Mechanical Properties of Swelled Vulcanizates of Polar Diene Elastomers

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ABSTRACT: Rubber elements, which usually form a major part of different isolators of vibrations, are generally easily swelled by oils, greases, or fuels. This leads to meaningful changes of their mechanical characteristics and shortening of durability of rubber components in service. The influence of the semisynthetic motor oil on mechanical and, particularly, dynamic properties of swelled vulcanizates of the polar diene rubber, chloroprene (CR) and acrylonitrile-butadiene (NBR), is estimated in this article. These elastomers, as is widely known, are resistant to the mineral oils absorption. However, our investigations showed that even a small degree of swelling of the vulcanizates causes decrease of their mechanical properties and considerable changes of the dynamic characteristics of the samples. The obtained results have shown the need to take into account the environment in which isolators of vibrations and dampers have worked, while designing the suitable composition of rubber compounds. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2010–2015, 2006

Key words: swelled rubber; mechanical properties; dynamic properties; dynamic modulus; reinforcement

INTRODUCTION

Dampers, bearings, and other isolators of vibrations (vibro-isolators) are used in many industries. During their service, they are often exposed to contact with oils, greases, or fuels. The rubber elements, which are usually major parts of the vibro-isolators, bearings, and dampers, are usually nonresistant to oils, greases, or fuels and therefore are swelled by them. This causes the change of their dynamic characteristics (particularly moduli and a loss angles) and shortening of the time of the exploitation.[1–4]

There are abundance of papers concerning the influence of many factors on the mechanical and the dynamic properties of rubbers.[5–9] However, only few of them take into account the significance of the problem (practically and theoretically) of the influence of swelled vulcanizates by liquids (such as, e.g., oils) on their mechanical and, particularly, their dynamic properties. In this field, only a few titles were found. For example, Gajewski[1] examined the influence of swelling of a natural, isoprene and butadiene rubber by benzene, dibutyl phthalate, and higher hydrocarbons on the static and the dynamic properties (by using the torsion pendulum). He reported that a small degree of swelling caused a small increase of angles of the phase shift of vulcanizates, but if degree of swelling was higher then phase angles were decreased significantly. He explained it as a result of a destruction of a filler network by pressure of absorbed liquids. Busfield et al.[2] studied the influence of swelling linked to the prior stress applied to samples on dynamic properties of natural rubbers. They used, as Gajewski did, the free oscillating technique. The researchers used dibutyl adipate and unknown oils as the swelling fluids. When samples were immersed in fluids of low viscosity, high decrease of the storage and the loss components of the dynamic moduli (G^*) were observed. However, in case of high degree of swelling by viscous liquids the loss modulus G'' increased, which they tried to explain by "the high internal viscosity of rubber caused by viscous liquids." Similar results for vulcanizates of nonpolar diene rubbers were described by Rzymski and Jentzsch.[3]

In the literature, there is a noticeable shortage of reports dealing with the influence of oils on the mechanical and the dynamic properties of polar diene rubbers, e.g., the chloroprene and the nitrile rubbers. The vulcanizates based on these rubbers swelled in oils only to a limited degree, although the aforementioned publications[1–3] show that even limited swelling may cause hazardous changes of rubber parts performance. That is why we have decided to investigate the influence of CR and NBR rubbers swelled by semisynthetic motor oils on the mechanical and dynamic properties of the vulcanizates. Our research, as well as the

TABLE I
Compositions of Rubber Compounds of CR Vulcanizates and T_{90} Times of Vulcanization

Components/sample	CR 0	CR 10	CR 20	CR 30	CR 50	CR 70
CR S40	100	100	100	100	100	100
Stearic acid	5	5	5	5	5	5
Zinc oxide	5	5	5	5	5	5
Magnesium oxide	4	4	4	4	4	4
Dibutyl phthalate	10	10	10	10	10	10
CB N550	0	10	20	30	50	70
IPPD	1	1	1	1	1	1
ETU	0.5	0.5	0.5	0.5	0.5	0.5
TMTD	0.5	0.5	0.5	0.5	0.5	0.5
Sum	126	136	146	156	176	196
Measured T_{90}[min]	17.62	14.95	18.43	13.3	10.87	12.64

practical benefits such as determination of risk caused by interaction of mineral oils with CR and NBR rubbers, may also make a considerable contribution to understanding of the reinforcement phenomena of elastomers by fillers.

EXPERIMENTAL

Materials

Chloroprene rubber (CR, Denka S40, Denka, Japan); acrylonitrile-butadiene rubber (NBR, KER N33, 33% of acrylonitrile, Dwory S.A., Poland); N-tert-butyl-1,3-benzothiazole-2-sulfenamid (TBBS, Vulkacit NZ, Bayer, Germany); imidazoline-2-thione (ETU, Vulkacit NPV/C, Bayer, Germany); N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD, Dusantox IPPD, Duslo, Slovakia); tetramethylthiuram disulfide (TMTD, Vulkafil TMTD, Bayer, Germany); 1,2-dihydro-2,2,4-trimethylquinoline polymerized (TMQ, NaugardTMQ, Uniroyal); N-cyclohexyl-1,3-benzothiazole-2-sulfenamide (CBS, Vulkacit CZ/EG, Bayer, Germany); carbon black N550, N220 (both types of CB Degussa, Germany); others: sulfur (Siarkopol, Poland), dibutyl phthalate (Boryszew, Poland), stearic acid (Brentag, Poland), magnesium oxide (The C.P.Hall Company, USA), zinc oxide (Huta Olawa, Poland), semisynthetic motor oil 10W/40 (Orlen, Poland; mixtures of hydrotreated heavy paraffinic, hydrotreated light paraffinic, solvent-dewaxed heavy paraffinic –in summary >70%; poli(1-decen) –<15%; zinc diphosphate –<1%).

Samples preparation

For the dynamic tests, the cylindrical shaped (diameter 18 mm, height 25 mm) samples of CR vulcanizates and NBR vulcanizates, with different contents of carbon black, were prepared. For the mechanical tests, standard plates with 2 mm thickness were made, from which the samples of the dumbbell shape (II type) were cut, according to ISO 37 : 98. The rubber compounds shown in Tables I and II were prepared using a roll mill. Ingredients were added in the following order: elastomer, zinc oxide or magnesium oxide, stearic acid, carbon black, plasticizers, accelerators, and sulfur. The compounds were homogenized for about 20 min. The samples were vulcanized in a laboratory press, at 150°C, during T_{90} + 2 min (for mechanical properties) or T_{90} + 5 min (in case of the dynamic tests). Because of their diameters, the samples for the dynamic tests were vulcanized a little

TABLE II
Compositions of Rubber Compounds of NBR Vulcanizates and T_{90} Times of Vulcanization

Components/sample	NBR 0	NBR 10	NBR 20	NBR 30	NBR 50	NBR 70
Ker N33	100	100	100	100	100	100
Stearic acid	2	5	5	5	5	5
Zinc oxide	5	5	5	5	5	5
Dibutyl phthalate	5	5	5	5	5	5
CB N220	0	10	20	30	50	70
IPPD	1	1	1	1	1	1
TMQ	1.5	1.5	1.5	1.5	1.5	1.5
CBS	1.5	1.5	1.5	1.5	1.5	1.5
TMTD	1.5	1.5	1.5	1.5	1.5	1.5
Sulfur	1	1	1	1	1	1
Sum	117.5	130.5	140.5	150.5	170.5	190.5
Measured T_{90} [min]	10.04	26.25	28.78	24.57	18.08	14.07

TABLE III
Degree of Rubber Swelling for NBR Vulcanizates,
Samples for Dynamic and Mechanical Properties

	Δm (%)	Δv (%)
Samples for dynamic tests		
NBR 0	−0.7	−0.5
NBR 10	−0.7	−0.4
NBR 20	−0.6	−0.4
NBR 30	−0.6	−0.3
NBR 50	−0.5	−0.4
NBR 70	−0.5	−0.2
Samples for mechanical tests		
NBR 0	−1.9	−1.4
NBR 10	−1.7	−1.1
NBR 20	−1.8	−1.2
NBR 30	−1.3	−0.5
NBR 50	−1.1	−0.8
NBR 70	−1.1	−1.2

longer to obtain the same level of crosslinking. T_{90} values for each compound are shown in Tables I and II. Part (half) of the samples quantity were swelled by the semisynthetic motor oil, heated up to a temperature of 70°C, by immersing the samples in it for 24 h (tests of swelling degree as function of oil temperature and swelling time was done to optimize the swelling procedure). The procedure ensured that at the equilibrium degrees of swelling all samples were achieved. Before measurement of the mechanical properties, the samples were wiped with blotting-paper.

Measurements

The vulcametric properties of the compounds were examined using rotorless rheometer (Monsanto Rheometer Mv2000), according to ISO 3417 : 98, at 150°C, during 45 min.

For the dynamic measurements, the D8 apparatus produced by H. W. Wallace was used. The sample was sheared in the range 0.002–0.365 of relative amplitudes of deformation, at the frequency of 0.25 Hz, were applied in ambient temperature. The complex modulus G*, their component and angle of the phase shift (the loss angle) were determined. A rubber cylinder was glued to the metal plates, to fix it to the measuring device.[10]

Mechanical properties: the tensile strength (TS_b), the moduli (S_e 100%, S_e 200%, S_e 300%), and the elongation at break (E_b) were done, according to ISO 37 : 98 (Zwick 1445); the Shore A hardness was performed according to PN-80/C-04 238 (Zwick 7201); the tear strength (T_s) was measured, according to ISO 34–1 : 98 —A method (Zwick 1445).

RESULTS AND DISCUSSION

Swelling tests of the vulcanizates

The samples for the dynamic and the mechanical measurements of CR and NBR vulcanizates were swelled

in the semisynthetic motor oil. The preliminary tests were carried out to find the most effective condition of the swelling procedure (it is described in the experimental parts of this paper). As it was expected, for the vulcanizates of NBR, increase of mass or volume were not observed (Table III). The negative change of mass and volume of NBR samples is due to extraction of low molecular ingredients of the vulcanizates. The samples of CR vulcanizates for the dynamic tests swelled only in a slight degree from about 1.6–2.7% volumetric. The CR samples for the mechanical tests swelled to higher level from 7 to 15% volumetric (Table IV). The considerable differences in the degree of swelling of the samples for the dynamic and the mechanical properties may result from the differences of the size of the surface and the thickness of both kinds of the samples.

Influence of swelling on the dynamic properties of the vulcanizates

The dynamic measurements of both nonswelled and swelled vulcanizates were carried out. Comparative results of the dynamic moduli G* and the loss angles are shown in Figures 1–4.

Despite the slight degree of the swelling of CR vulcanizates, a considerable increase of the loss angle values of the swelled samples compared with those of nonswelled was observed (Fig. 2). In the light of the mechanism, which clarifies a damping phenomenon of rubber, based on energy dissipation by molecular slippage,[5] those results are unexpected. Considering the fact that in the swelled samples loosening of elastomer chains occurs, an opposite situation was expected. These results are in agreement with Payne's mechanism, which relies on breaking of weak bonds between filler–elastomer and filler–filler matrix.[8,11] Increase of the loss angles means that greater number of

TABLE IV
Degree of Rubber Swelling for CR Vulcanizates,
Samples for Dynamic and Mechanical Properties

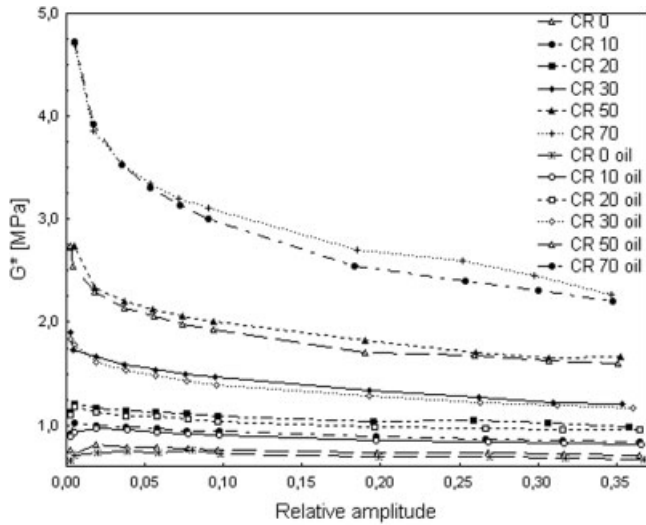|	Δm (%)	Δv (%)
Samples for dynamic tests		
CR 0	1.7	2.7
CR 10	1.6	2.6
CR 20	1.3	2.2
CR 30	1.2	2.1
CR 50	1.0	1.8
CR 70	0.8	1.6
Samples for mechanical tests		
CR 0	9.9	15.0
CR 10	7.9	12.7
CR 20	7.3	11.8
CR 30	6.8	11.4
CR 50	4.7	8.4
CR 70	3.6	7.0

Figure 1 Effect of strain amplitude on dynamic moduli of CR vulcanizates before and after swelling.

these bonds undergo destruction in the swelled systems. Other explanation of the obtained results is the use of the mechanism proposed by Wang.[6] His model explains damping by the mechanism of forming of joint rubber shells around filler particles. However, it can be accepted that the swelling of the vulcanizates leads to weakening of the layer of the elastomers surrounding the filler particles, which increases the level of the loss angle. It is understood that the deformation of this layer will be higher, because modulus G* is lower, which means that higher number of filler–elastomer bonds may be damaged.[9] This can mean that a larger number of physical bonds of filler–elastomer or/and filler–filler break temporarily and more mechanical energy would be dissipated.
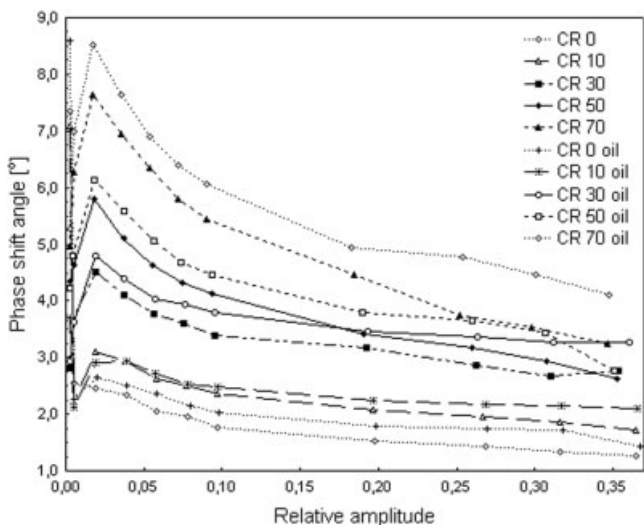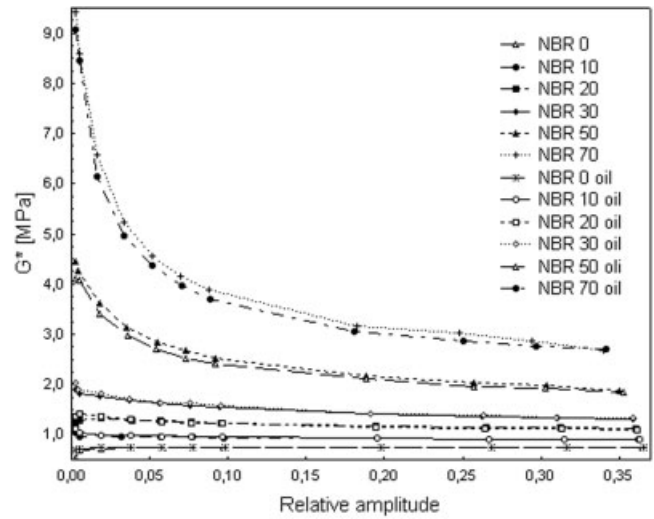

Figure 3 Effect of strain amplitude on dynamic moduli of NBR vulcanizates before and after swelling.

In spite of that, NBR vulcanizates exposed to the oil did not point out to the mass or the volume changes similar to the behavior of the moduli or the loss angles, as was observed in the case of CR vulcanizates (Figs. 3 and 4). However, as is indirectly shown by the decrease of the hardness after swelling tests (Table VI), the absorption of the oil occurred to some extent. It is possible that in NBR samples certain quantities of the components of vulcanizates were washed out, and the lack of changes of the mass or the volume is the effect of equilibrium of the swelling and the washing processes.

Influence of swelling on the mechanical properties of the vulcanizates

The results of measurements of the mechanical properties of the samples CR and NBR before and after
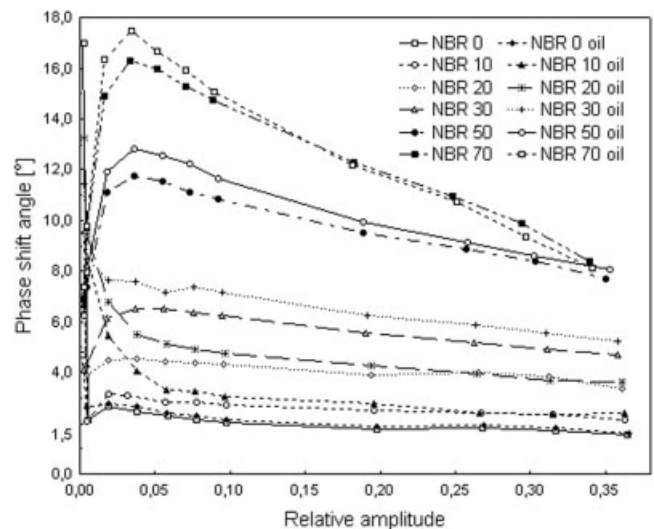

Figure 2 Effect of strain amplitude on loss angles of CR vulcanizates before and after swelling.

Figure 4 Effect of strain amplitude on loss angles of NBR vulcanizates before and after swelling.

TABLE V
Mechanical Properties of CR Vulcanizates Before and After Swelling

	Hardness (ShA)	E_b (%)	TS_b (MPa)	S_e 100% (MPa)	200% (MPa)	300% (MPa)	T_s (kN/m)
Before oil treatment							
CR 0	39	495	13.9	1.1	1.3	1.8	7.1
CR 10	47	547	17.1	1.3	2.3	4.7	7.0
CR 20	52	513	20.1	1.9	4.3	8.8	6.4
CR 30	59	396	19.4	2.9	7.7	14.2	7.0
CR 50	74	259	19.3	6.3	14.7	—	7.0
CR 70	82	185	19.5	10.3	—	—	4.4
After oil treatment							
CR 0	32	633	9.7	0.7	0.9	1.1	3.0
CR 10	39	547	14.7	1.0	1.7	3.3	4.2
CR 20	44	419	16.0	1.7	7.3	11.8	4.0
CR 30	51	360	18.5	2.7	7.9	14.4	5.0
CR 50	65	233	18.3	7.0	16	—	5.0
CR 70	74	149	17.5	7.0	—	—	3.2

swelling in the selected oil are shown in Tables V and VI. In the swelled vulcanizates of CR (compared with nonswelled one), the decrease of all properties (TS_b, E_b, T_s, hardness, excluding E_b for samples of CR with 0 and 10 phr CB load) was observed (Table V). The decrease of the properties can be explained by weakening of the filler–elastomer and filler–filler interactions. At lower filler amounts (30 phr), decrease of the mechanical properties is higher than in the samples with higher content of the filler. Those differences result from lower degree of swelling of the vulcanizates with higher load of the filler. However, it is known that in the range ≤30 phr of the filler content it is difficult to expect that the filler net exists. So, it seems probable that the fall of the mechanical properties is caused mainly by the weakening of filler–elastomer interactions and the rubber matrix itself. However, in the vulcanizates with the filler amount in the range of 50–70 phr, there is no doubt that the filler network exists and filler–filler interactions are numerous. Joining this observation with lesser fall of the mechanical properties (in this range of the filler content), it may be stated that filler–filler interactions are less weakened than filler–elastomer interactions by the oil absorption of the samples.

The mechanical properties of NBR vulcanizates in relation to the filler amount and the swelling degrees (Table VI) are less clear than those obtained for CR vulcanizates, which results from the lesser absorption of the oil. However, similar to the CR samples, in case of the filler loads less than or equal 30 phr, the fall of the mechanical properties was significant. In the sam-

TABLE VI
Mechanical Properties of NBR Vulcanizates Before and After Swelling

	Hardness (ShA)	E_b (%)	TS_b (MPa)	S_e 100% (MPa)	200% (MPa)	300% (MPa)	T_s [kN/m]
Before oil treatment							
NBR 0	49	400	3.7	1.2	1.7	2.3	1.7
NBR 10	54	435	10.5	1.5	2.5	4.5	3.3
NBR 20	59	416	14.4	1.8	3.6	7.3	5.3
NBR 30	64	439	20.5	2.5	7.3	11.2	5.0
NBR 50	74	367	23.6	4.0	10.5	18.4	6.4
NBR 70	84	276	24.6	6.6	17.1	—	7.0
After oil treatment							
NBR 0	43	376	3.1	1.2	1.7	2.3	1.6
NBR 10	50	390	7.8	1.5	2.5	4.6	3.2
NBR 20	54	355	9.9	1.7	3.4	7	5.7
NBR 30	60	400	17.2	2.2	4.9	10.1	6.7
NBR 50	70	357	24.0	4.0	10.9	19.3	6.2
NBR 70	83	286	25.5	6.5	17.6	—	7.3

ples containing 50 phr or higher amounts of filler, the mechanical properties practically did not change. Because similar characters of changes of the properties (although to some extent) were observed for the NBR vulcanizates to those in the CR case, it can be assumed that the mechanisms in both cases are similar, that is, filler–filler interactions limit the negative influence of oil on the properties of vulcanizates.

CONCLUSIONS

Rubber goods are frequently used for such applications in which they undergo cyclic deformations at a certain frequency or over a range of frequencies. Therefore, temperature and extent of deformations varied considerably during exploitation. For this sort of application, the dynamic properties of the rubber goods are very important because of their influence on the fatigue life and the operating characteristics.

Even negligible swelling of CR and NBR vulcanizates in the semisynthetic motor oil causes considerable changes of their dynamic properties—the increase of the loss angles and decrease of the complex moduli G* are observed. Those results show that proposed mechanism of the "damping" phenomenon, so-called "molecular slippage," is incorrect.

The mechanical properties (TS_b, E_b, S_e 100%, S_e 200%, Se 300%, hardness, and Ts) of swelled CR and NBR vulcanizates, in spite of a small degree of swelling (in the samples with filler amount up to 30 phr), are significantly lower than for the nonswelled vulcanizates. Those differences may arise from the different degree of swelling and the fact that absorbed oil weak-

ens interactions of the filler–rubber matrix stronger than filler–filler interactions.

The differences of the dynamic properties of the swelled and nonswelled vulcanizates with filler over 30 phr are not significant. It confirms that the strong filler–filler interactions constrain the penetration of the vulcanizates structure by the oils.

From the practical point of view, the presented results turn attention toward designing of rubber vibro-isolating systems, by selection of suitable composition of rubber compounds, taking into account the environment in which the vibro-isolators will be expected to work. The increase of the loss angle as a result of swelling will lead to the dissipation of more mechanical energy during exploitation and probably higher temperature of the rubber goods. The higher temperature may accelerate the aging processes of rubber and shorten the durability of the vibro-isolators.

References

1. Gajewski, M. Polimery–Tworzywa Wielkocząsteczkowe 1974, 19, 244.
2. Busfield, J. J. C.; Deeprasertkul, C.; Thomas, A. G. Polymer 2000, 41, 9219.
3. Rzymski, W. M.; Jentzsch, J. Plaste und Kautchuk 1990, 37, 48.
4. Shaefer, R. J Rubber World 1995, 222, 16.
5. Dannenberg, E. M. Rubber Chem Technol 1975, 48, 410.
6. Wang, M.-J. Rubber Chem Technol 1998, 71, 520.
7. Medalia, A. I. Rubber Chem Technol 1978, 51, 437.
8. Payne, A. R. J Polym Sci 1962, 6, 57.
9. Magryta, J. Eur Polym J 1991, 27, 359.
10. Młoźniak, D.; Magryta, J. Elastomery 2004, 8, 18.
11. Payne, A. R.; Whittaker, R. E. Rubber Chem Technol 1971, 44, 440.