

Efficiency of Some Dinitrodiamines and Dinitrodiamides in Improving Dynamic Properties of Vulcanized Rubber

A. KLÁSEK,¹ E. FILIPOVIČOVÁ,¹ J. ŠPAČEK²

¹ Department of Chemistry and Environmental Technology, Faculty of Technology, Tomas Bata University, Nám. TGM 275, 762 72 Zlín, Czech Republic

² Department of Rubber and Plastics Technology, Faculty of Technology, Technical University of Brno, 762 72 Zlín, Czech Republic

Received 13 April 1998; accepted 13 October 2000

ABSTRACT: The effect of some dinitrodiamines and dinitrodiamides on dynamic properties of vulcanized rubber have been investigated. Rubber compounds based on NR/BR were used for these experiments. It has been established that only the use of dinitrodiamines contribute to the increase of impact resilience in comparison with the unmodified compound. The results of carbon gel content assessment suggest that, under given conditions, dinitrodiamides do not form bonds between rubber and carbon black and, therefore, do not influence the dynamic properties of vulcanized rubber. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1439–1443, 2001

Key words: rubber; dynamic properties; resilience; heat build-up; dinitrodiamines; dinitrodiamides; coupling agents

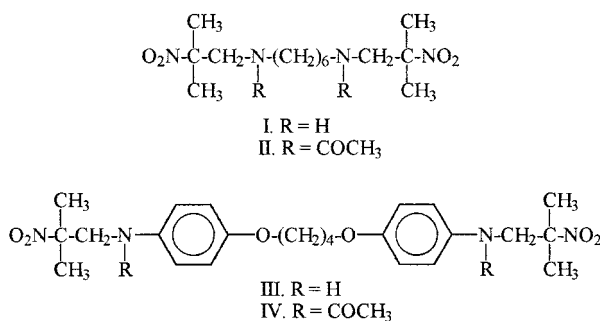
INTRODUCTION

One of the ways to improve dynamic properties of rubber is to add compounds designated as coupling agents. These compounds decompose in the course of mixing and vulcanization and form chemical bonds between rubber and carbon black. The consequence of this is the improvement of carbon black dispersion and decrease of energetic losses at the interface. The values of resilience increase and contemporary decrease of heat build-up can be observed. The value of loss factor $\tan \delta$ improves as well. Different nitroso compounds,^{1–5} especially *N*-nitrosoamines, were used for that purpose. Regarding the fact that *N*-nitroso compounds are potential carcinogens, other

compounds have been searched which would not be health defective but would give the same effect as *N*-nitrosoamines. A group of Japanese authors^{6–8} described dinitrodiamines as such compounds. These compounds not only increase resilience and decrease heat build-up of vulcanized rubbers, but in addition, do not practically influence tensile characteristics and favorably change the frequency dependence of dynamic modulus and the temperature dependence of $\tan \delta$. The application of dinitroamines describe more than 50 patents which have been reviewed.⁹ As a most effective compound from this group, *N,N'*-bis(2-methyl-2-nitropropyl)-1,6-diaminohexane (I, Scheme 1) is presented, which is commercially available as SumifineTM 1162. We have tried in our study⁹ to deduce the causes of different efficiencies of various dinitrodiamines. It was found that an efficient coupling agent should have such a structure which, under its thermal decomposition, makes possible the formation of flexible biradical of the chain length 1.1 nm at least. On the

Correspondence to: A. Klásek (klasek@ft.utb.cz).
Contract grant sponsor: Grant Agency of the Czech Republic; contract grant number: 104/94/0104.

Journal of Applied Polymer Science, Vol. 81, 1439–1443 (2001)
© 2001 John Wiley & Sons, Inc.



Scheme 1

basis of the conclusions of the study, we have prepared¹⁰ some new dinitrodiamines with aliphatic or aliphatic-aromatic connecting chain between functional groups and tested¹¹ the efficiency of them in a model compound on the basis of natural rubber. From the analyses of results, we have concluded that the molar efficiency of such tailored coupling agents is comparable or even higher than that of compound I.

In this work we present the results achieved by application of *N,N'*-bis(2-methyl-2-nitropropyl)-1,6-diacetamidohexane (II), *N,N'*-bis[4-(2-methyl-2-nitropropyl)aminophenoxy]-butane (III), and *N,N'*-bis(2-methyl-2-nitropropyl)-1,4-bis(4-acetamidophenoxy)butane (IV) as coupling agents in a different rubber compound than the one used in our previous work.¹¹ The results are compared with the result reached by the application of compound (I).

EXPERIMENTAL

Materials

All the coupling agents under investigation have been prepared according to the published¹⁰ procedure. Elastomers used were Buna cis 132 (BR) (Chemische Werke Buna, Schopau, Germany) and SMR-10 (NR) (Natural Rubber Producers Association, Malaysia). Carbon black HAF (Nigros K) and ISAF (Nigros I) (Urxovy Zavody, Valasske Mezirici, Czech Republic) were employed.

Preparation of Compounds

Components were mixed in the ratio shown in Table I in a 1.7-dm³ Banbury BC laboratory mixer. At first, rubbers were homogenized and mixed with all additives with the exception of vulcanization system at 5 min at 90 rpm and a

Table I Compound Formulation

BR (Buna cis 132)	14.45phr
NR (SMR-10)	85.55
Carbon black N-330 (Nigros K)	15.00
Carbon black N-220 (Nigros I)	35.00
Stearic acid	2.00
Zinc oxide	4.00
phenyl- β -naphthylamine	1.51
<i>N</i> -isopropyl- <i>N'</i> -phenyl- <i>p</i> -phenyldiamine	1.51
Paraffin 58/62	1.00
Process oil	2.00
Coupling agent (as shown)	0.67
Santocure MOR	1.29
Sulphur	1.64

pressure of 0.3 MPa. Discharge temperature was 150°C. The vulcanization system was admixed on a two-roll mill 150 × 400 mm for 5 min at 50–60°C. Vulcanization was executed in a hydraulic press at 160°C; the cure time was determined in accordance with vulcanization characteristics of particular compounds.

Test Methods

Vulcanization characteristics were measured on an oscillating disc vulcameter standard (Research institute of Rubber and Plastics Technology, Zlín, Czech Republic) at 160°C. Tear strength was determined by the Graves method and impact resilience was determined on a Lüpke elastometer at laboratory temperature. Heat build-up was measured by DPGi method (bending fatigue resistance and heat build-up apparatus, VEB Thüringer Industrie Werke, Rauenstein, Ger-

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

Property	Coupling Agent				
	Blank	I	II	III	IV
T_2 (min)	2.1	1.1	2.0	1.6	2.1
T_{90} (min)	5.3	3.4	5.0	4.3	5.4
H (Shore A)	60	62	62	63	62
TS (MPa)	24.6	25.5	25.1	26.1	26.8
M_{300} (MPa)	14.1	16.8	15.7	15.8	14.3
EB (%)	475	440	506	478	514
G (N mm ⁻¹)	73.0	83.5	84.1	81.1	93.1
R (%)	55	63	55	61	53
ΔT (°C)	77	80	82	77	87
GC (%)	55.1	61.1	55.2	60.8	56.1

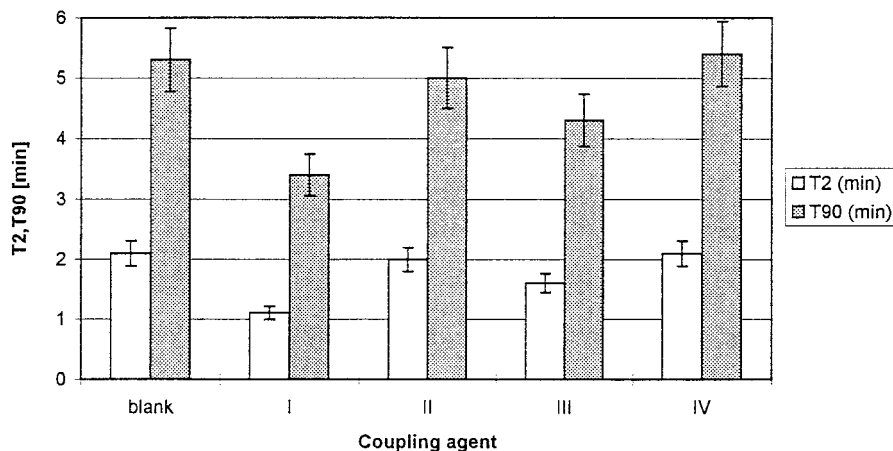


Figure 1 Influence of coupling agents on vulcanization parameters.

many) at 1000 rpm, deformation bending radius of 50 mm, and laboratory temperature. The increase of sample temperature (ΔT) was measured after 30 min. The gel content was determined by the following method.

The sample of rubber compound (~ 0.5 g) was weighed with the accuracy of four decimal digits, put into a small polyamide monofilament basket, hung on a stopper with a hook, and then placed in a 250-mL conical flask filled with 200 mL toluol. Samples were extracted in toluol for 5 days at room temperature, with one change of toluol on the fourth day. Samples in the baskets were removed from flasks, left to dry freely in the air for 24 h, and then dried in the oven with air circulating at 115°C to the constant weight. The gel content was calculated from the weights before and after extraction and the known polyamide baskets weights. Other parameters were deter-

mined by the usual methods. Coupling agents were tested in comparison with the blank compound (having no coupling agent) always on the row of four compounds which were mixed consecutively; average values are given in Table II. The error bars of experiments are included in the figures.

The following characteristics were used:

T_2	scorch time (min);
T_{90}	optimal vulcanization (min);
H	hardness (Shore A);
TS	tensile strength (MPa);
M_{300}	modulus 300% (MPa);
EB	elongation at break (%);
G	tear resistance, Graves ($N\ mm^{-1}$);
R	impact resilience (%);
ΔT	heat build-up, DPGi method (°C);
GC	gel content (%).

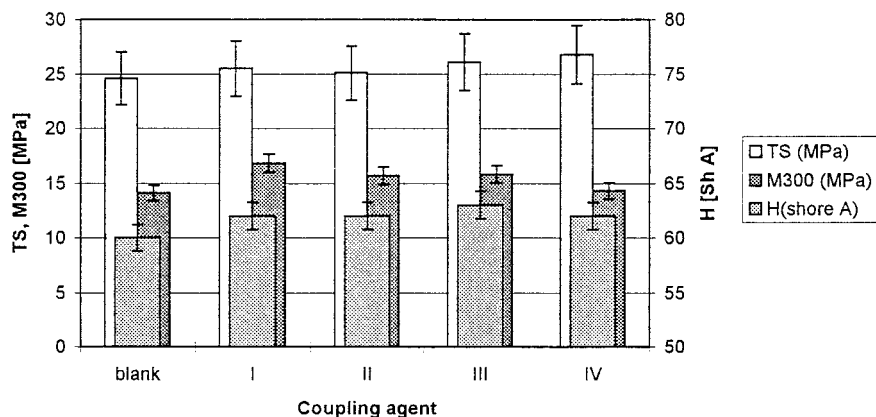


Figure 2 Influence of coupling agents on some mechanical properties.

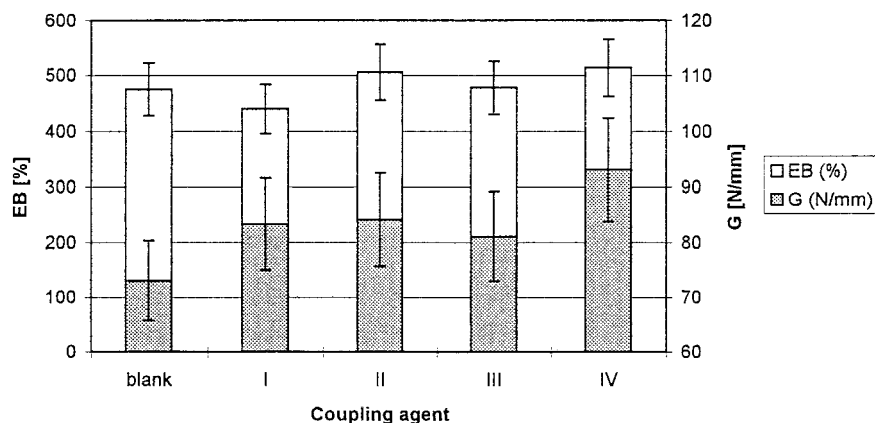


Figure 3 Influence of coupling agents on elongation at break and tear resistance.

RESULTS AND DISCUSSION

As can be seen from Table II, the values of vulcanization optimum are lower for coupling agents I and III, containing secondary amine group. The effect has been already observed¹² and for removing this, the addition of imides was recommended. With acetyl derivatives II and IV, the values of vulcanization optimum in comparison with blank do not change (Fig. 1). Thus, in this respect agents II and IV behave differently in the compound of the composition given in Table I than we observed previously,¹¹ where the compound based on NR alone was employed. Similar influence shows the tested coupling agents on the value of scorch time T_2 (Fig. 1). Mechanical properties of vulcanized rubber are changed only slightly by the addition of coupling agents (Fig. 2); a small increase of modulus (significant with coupling agent I), tensile strength, and hardness may be seen, which

is in accordance with our previous results.¹¹ Influence of coupling agents on elongation at break is shown in Figure 3. The decrease of EB value in the case of agent I is in accordance with higher modulus. The changes of tear resistance (Graves) with the addition of coupling agents are shown in Figure 3. In all cases the value of G is increased in comparison with blank; with dinitrodiamine IV the increase is more expressive. This result is again opposite to the case where only the compound based on NR was used and points out that the mechanism of dinitroamines action is obviously dependent on the composition of compound. From the standpoint of application purposes, the most important parameters are impact resilience and heat build-up, which are shown in Figure 4. According to the presumption, resilience is increased by the addition of dinitroamines I and III; the increase of values is analogical to the results observed in our previous work.¹¹ However, although by us-

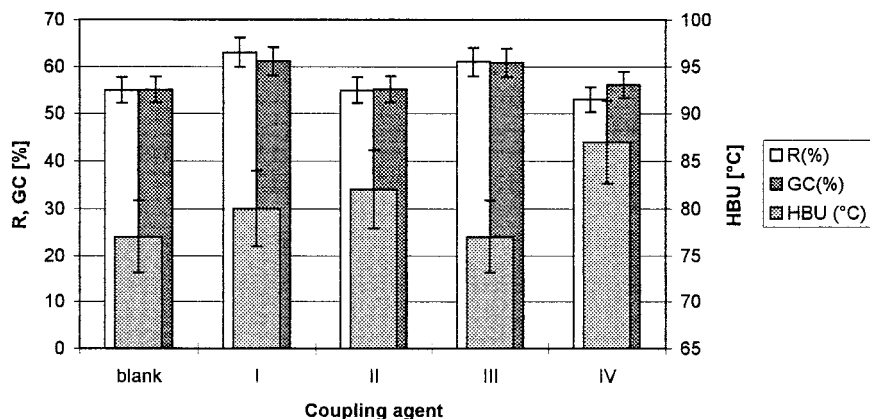


Figure 4 Influence of coupling agents on dynamic properties and gel content.

ing NR the resilience was increased even in the case of dinitroamides II and IV, with the compound used in this work, resilience is not increased in comparison with blank. The greatest surprise, however, brings the application of coupling agents in the case of heat build-up (Fig. 4). It is possible to say that with the exception of aromatic dinitrodiamine III, which has the same value of heat build-up as blank, the other coupling agents increase heat build-up, especially dinitrodiamide IV. It is necessary to point out that even the compound used without any coupling agent has considerably lower heat build-up than the compound used in our previous work.¹¹ The difference is not only in basic elastomers employed, but also in carbon black type and content, and the vulcanization system as well. It is possible to state that coupling agents influence dynamic properties of vulcanized rubber prepared from the compound under investigation substantially less than that of simple compound based on natural rubber alone. However, it cannot be said whether only the change in basic elastomer composition is substantial in this case, because other characteristics of the compound are changed also.

To verify that the mechanisms of the action of biradicals originate by thermal decomposition of coupling agents, we have measured the carbon black gel content in all compounds. It appears that the increase of carbon gel content, demonstrating the formation of the crosslinks, comes only by secondary dinitrodiamines I and III, which is in agreement with the change of impact resilience (Fig. 4). It is possible that dinitrodiamides either are stable at given conditions or decompose by a mechanism other than dinitrodiamines and, therefore, do not afford crosslinked products. On the other hand, a favorable influence of the addition of dinitrodiamides on mechanical properties and tear resistance is of interest.

CONCLUSIONS

The interpretation of results with application of the coupling agents under investigation on differ-

ent characteristics of vulcanized rubber demonstrates that (1) fundamental importance for the efficiency of coupling agents has the composition of compounds; (2) dinitrodiamides, which in natural rubber compounds are only slightly less efficient than dinitrodiamines, do not improve dynamic properties of compounds under investigation; nevertheless, an improvement of mechanical properties and tear resistance may be seen; (3) increased carbon black gel by application of dinitrodiamines shows that even in such a compound chemical bonds between rubber and carbon black may be formed by action of biradicals from thermal decomposition; (4) unchanged carbon black gel content after application of dinitrodiamides in comparison with blank shows that these compounds, under given conditions and compound formulation, are stable or decompose in a different way than dinitrodiamines.

REFERENCES

1. Walker, L. A.; D'Amico, J. J.; Mullins, D. D. *J Org Chem* 1962, 27, 2767.
2. Payne, A. R.; Swift, P. M.; Wheelans, M. A. *J Rubber Res Inst Malays* 1969, 22, 275.
3. Hamed, P.; Walker, L. A. *Rubber World* 1971, 164, 51.
4. Leeper, H. M.; Gable, C. L.; D'Amico, J. J.; Tung, C. C. *Rubber World* 1956, 135, 413.
5. D'Amico, J. J.; Tung, C. C.; Walker, L. A. *J Am Chem Soc* 1959, 81, 5957.
6. Okita, T.; Yamaguchi, T.; Kurimoto, I.; Ohashi, K. *Novel Carbon Black/Rubber Coupling Agents; Meeting of the Rubber Div., American Chemical Society: Cincinnati, OH, Oct. 18-21, 1988.*
7. Yamaguchi, T.; Kurimoto, I.; Ohashi, K.; Okita, T. *Kautsch Gummi Kunstst* 1989, 42, 403.
8. Yamaguchi, T.; Kurimoto, I.; Nagasaki, H.; Okita, T. *Rubber World* 1989, 199 (5), 30, 38.
9. Klásek, A.; Kafka, S. *Plasty a kaučuk (Czech)* 1995, 32, 132.
10. Kafka, S.; Klásek, A.; Sedmera, P. *Collect Czech Chem Commun* 1995, 60, 1419.
11. Klásek, A.; Špaček, J.; Čuřík, R.; Kafka, S. *J Appl Polym Sci* 1996, 61, 1137.
12. Nagasaki, H.; Inui, N.; Yashigo, S. *Eur Pat Appl* 410,152, 1991 (Chem Abstr 1991, 115, 116173).