows practically no change in the stress-strain behavior on the number of deformation cycles and practically no hysteresis.

In the interpretation of this behavior, we should like to exercise restraint to avoid adding a further hypothesis to the numerous theories about the still not yet completely clarified phenomenon of the Mullins effect. However, high elongation set in the range of 100% elongation in conjunction with a strengthening of the material suggests the idea of a drawing process to which the elastomer/carbon black system is subjected. Thus, novel thermoplastic polyether/ester elastomers from polytetrahydrofuran and terephthalic acid, described by Hoeschele and Witsiepe,²² show a stress-strain behavior (Fig. 7) which to a lesser extent is also exhibited by the powder compound. Hoeschele and Witsiepe ascribe the broad plateau of the thermoplastic elastomer to plastic flow and to an orientation of crystalline regions. In the case of powdered rubber compounds from carbon black and SBR there are no pronounced crystalline deformable regions, but consolidated rubber zones which also should be capable of plastic flow and reorientation.

Electron Microscopic Examination

In order to examine differences between a pressed powder vulcanizate and a conventional mill-mixed compound, electron-microscopic investigations were carried out. Figure 8 shows scanning electron micrographs with 6000 times magnification on fractures of a powder compound sample with color black; for comparison, two mill-mixed compounds with F-28 and with standard SBR-1500 are shown. The roughness of the surface increases from the mill-mixed compound with SBR-1500 over the powder compound to the mill-mixed compound with F-28 polymer. In the case of the powder compound,

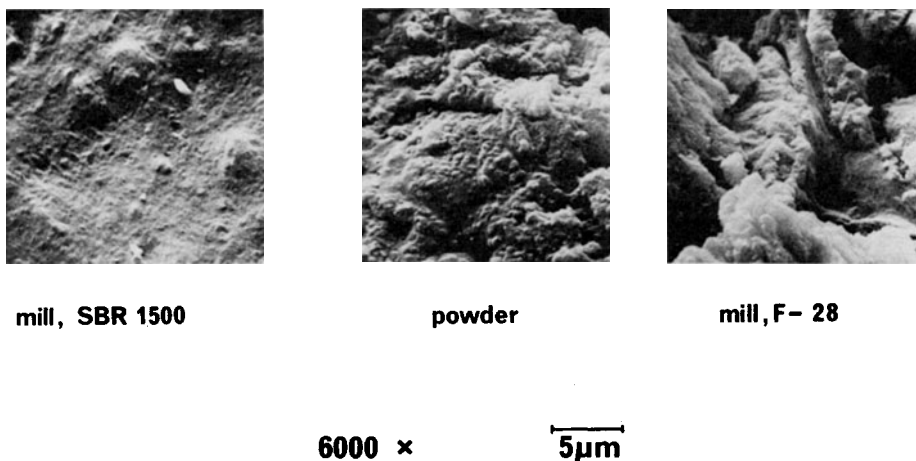


Fig. 8. SEM photographs of fracture areas of powder compounds and mill-mixed compounds containing color black (compound I).

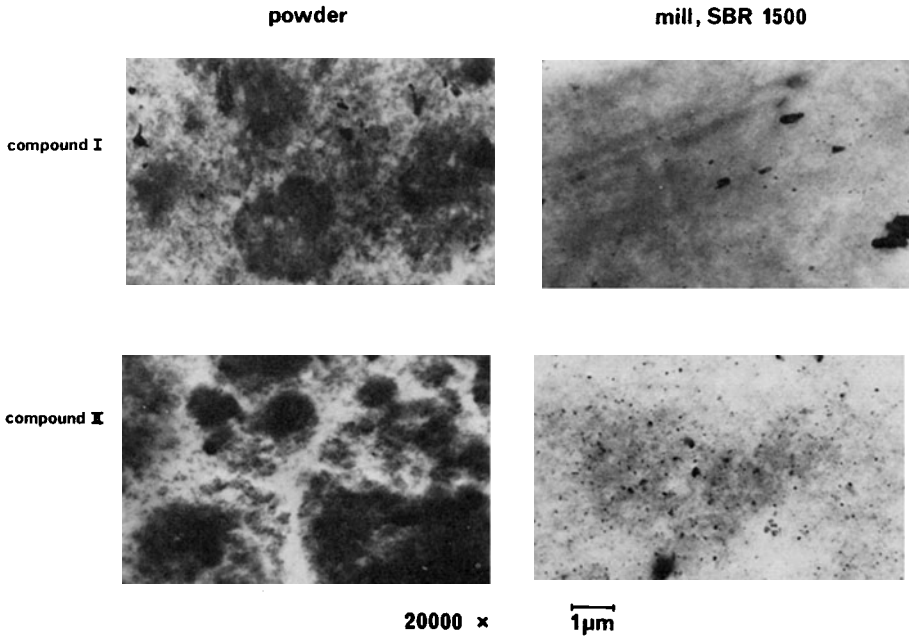
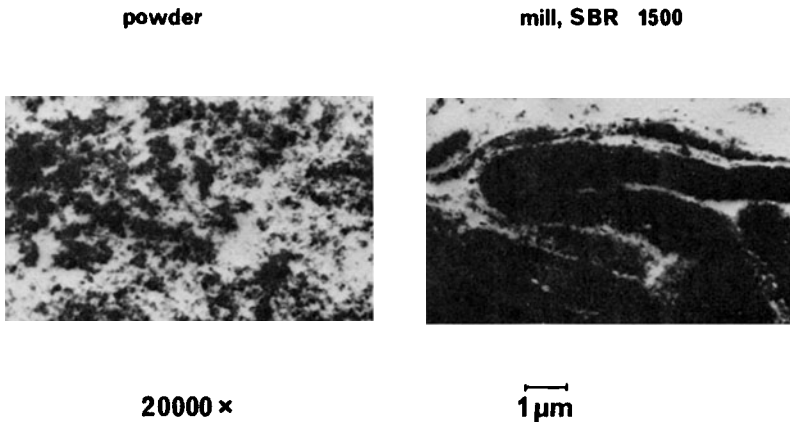


Fig. 9. TEM photographs of ultrathin cuts of powder compounds and mill-mixed compounds containing color black.

we can notice spherical structures in the μm region which are not visible in both mill-mixed comparison compounds.

Figure 9 shows transmission electron micrographs on ultrathin cuts at 20,000 times magnification (courtesy of Prof. Donnet at Mulhouse). The two upper micrographs were obtained from the same samples, the fractures of which were shown in Figure 8. The samples consist of powder and mill-mixed compounds containing color black vulcanized according to compound-



Cabot Rating:

B1

A3

Fig. 10. TEM photographs of ultrathin cuts of powder compounds and mill-mixed compounds containing HAF black N-326 (compound II).

ing formulation I. The two lower pictures were obtained from vulcanizates with compounding formulation II. With both powder compounds, spherical structures can be identified which are not present in the mill-mixed comparison compounds; the powder compounds show a somewhat less homogeneous picture than the mill-mixed comparison compounds. This is remarkable since the carbon black distribution according to the Cabot scale corresponds to A 1 for the powder compound; the mill-mixed compound has apparently inferior C 3 dispersion (lower pictures).

Figure 10 shows the same for HAF black containing powder and mill-mixed compounds. The powder compound shows a quite homogeneous carbon black distribution; spherical structures are hardly noticeable, while in contrast the mill-mixed compound shows an inhomogeneous, strangely whirled carbon black structure not to be expected from its A 3 value on the Cabot scale. However, the HAF carbon black used here is a low-structure carbon black (Printex 300) which is known to be difficult to distribute.

As a result of these morphological investigations, it might be concluded that with the powder compounds spherical structures can be detected which indicate an inhomogeneity of the carbon black distribution in the microregion. These inhomogeneities cannot be detected with the usual transmitted light-microscopic procedure upon which, e.g., the Cabot carbon black distribution scale is based. In fact, their cause can only be found in the special compounding procedure at which the carbon black/vulcanization agent dispersion is fed into an excess of the SBR latex. The inhomogeneities should disappear if such a process is conducted continuously, e.g., by combining the two dispersions as liquid films.²³ In this case, no excess of a component would occur and all preconditions for an even carbon black distribution should be provided.

CONCLUSIONS

It was shown that with the use of extremely fine-sized carbon blacks, like color black HCC-I, tensile values up to 20 MN/m² can be obtained also with powder vulcanizates. This corresponds to a distinct reinforcing effect of a rubber compound which was prepared in the latex state and which as powder was not subjected to any shear stress. On the other hand, powder vulcanizates, which are compounded this way, and vulcanized under pressure, show high hardness and after mechanical stress suffer a number of irreversible changes which are characterized by high elongation set and strong stress softening and which make them little suitable for a practical application in competition with conventional compounds. However, there is some evidence that these deficiencies may become strongly reduced by the action of even small shear forces, as they can be applied, e.g., by means of a shear cell.²⁴

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References

1. H. Schilling, G. Angerer, T. S. Ng, and H. Wolf, *Angew. Makromol. Chem.*, **35**, 131 (1974).
2. H. Schilling, G. Angerer, and T. S. Ng, *Angew. Makromol. Chem.* **36**, 1 (1974).

3. G. Angerer and H. Schilling, *Colloid & Polymer Sci.*, **253**, 206 (1975).
4. J. Schwedes, *Fließverhalten von Schüttgütern in Bunkern*, Verlag Chemie, Weinheim, 1968, p. 4.
5. K. H. Nordsiek and G. Berg, *Polymer Age*, **56**, 60 (1975).
6. T. R. Goshorn and F. R. Wolf, *Rubber Age*, **79** (11), 77 (1965).
7. B. A. Dogadkin, L. G. Senatorskaya, V. I. Guseva, A. V. Suslyakov, and P. I. Zakharchenko, *Koll. Zhur.* **18** (5), 528 (1956).
8. F. Drogin, Proceedings International Rubber Conference, Washington, ACS, 1959, p. 486.
9. B. I. Mikhant'ev, S. A. Kretinin, and V. P. Shatalov, Tr. Labor. khim. vys. soed. Vovonezh. Univ., 1962, Vyp. 1, pp. 162-169; *Rubber Abstr.* **41** 5412 (1963).
10. F. Zeppernick, *Kautschuk u. Gummi, Kunststoffe*, **18**, 231 and 313 (1965).
11. G. Alliger, Review of the Overall Progress in the Field of Powder and Liquid Elastomer-Their Potential and Future, ACS Rubber Division Meeting, Oct. 5, 1972, Cincinnati, Ohio.
12. C. M. Leigh-Dugmore, in *The Applied Science of Rubber*, W. J. S. Naunton, Ed., E. Arnold, London, 1961, Chap. VII, p. 475.
13. J. W. Adams and L. H. Howland, in *Synthetic Rubber*, G. S. Whitby, Ed., Wiley, New York and London, 1954, p. 668.
14. H. J. Janssen and K. V. Weinstock, *Rubber Chem. Technol.*, **34**, 1485 (1961).
15. J. C. Ravey, S. Premilat, and P. Horn, *Eur. Poly. J.*, **6**, 1527 (1970).
16. A. I. Medalia, E. M. Dannenberg, F. A. Heckman, and G. R. Cotten, *Rubber Chem. Technol.*, **46** (5), 1239 (1973).
17. T. S. Ng, *Angew. Makromol. Chem.*, **44**, 165 (1975).
18. H. Wesslau, *Makromol. Chem.* **69** 213 (1963).
19. H. A. Braendle, *Rubber World*, **136** (6) 835 (1957).
20. E. M. Dannenberg, E. Hagopian, J. P. Hall, Jr. and A. I. Medalia, *Trans. Inst. Rubber Ind.*, **37** (1), 1 (1961).
21. J. A. C. Harwood, L. Mullins, and A. R. Payne, *J. Inst. Rubber Ind.*, **1**(1/2), 17 (1967).
22. G. K. Hoeschele and W. K. Witsiepe, *Angew. Makromol. Chem.*, **29/30**, 267 (1973).
23. DAS 1 280 545 (1968) Chemische Werke Hüls AG, Erf.: P. Bernemann, F. Engel, and E. Pflegerl, *C. A.*, **70**, 12442 (1969).
24. G. Angerer and H. Schilling, results to be published.

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