

Efficiency of Some Novel Carbon Black/Rubber Coupling Agents

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SYNOPSIS

The effect of some new synthesized carbon black/rubber coupling agents without nitrogroups have been investigated in comparison with one commercially available coupling agent *N,N'*-bis(2-methyl-2-nitropropyl)-1,6-diaminohexane (SumifineTM 1162). Rubber compounds based on natural rubber and carbon black N-220 were used for these experiments. Tensile properties, impact resilience, and heat buildup of vulcanized rubber are improved with all coupling agents under investigation in comparison with the unmodified compound. Any positive effect of coupling agents appears also in tear resistance, dynamic flow, and permanent set. The correlation between the efficiency and chemical structure of coupling agents is discussed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

It is well known that improvement of dynamic properties of vulcanized rubbers is possible by the control of microstructure or molecular weight distribution of rubber, by changing composition of the compounds or by addition of ingredients known as coupling agents. These agents are decomposed under heating forming bonds between rubber and carbon black. Carbon black dispersion is improved by this and energetic losses at the interface are decreased, which leads to the increase of resilience and to the decrease of heat build-up at the same time. The value of loss factor $\tan \delta$ is improved as well. Different nitroso compounds are known¹⁻⁸ as improvers of dynamic properties of vulcanized rubber.

However, all nitroso compounds have unfavorable health effects. Even though they alone are nonvolatile, volatile carcinogenic N-nitrosoamines can be formed by their reaction with secondary amines originating from decomposition of some accelerators.^{9,10}

Compounds containing no nitroso group, and improving the dynamic properties of vulcanized rub-

bers by the creation of chemical bonds between carbon black and rubber matrix were described by the group of Japanese authors.¹¹⁻¹³ They described the synthesis and testing of more than 20 compounds of dinitrodiamine type, originating by the aldol condensation of aliphatic nitrocompounds with formaldehyde in the presence of diamines (Mannich reaction).

The most effective compound tested was *N,N'*-bis(2-methyl-2-nitropropyl)-1,6-diaminohexane (I), the addition of which to the compound based on natural rubber caused an increase of resilience and decrease of heat buildup of vulcanized rubbers. There are other advantages of application of substance I to the rubber compounds: e.g., practically unchanged tensile properties, favorable change of frequency dependence of dynamic modulus G' (antivibration properties) and of temperature dependence of $\tan \delta$ (lower fuel consumption and better wet-grip and ice-grip at the same time), and decrease of electrical conductivity. These effects appeared in the presence of all sorts of carbon black. The formation of chemical bonds between rubber and carbon black was proven by the increase of gel content by 50% in comparison to the unmodified compounds, and also by physicochemical methods proving the presence of reactive sites on carbon black. However,

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Table I Compound Formulation

NR (RSS #2)	100 phr
Carbon black ISAF (Nigros I)	45
Stearic acid	3
Zinc oxide	5
Process oil	5
Coupling agent	0.7
N-cyclohexyl-2-benzothiazolesulfenamide (Sulfenax CB)	1
Sulfur	2

the authors did not investigate possible causes of the different activity of the tested dinitrodiamines. This also concerns the subsequently more than 50 patents on the utilization of dinitrodiamines since 1995, which have been reviewed.¹⁴

In our study,¹⁴ we tried to elucidate the causes of different activity of the different dinitrodiamines described in Refs. 11–13 and, therefore, we compared the published effects of different dinitrodiamines always inside this structurally homogeneous group. We expressed the efficiency of different dinitrodiamines as the change of the respective property caused by the addition of 1 mmol of dinitrodiamine to 100 g of rubber. After this comparison, we have accepted the hypothesis that the efficiency of dinitrodiamines is probably connected with the length and flexibility of the biradical that is formed by their thermal decomposition. If the biradical is short with little flexibility, the probability of bond formation between carbon black and rubber decreases and such a biradical obviously becomes inactive in consequence of a recombination or chain transfer. However, the long biradicals after binding of one of their ends to the substrate (rubber or carbon black) originate the long and flexible chains with unpaired electron at their ends. With the increasing length and flexibility of these monoradical chains their mobility increases and, therefore, the probability of interconnection of carbon black with rubber increases. With aromatic dinitrodiamines, which generally have lower flexibility, this probability is lower, but increases with the increasing number of flexible groups between aromatic nuclei.

We deduced¹⁴ that an efficient coupling agent should have a length of biradical chain approximately 1.1 nm at least, and should have high flexibility that can be expressed by the ratio between end distances in fully stretched and completely coiled conformation. The most efficient compound I (commercially available as SumifineTM 1162) conforms best to this criterion and, due to its low mo-

lecular weight, is the most effective of the coupling agents so far prepared.

The results of this analysis suggested our interest in further study of analogous dinitrodiamines. Therefore, we prepared¹⁵ the set of model dinitrodiamines that conform to our anticipation on structural parameters for an efficient coupling agent. Because the influence of further substitution at nitrogen atoms of dinitrodiamines has not been done yet, some of the prepared derivatives are substituted at the nitrogen atoms with alkyl or acyl groups.

In this article we describe the effect of five new synthesized¹⁵ dinitrodiamines and dinitrodiamides (II–VI) onto some basic properties of vulcanized rubber in comparison with that of the highly efficient^{11–13} coupling agent I (SumifineTM 1162).

EXPERIMENTAL

Materials

All coupling agents under investigation (II–VI) were prepared in our laboratory. The syntheses are described in Ref. 15. The reference coupling agent I was prepared according to procedure.¹¹ Elastomer used in this investigation was NR (RSS #2), the carbon black was ISAF (Nigros I) type.

Preparation of Compounds

Components were mixed in the ratio shown in Table I in a 0.4 dm³ Pomini Farrell laboratory mixer. At first, NR was mixed with all additives with the exception of the vulcanization system and the mixture was kneaded for 6 min at 89 rpm. Discharge temperatures were 150°C (A) or 170°C (B) achieved by preheating the mixer (both chamber and rotors) by steam. The vulcanization system was admixed to the compounds on a two-roll mill 110 × 240 mm for 4 min at 50–60°C. Vulcanization was executed in a hydraulic press at a temperature of 155°C, the cure time was determined from the vulcanization characteristics measurements.

Test Methods

Vulcanization characteristics were measured on an oscillating disc vulcameter Standard (manufactured by Research Institute of Rubber and Plastics Technology, Zlín) at 155°C. Tear strength was determined by the Graves method and impact resilience on a Lüpke elastometer at laboratory temperature.

Table II Influence of Coupling Agents on the Properties of the Rubber Composition

Property	Coupling Agent							
	DT ^a	Blank	I	II	III	IV	V	VI
<i>MW</i> (g · mol ⁻¹)	—	—	318	498	402	474	502	558
<i>n</i> (mmol)	—	—	2.20	1.41	1.74	1.48	1.39	1.25
<i>T</i> ₂ (min)	A	1.9	2.3	2.3	2.5	1.8	2.3	2.6
	B	1.6	2.2	2.4	2.4	1.8	2.2	1.6
<i>T</i> ₉₀ (min)	A	8.8	6.1	6.0	6.5	5.5	5.9	6.7
	B	9.0	6.0	5.7	6.4	5.4	6.0	5.0
<i>R</i> _V (Nm · min ⁻¹)	A	2.5	3.4	3.5	3.3	3.2	3.2	3.3
	B	2.5	3.5	3.5	3.3	3.2	3.4	3.3
<i>H</i> (Shore A)	A	61	64	63	62	65	63	64
	B	61	63	62	63	65	61	64
<i>M</i> ₁₀₀ (MPa)	A	2.4	2.9	2.8	2.8	3.0	2.7	2.6
	B	2.2	3.0	2.8	2.8	3.1	2.8	3.0
<i>M</i> ₃₀₀ (MPa)	A	11.7	14.5	13.5	14.2	15.0	13.9	13.5
	B	11.5	14.7	13.7	14.7	15.4	14.2	15.5
<i>TS</i> (MPa)	A	24.3	27.5	27.8	28.1	28.4	27.6	27.6
	B	22.4	27.8	27.7	27.5	28.3	28.4	27.5
<i>EB</i> (%)	A	520	500	540	532	516	522	532
	B	524	512	533	510	502	540	492
<i>G</i> (N · mm ⁻¹)	A	26.0	64.6	56.6	63.2	57.8	53.0	65.7
	B	47.0	54.8	62.8	48.9	73.5	58.3	54.7
δG (N · mm ⁻¹ · mmol ⁻¹)	A	—	17.5	21.7	21.4	21.5	19.4	31.8
	B	—	3.5	11.2	1.1	17.9	8.1	6.2
<i>R</i> (%)	A	52	60	57	57	59	58	56
	B	53	62	59	57	60	59	58
δR (% · mmol ⁻¹)	A	—	3.6	3.5	2.9	4.7	4.3	3.2
	B	—	4.1	4.2	2.3	4.7	4.3	4.0
ΔT_D (°C)	A	110	84	92	90	90	87	93
	B	107	82	89	91	89	87	90
$\delta(\Delta T_D)$ (°C · mmol ⁻¹)	A	—	-11.8	-12.8	-11.5	-13.5	-16.6	-13.6
	B	—	-11.4	-12.8	-9.2	-12.2	-14.4	-13.6
ΔT_G (°C)	A	29	19	24	25	20	23	25
	B	29	18	24	21	20	22	23
$\delta(\Delta T_G)$ (°C · mmol ⁻¹)	A	—	-4.5	-3.6	-2.3	-6.1	-4.3	-3.2
	B	—	-5.0	-3.6	-4.6	-6.1	-5.0	-4.8
<i>DF</i> (%)	A	2.1	1.0	1.3	1.3	1.1	1.0	1.1
	B	1.8	1.1	1.2	0.9	1.1	0.9	1.0
<i>PS</i> (%)	A	2.1	1.2	1.4	1.3	1.5	1.3	1.4
	B	1.7	1.3	1.3	1.3	1.4	1.2	1.2

^a Discharge temperature (DT) of the rubber batch: (A)—150°C, (B)—170°C.

Heat buildup was measured on a Goodrich flexometer at frequency 30 Hz with a load of 1 MPa and stroke of 5.7 mm at laboratory temperature. The increase of sample temperature (ΔT_G) was measured after 25 min. The heat build-up with the DPGi method was measured at 1000 rpm, deformation bending radius of 50 mm, and laboratory temperature. The increase of sample temperature (ΔT_D) was measured after 30 min. Other parameters were de-

termined by the usual methods. The error bars of experiments are included in the figures.

The following characteristics were used:

MW molecular weight (g · mol⁻¹)
n molar amount (mmol)
*T*₉₀ optimal vulcanization (min)
*T*₂ scorch time (min)
*R*_V rate of vulcanization (Nm · min⁻¹)

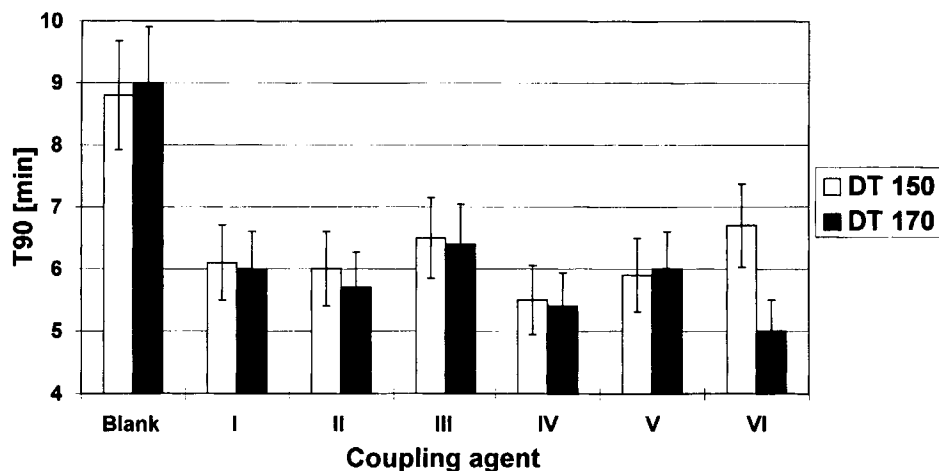
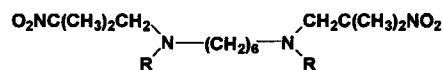


Figure 1 Influence of coupling agents and discharge temperature on vulcanization optimum.

TS tensile strength (MPa)
 M_{100} modulus 100% (MPa)
 M_{300} modulus 300% (MPa)
 EB elongation at break (%)
 G tear resistance—Graves ($N \cdot mm^{-1}$)
 H hardness (Shore A)
 R impact resilience (%)
 ΔT_D heat buildup—DPGi method ($^{\circ}C$)
 ΔT_G heat buildup—Goodrich ($^{\circ}C$)
 DF dynamic flow (%)
 PS permanent set (%)

noxybutane (I–VI), were used for testing. The first of them is the commercially available coupling agent Sumifine™ 1162, but all the compounds were prepared¹⁵ in our laboratory.



I. R = H II. R = CH₂Ph III. R = COCH₃



IV. R = H V. R = CH₃ VI. R = COCH₃

RESULTS AND DISCUSSION

The *N,N'*-bis(2-methyl-2-nitropropyl) derivatives of 1,4-diaminohexane and 1,4-bis-(4-aminophe-

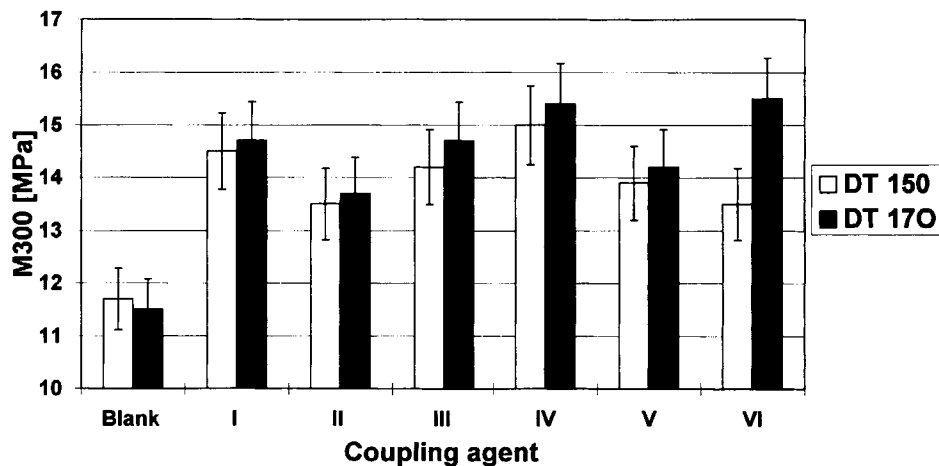


Figure 2 Influence of coupling agents and discharge temperature on modulus M300.

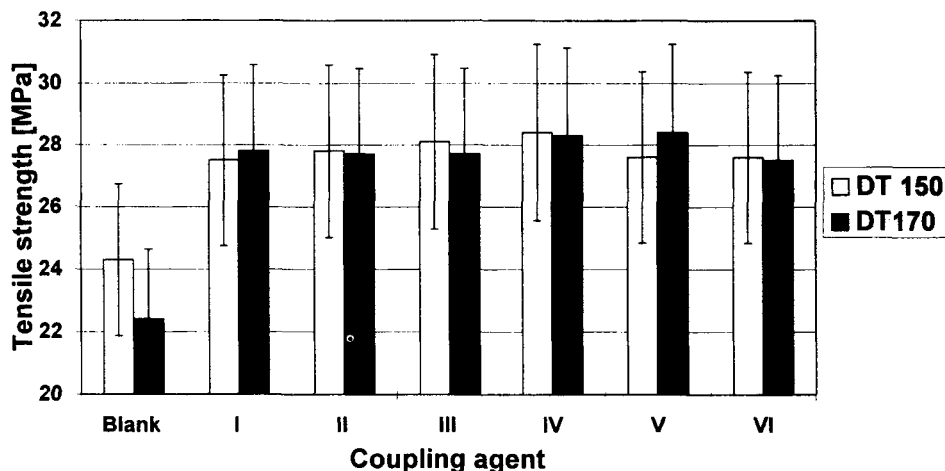


Figure 3 Influence of coupling agents and discharge temperature on tensile strength.

The change of properties related to the molar amount of coupling agent was also used for comparison of the efficiency of prepared dinitrodiamines because only in this way is it possible to express the dependence of properties on the chemical structure. These relative molar values are designated with the symbol δ , the manner of the calculation is shown in eq. (1):

$$\delta(X) = (X_C - X_B)/n \quad (1)$$

where X_B and X_C are properties of blank compound and compound with tested coupling agent, respectively, and n is molar amount of coupling agent.

The considerable dependence of the results on the temperature of compound preparation was observed in the preliminary experiments. Therefore, the compounds (formulation is given in Table I)

were prepared on Banbury mixer at two different discharge temperatures (150 and 170°C). The results are given in Table II.

As can be seen from this table, the value of optimal vulcanization (T_{90}) is essentially unchanged by the type of coupling agent and by the temperature of mixing, but in comparison with the blank compound it is decreased by 2 min on average (Fig. 1). This effect was observed earlier¹⁶ and the addition of N-imides to the compound was recommended for its elimination. The opposite effect can be observed in the case of scorch time (T_2) (after addition of coupling agent the scorch time increases) but, with the exception of dinitrodiamide VI, the influence of discharge temperature was not observed. With all the coupling agents under testing, the rate of vulcanization is the same at both discharge temperatures (again with the exception of dinitrodiamide

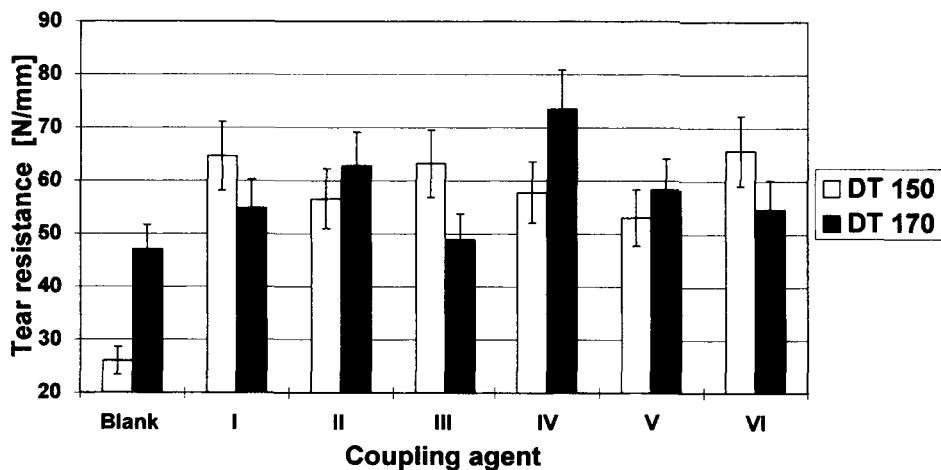


Figure 4 Influence of coupling agents and discharge temperature on tear resistance.

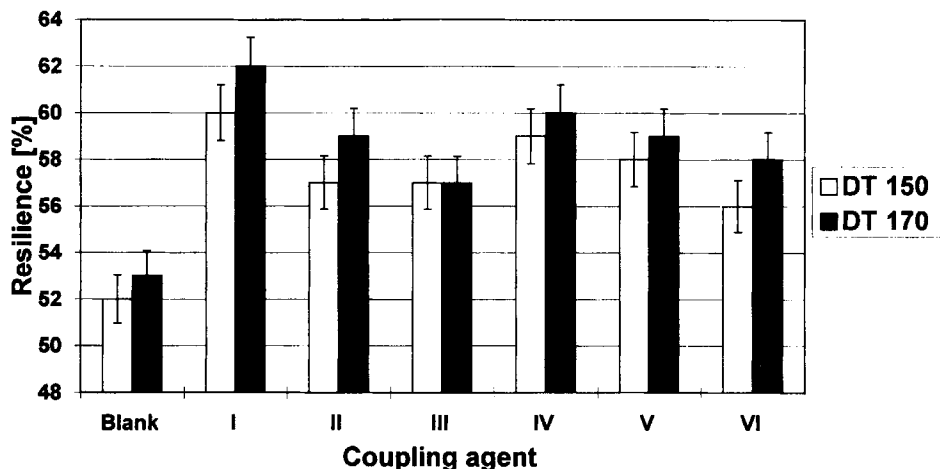


Figure 5 Influence of coupling agents and discharge temperature on impact resilience (Lüpke).

VI) and is higher than for the blank compound. The described effects are favorable from the reason that the vulcanization curve is approaching the ideal one where scorch time is sufficiently long followed by a high rate of vulcanization.

The results show that only a few properties change by the addition of coupling agents to the rubber compounds. Tensile properties are improved in all cases and are not significantly influenced by discharge temperature. Tensile strength (Fig. 2) is not influenced by the type of coupling agent, but in comparison with the blank, tensile strength is remarkably increased. The influence of discharge temperature is visible only with the blank compound and is a negative one. Similar results were obtained for all moduli (Fig. 3).

The variation in tear resistance (Graves) with coupling agents and discharge temperature is shown in Figure 4. Distinct differences between the blank and all coupling agents can be seen. The best results, at a discharge temperature 150°C, are with coupling agents I, III, and VI. It is interesting that the behavior of dinitrodiamides III and VI is analogous to that of Sumifine™ 1162 (I). It indicates that dinitrodiamides may also be thermally decomposed by a similar mechanism as secondary dinitrodiamines. The increase of tear resistance at higher discharge temperature can be seen with both tertiary dinitrodiamines II and V. An exception from the comparable behavior of the tested compounds is secondary dinitrodiamine IV. The cause of highly increased tear resistance in the presence of this compound at

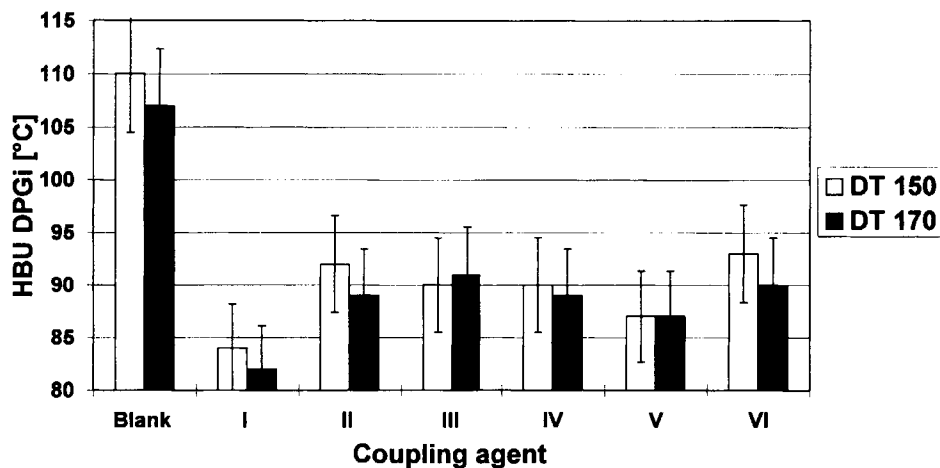


Figure 6 Influence of coupling agents and discharge temperature on heat buildup (DPGi).

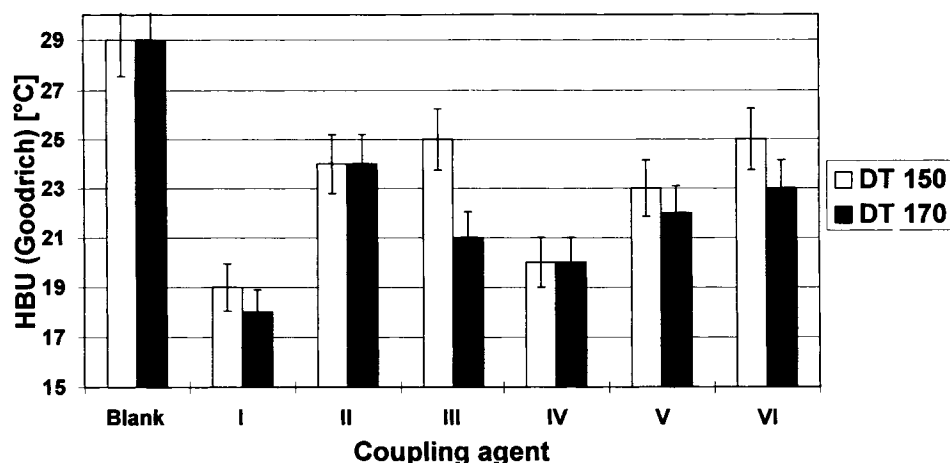


Figure 7 Influence of coupling agents and discharge temperature on heat buildup (Goodrich).

a higher discharge temperature cannot be explained for the time being.

The positive influence of both coupling agent and higher discharge temperature can be seen by Lüpke impact resilience (Fig. 5). All coupling agents favorably influence the increase of impact resilience in comparison with the blank; the substance I is most efficient. The favorable influence of discharge temperature may be explained by the more efficient decomposition of the coupling agent. As a consequence, more coupling bonds are formed between the phases. The comparable effect of dinitrodiamides III and VI with that of dinitrodiamines is surprising. However, it is known from the literature¹⁷ that some derivatives of dinitrodiamines, for example, their salts, are also efficient.

The variation in DPGi heat buildup for different coupling agents with discharge temperature is shown in Figure 6. All agents under investigation have a pronounced effect in comparison with the blank; most influential appears to be I. With the exception of III and V, the higher discharge temperature decreases heat buildup. Similar results are evident in the case of Goodrich heat buildup (Fig. 7). Compounds discharged at 170°C have equal or lower heat buildup than those discharged at 150°C. Again, Agent I is most efficient. The results of the testing of heat buildup by both methods is (taking account of experimental errors) comparable.

Dynamic flow (Goodrich) dependence on coupling agent and discharge temperature is shown in Figure 8. All the coupling agents decrease dynamic

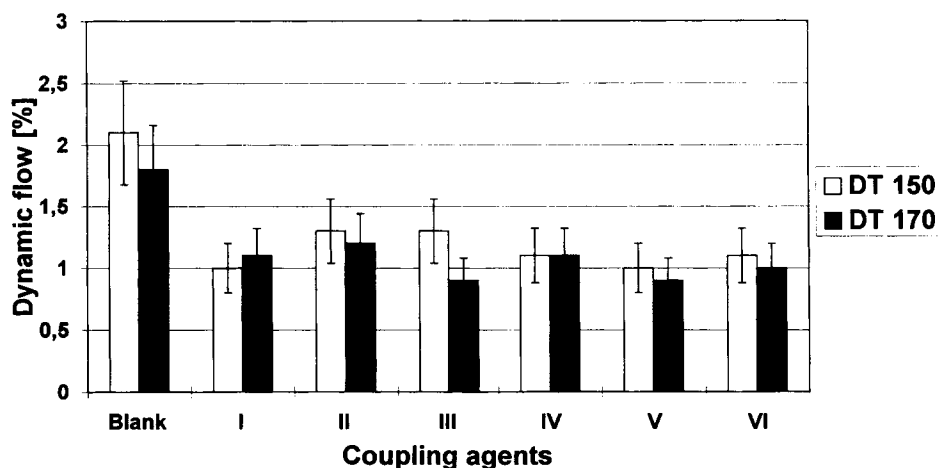


Figure 8 Influence of coupling agents and discharge temperature on dynamic flow.

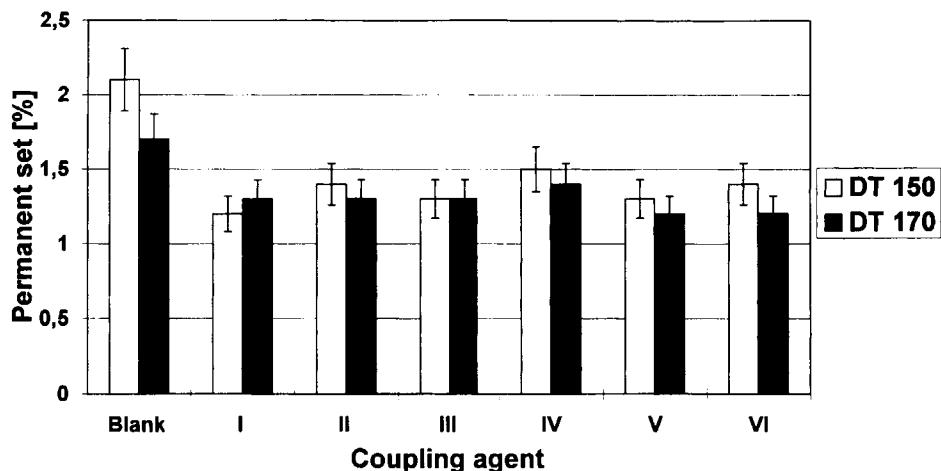


Figure 9 Influence of coupling agents and discharge temperature on permanent set (Goodrich).

flow of vulcanized rubbers in comparison with the blank. Differences between coupling agents are not significant, in most cases the value of dynamic flow is better with the increase of discharge temperature, which is in accordance with the increase of resilience and the decrease of heat buildup. The exception is secondary dinitrodiamine I, where the increase of dynamic flow value occurs at higher discharge temperature. Entirely analogous is the dependence of permanent set on coupling agent and discharge temperature (Fig. 9). Like other values measured with the Goodrich flexometer, permanent set is positively influenced by all coupling agents used in these experiments; the effect of discharge temperature is not very significant.

A more illustrative presentation of the influence of the chemical structure of tested coupling agents on the dynamic properties of vulcanized rubber can be obtained by using the relative molar values of some properties, which are defined by eq. (1). Figure 10 shows the influence of coupling agents on the increase of the impact resilience values converted to the dosage of 1 mmol of coupling agent to 100 g of rubber. Figures 11 and 12 show analogous influences on the reduction of the absolute values of heat buildup. From the comparison of these figures, it follows that the influences are similar for all coupling agents.

Aliphatic (I) as well as aromatic (IV) secondary dinitrodiamines show approximately the same in-

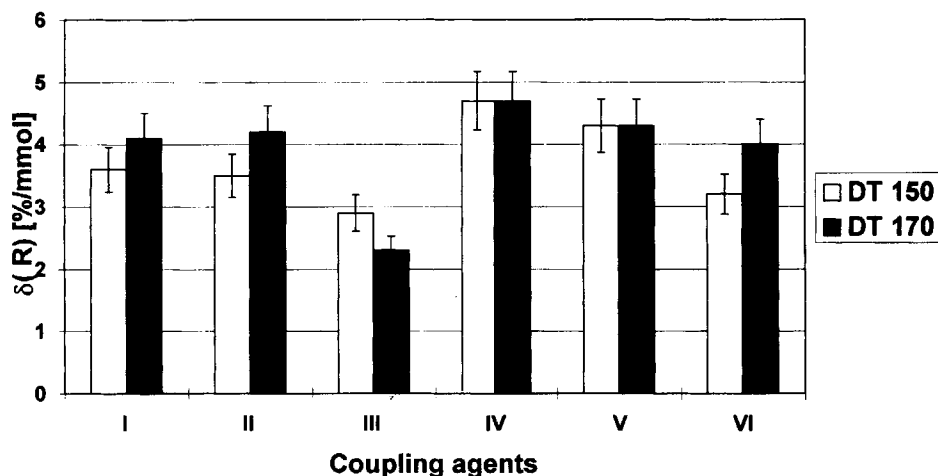


Figure 10 Influence of coupling agents and discharge temperature on relative molar resilience (Lüpke).

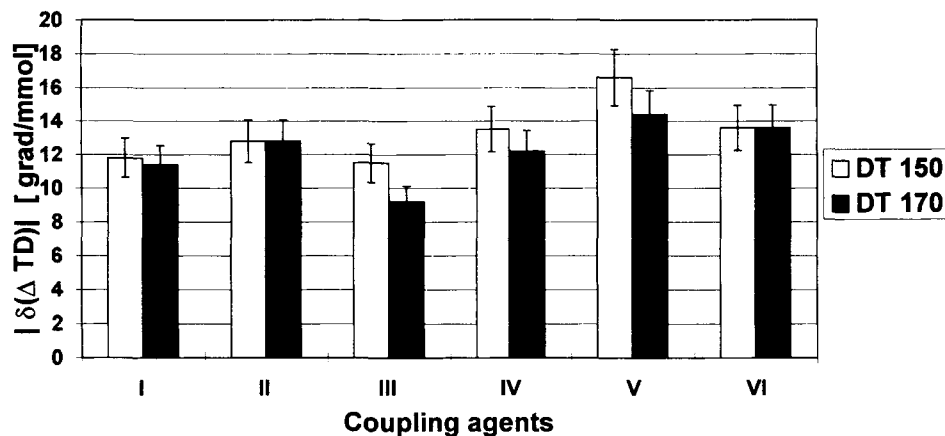


Figure 11 Influence of coupling agents and discharge temperature on the absolute value of relative molar heat buildup (DPGi).

fluence on the resilience increase and the reduction of heat buildup. The aromatic compound IV is a bit more efficient than the aliphatic one. The influence of discharge temperature is negligible in comparison with the blank at the same discharge temperature. This shows that sufficient breakdown of coupling agent and the formation of radicals for the buildup of couplings between rubber and carbon black already occurred at the temperature of 150°C. Aliphatic (II) and aromatic (V) tertiary dinitrodiamines also have comparable effects (the aromatic ones are again a bit better), and not only together, but even in comparison with secondary dinitrodiamines I and IV. The higher molar efficiency of aromatic coupling agents might be connected with the higher stability of an amine radical in conjugation with a benzene ring. The influence of discharge temperature is negligible. The lowest molar efficiency, for resilience

increase and reduction of heat buildup, was obtained in the case of dinitrodiamides III and VI (by about 25%). It is evident that amide radicals from thermal decomposition behave differently from amine radicals; however, we have not any experimental results to explain this phenomenon yet.

CONCLUSION

The presented interpretation of the effects of the coupling agents under investigation on various characteristics of vulcanized rubber shows that all the tested substances have a positive influence on impact resilience and heat buildup; mechanical properties are improved as well. This confirms that substances based on the dinitrodiamine structure can be substituted for usually used nitrosocom-

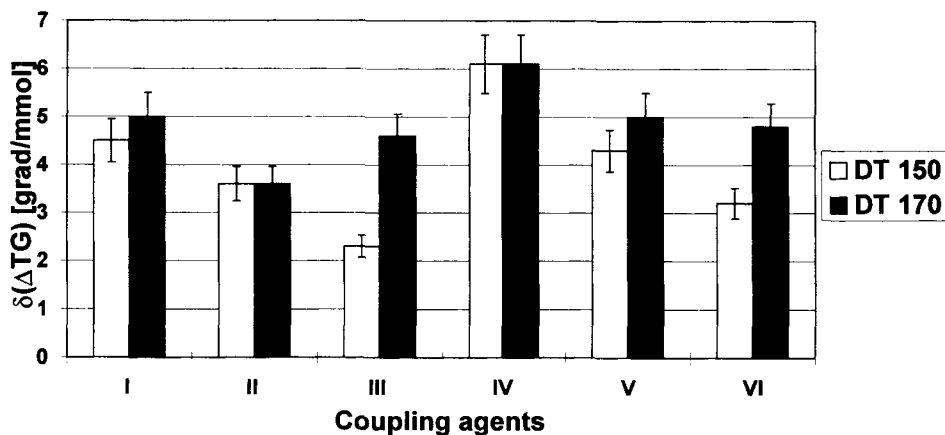


Figure 12 Influence of coupling agents and discharge temperature on the absolute values of relative molar heat buildup (Goodrich).

pounds, which bring health hazards. From the analysis of the results it can be concluded that: (1) the efficiency of dinitrodiamines with comparable lengths of biradical chain from their thermal decomposition depends above all on the size of their molecules; (2) the efficiency of tested dinitrodiamines expressed in molar amounts is comparable, which shows that the length of the biradical obviously plays the substantial role; (3) the influence of substitution at the nitrogen atoms was not proved; secondary and tertiary dinitrodiamines have approximately the same molar efficiency; (4) aromatic derivatives have greater molar efficiency than aliphatic ones; (5) the influence of discharge temperature within 150 and 170°C is not very pronounced; (6) dinitrodiamides are less efficient than dinitrodiamines; and (7) dinitrodiamines with the molecule as small as possible (but with the sufficiently long chain between nitrogen atoms) are from the practical point of view most advantageous because the same effect is afforded at a smaller dosage by weight.

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