Sulfur and peroxide curing of Rubber Compounds based on NR and NBR. Part I: cross-linking and physical-mechanical Properties

1. Introduction
Vulcanization or curing is one of the most important processes in rubber technologies. During that, plastic rubber compound changes into high elastic final product – vulcanize by running parallel and subsequent physical, but mainly chemical reactions at high temperature and high pressure. A lot of curing systems have already been developed within the history, such as sulfur, peroxide, phenolic resins, quinones, etc. Among them, peroxide and mainly sulfur curatives are the most widely used.

Vulcanization with sulfur is the oldest process in cross-linking of unsaturated elastomers [1-3]. Sulfur curing systems consisting of at least three ingredients – sulfur, activators and accelerators leads to the forming of sulfidic cross-links with various lengths (monosulfidic C-S-C, disulfidic C-S-S-C and polysulfidic C-S-C, x = 3-6) between macromolecular chains [4, 5]. Generally, sulfur cured vulcanizates exhibit good elastic and dynamic behavior and possess high values of tensile and tear strength. Sulfur curing of rubber is very complex and intricate process and the mechanism of cross-linking is still not clearly understood.

On the other hand, cross-linking of rubber with peroxides is relatively simple process results in forming carbon-carbon linkages between macromolecular chains [6]. C-C bonds have higher dissociation energy compared to sulfidic cross-links, therefore the main advantage of peroxide cured vulcanizates is good heat ageing resistance [7]. Good electrical properties, low compression set and non-staining of the finished parts are next benefits of peroxide cured vulcanizates. In order to improve the cross-linking efficiency and properties of peroxide cured elastomers, the multifunctional co-agents are very often used. Co-agents are typically low molecular weight organic molecules with high reactivity towards free radicals. During the curing process, they undergo homopolymerization reaction and easily graft to elastomer chains to form complex cross-linked network [8]. The two types of elastomers were chosen for the experiments. Natural rubber NR has unique properties, which distinguish it from other synthetic rubber. It is an unsaturated, non-polar elastomer with highly stereo-regular structure, containing 99.9% of cis-1,4-isoprene structural units. Due to this, it is crystalizing elastomer with almost ideal elastic and hysteresis properties.

Acrylonitrile-butadiene rubber NBR is a synthetic unsaturated co-polymer, consisting of cis-, trans-1,4, and 1,2-butadiene structural units and polar acrylonitrile structural units, which ranks it among polar elastomers. Due to the irregularity of macromolecular chains, it is non-crystallizing elastomer with good resistance to non-polar solvents.

The present work was focused on the preparation of rubber compounds based on NR and NBR by applying of mixed sulfur and peroxide curing systems. A combination of both curing systems in cross-linking of elastomers should combine the patterns of sulfidic bridges and C-C linkages. The main aim was to suppress the main negatives of both curing systems and possibly to highlight their benefits.

Authors
Ján Kruželák, Richard Sýkora, Ivan Hudec, Bratislava, Slovakia

Corresponding author: Ján Kruželák, Department of Plastics and Rubber Institute of Polymer Materials Faculty of Chemical and Food Technology Slovak University of Technology Radlinského 9, 812 37 Bratislava, Slovakia E-Mail: jan.kruzela@stuba.sk Telephone: + 421 02 5932589
Discover more interesting articles and news on the subject!

www.kgk-rubberpoint.de

Entdecken Sie weitere interessante Artikel und News zum Thema!
2. Experimental

2.1 Materials

The two types of elastomers were tested, natural rubber NR (SMRS, Mardec, Malaysia) and acrylonitrile-butadiene rubber NBR (SKN3345, content of acrylonitrile 31-35%, Sibur International GmbH, Russia). The rubber compounds have model character and they contained only the ingredients of curing systems. Peroxide curing system consisted of dicumyl peroxide DCP as peroxide curing agent and ethylene glycol dimethacrylate EGDA as co-agent. Both chemicals were supplied from Merck Schuchardt OHG, Germany. Sulfur curing system was consisted of zinc oxide (Slovlak, Košeca, Slovakia), stearic acid (Setuza, Ústí nad Labem, Czech Republic), N-Cyclohexyl-2-benzothiazole sulfenamide CBS (Duslo, Šaľa, Slovakia) and sulfur (Siarkopol, Tarnobrzeg, Poland).

2.2 Methods

2.2.1 Preparation and curing of rubber compounds

The mixing of rubber compounds was carried out in laboratory mixer Brabender at the rotor speed 50 rpm and temperature 90°C. The amount of feedstock was about 60g. First, the rubber was plasticated for 3 minutes, than the ingredients of curing systems were introduced. The mixing process then continued for 4 minutes. After that the blends were homogenized in two roll calender.

There were prepared 5 types rubber compounds. The first one was prepared only with peroxide curing system, by contrast the last one only with sulfur curing system. In the rest three types rubber formulations, the mutual ratio of sulfur and peroxide was uniformly changed so that the amount of curatives in all rubber compounds was kept constant. The rubber compounds were designated according to which content and ratio of peroxide and sulfur they contain. The detailed composition of rubber compounds and their designations are presented in Tab. 1.

The prepared rubber compounds were cured at 160°C and 15 MPa by using hydraulic press Fontijne in form of thin rubber sheets (width 15 x 15 cm, thickness 2 mm). The time of vulcanization was equal to optimum cure time $t_{c90}$, which was determined from the corresponding curing isotherms measured by Rheometer Monsanto.

2.2.2 Determination of cross-link density of vulcanizates

The determination of cross-link density $\nu$ is based on equilibrium swelling of samples in suitable solvent. Xylene, as non-polar solvent was used for swelling of vulcanizates based on NR and acetone, as polar solvent was used for swelling of vulcanizates based on NBR. The samples of vulcanizates were immersed in solvents and their weight was periodically measured within the time, until the equilibrium swelling was reached, i.e. the weight of samples was stabilized on the constant value. The cross-link density was calculated based upon equilibrium swelling degree by using the Flory-Rehner equation [9].

2.2.3 Determination of physical-mechanical properties of vulcanizates

Physical-mechanical properties of the prepared vulcanizates were measured in accordance with the valid technical standards, on the double side dumbbell-shaped test specimens (length 10 cm, width 6.4 mm, thickness 2 mm), by using Zwick Roell/Z 2.5 appliance at cross-head speed of 500 mm/min. The hardness was measured by using durometer and the unit was expressed in Shore A.

<table>
<thead>
<tr>
<th>Tab.1 Composition of rubber compounds and their designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component</td>
</tr>
<tr>
<td>NR or NBR</td>
</tr>
<tr>
<td>ZnO</td>
</tr>
<tr>
<td>Stearic acid</td>
</tr>
<tr>
<td>Sulfur</td>
</tr>
<tr>
<td>CBS</td>
</tr>
<tr>
<td>DCP</td>
</tr>
<tr>
<td>EGDA</td>
</tr>
<tr>
<td>Designation of samples</td>
</tr>
</tbody>
</table>
3. Results and discussion

3.1 Influence of curing systems on curing process of rubber compounds

The curing isotherms for all tested rubber compounds are graphically illustrated in Figs. 1, 2. From them it is possible to see that the highest torque value showed samples cured only with peroxide system (S0-P1.5) in the case of both NR and also NBR based rubber compounds. From Fig. 1 it is evident that torque value of the sample cured only with sulfur system (S1.5-P0) declined when its maximum value was reached. This behavior, the so-called „reversion”, is a negative feature of sulfur cured rubber compounds based on NR, because this phase of curing is connected with destruction of previously formed cross-links. This does not happen when peroxide curing systems are applied in cross-linking of elastomers. As seen in Figs. 1, 2 the torque value of NR and NBR based rubber compounds cured only with peroxide system (S0-P1.5) was kept constant when its maximum value was achieved. The so-called „plato”, is the ideal case because the structure of formed cross-links and cross-link density is not changed. The values of the optimum cure time \( t_{c90} \) of rubber compounds based on NBR shows that the lowest scorch time showed samples cured only with peroxide (S0-P1.5) while the highest one exhibited samples cured only with sulfur system (S1.5-P0). As already mentioned, sulfur curing is a very complex process. A number of mutual and competitive chemical reactions run during this process, which may have substitute, addition and elimination character. The process of cross-linking can be controlled by selection of suitable curing additives, mainly accelerators, pre-vulcanization inhibitors, or vulcanization retarders. Generally, transition complexes formed from activators, accelerators and sulfur are formed in the first stage of sulfur curing. In that time, called induction period, cross-linking does not take place yet. The length of this period depends mainly on the type and amount of accelerator. CBS belongs to sulfur curing is very sensitive, therefore any sulfur (S0.75-P0.75), then a slight decrease of optimum cure time was recorded (Fig. 4).

As seen in Fig. 3, the scorch time of rubber compounds based on NBR was found to increase with increasing amount of sulfur and decreasing amount of peroxide in the applied curing systems. The scorch time of rubber compounds based on NR seems to be less dependent on the curing system composition (Fig. 3). In the case of both types rubber compounds, the lowest scorch time showed samples cured only with peroxide (S0-P1.5) while the highest one exhibited samples cured only with sulfur system (S1.5-P0), while three times longer optimum cure time exhibited the sample cured only with peroxide system (S0-P1.5). The optimum cure time of rubber compounds with mixed sulfur/peroxide systems almost linearly shortened with increasing content of sulfur and decreasing content of peroxide. By contrast, the values of \( t_{c90} \) of rubber compounds based on NBR passed over the slight maximum at the equivalent ratio of sulfur and peroxide (S0.75-P0.75), then a slight decrease of optimum cure time was recorded (Fig. 4).

From Fig. 4 it is shown that the shortest time for optimum curing of rubber compounds based on NR was required for the sample cured only with sulfur system (S1.5-P0), while three times longer optimum cure time exhibited the sample cured only with peroxide system (S0-P1.5). The optimum cure time of rubber compounds with mixed sulfur/peroxide systems almost linearly shortened with increasing content of sulfur and decreasing content of peroxide. By contrast, the values of \( t_{c90} \) of rubber compounds based on NBR passed over the slight maximum at the equivalent ratio of sulfur and peroxide (S0.75-P0.75), then a slight decrease of optimum cure time was recorded (Fig. 4).

Seeing the results presented in Fig. 5, it becomes evident that the highest values of the torque difference \( dM \) showed the samples cured either only with sulfur or peroxide system in case of both types rubber compounds. The \( dM \) values of rubber compounds cured with mixed sulfur /peroxide curing systems varied only very little in dependence on the curing system composition. The scorch time and also the optimum cure time of rubber compounds based on NBR were longer compared to corresponding for \( f_\alpha \) and \( t_{90} \) values of rubber compounds based on NR. This indicate, that the curing process of rubber compounds based on NR runs faster due to the presence of higher amount of reactive groups (mainly double bonds and \( \alpha \)-methylene hydrogen) present in the structure of natural rubber. On the other hand, higher values of the torque difference of rubber compounds based on NBR point out to the higher cross-link density of the equivalent vulcanizates.
3.2 Influence of curing systems on cross-link density

The character of dependences of cross-link density \( \nu \) on the curing system composition and also on the type of rubber correlates with the dependence of torque difference on both factors, confirming that higher cross-link density exhibited vulcanizates based on NBR, and mainly those cured either only with peroxide (S0-P1.5) or sulfur system (S1.5-P0) (Fig. 6). The highest cross-link density showed vulcanizate cured only with peroxide system (S0-P1.5), its value is about two times higher in comparison with the sample cured only with sulfur system (S1.5-P0) and almost three times higher compared to the samples prepared in the presence of mixed curing systems. The cross-link density of vulcanizates based on NR was much lower compared to \( \nu \) of NBR based rubber systems. Although the differences in the \( \nu \) values of vulcanizates based on NR were much lower, it can also be stated that samples cured only with sulfur (S1.5-P0) or peroxide system (S0-P1.5) showed slightly higher cross-linking degree in comparison with the samples cured with mixed vulcanization systems. It becomes also apparent that in both, NBR and also NR based rubber compounds, samples cured in presence of equivalent ratio of sulfur and peroxide (S0.75-P0.75) exhibited the lowest degree of cross-linking.

The biggest difference between the cross-link density of NR and NBR based vulcanizates were observed in the case of samples cured only with peroxide system (S0-P1.5). As shown in Fig. 6 the cross-link density of NBR based vulcanize S0-P1.5 was about six times higher compared to the equivalent vulcanize based on NR. Peroxide curing of elastomers is radical process. In the first step, the molecules of peroxide dissociate into free radicals at vulcanization temperature. The primary radicals can subsequently be fragmented into secondary radicals [10]. The peroxide free radicals subsequently react with macromolecules of rubber. The two mechanisms are suggested in peroxide cross-linking of unsaturated rubbers. Peroxide radicals species can react by addition to a double bond or by abstraction of \( \alpha \)-methylene hydrogens. Eventually both mechanisms might run simultaneously [11]. The macromolecular radicals formed during curing recombine to form cross-links. The primary mechanism in peroxide curing of natural rubber is abstraction of \( \alpha \)-methylene hydrogens from the macromolecular backbone by free peroxide radicals. Macromolecular radicals consequently undergo mutual recombination reactions to form cross-links [12]. From an analysis of the stoichiometry of peroxide cross-linking for natural rubber using DCP, it was concluded that this peroxide forms one mole of cross-links per mole of peroxide, i.e. they are quantitative cross-linking agents [13].

More complex mechanism of cross-linking with peroxides is supposed in the case of butadiene type elastomers. The peroxide free radicals can react with macromolecules of rubber by both mechanisms, by addition to a double bond or by abstraction of \( \alpha \)-methylene hydrogens. The formed macroradicals can, besides mutual recombination reactions, take also part in addition reactions onto the double bonds in macromolecular chains. It is expected the multiple addition of macroradicals on double bonds in polymer chains, which occurs before termination. The chain character of addition reactions results in high cross-linking efficiency, i.e. 10-50 for polybutadiene depending on the microstructure of polybutadiene. High cross-linking efficiency is achieved mainly for polybutadienes and its co-polymers with high amount of 1,2-structural units with side-chain vinyl groups, which are much more reactive towards radical addition reactions in comparison with double bonds situated in main polymer backbone [13]. The above outlined aspects seem to be reason for much higher cross-link density of peroxide cured vulcanizate based on NBR in comparison with equivalent vulcanizate based on NR.

As seen in Fig. 6, various degree of cross-linking was found to be determined also in structures of NR and NBR vulcanizates cured with sulfur system (S1.5-P0), although the difference between them was not as high as in the previous case. The mechanism of sulfur curing is very intricate and still not clearly elucidated. A sequence of parallel and consecutive reactions runs during this process in several steps. Generally accepted statement is that vulcanization with sulfur systems in unsaturated elastomers can be divided into three phases. In the first phase, the interaction of components of curing system leads to the forming of transition complexes, which together with rubber form active cross-linking agent. The second phase is characterized by forming of primary vulcanizate network with dominance of polysulfidic cross-links. During the third phase, this network is restructured in consequence of modification of cross-links (polysulfidic cross-links are transferred into di- and monosulfidic cross-links) and macromolecules of rubber (isomerization, dehydrogenation, cyclization) and the final spatial network of vulcanizate is formed. In term of chemism, ionic character of...
reactions leading to the forming of reactive cross-linking agent are preferred; in the next stages, reactions of radical character are also to be considered [1, 14]. The functional groups active in sulfur vulcanization of unsaturated rubbers are double bonds and α-methylene hydrogens present in their structural units. Compared to NBR, natural rubber exhibits higher amount of reactive centers; therefore it could be supposed that vulcanize based on NR should also have higher cross-link density. But seeing the results in Fig. 6, the reverse tendency was observed. Probably, what contributes to higher cross-link density of the vulcanize based on NBR are some addition reactions of macromolecular radicals, formed also during sulfur curing, on the in-chain double bonds and mainly on the side-chain vinyl units of NBR, thus making curing process more efficient.

In both, NR and also NBR based vulcanizates, the lowest cross-linking degree exhibited vulcanizates cured in the presence of equivalent ratio of sulfur and peroxide (S0.75-P0.75). The possible explanation of this might be some competitive reactions, which may consume free peroxide radical species and/or sulfur fragments, running simultaneously with the main cross-linking reactions.

3.3 Influence of curing systems on physical-mechanical properties
From Figs. 7-11 it becomes obvious that the physical-mechanical properties of tested materials were dependent on the composition of curing systems and on the type of rubber matrix, too.

As shown in Figs. 7-9, the dependences of moduli M100, M300 and the hardness of vulcanizates are in close connection with the dependences of cross-link density of both types vulcanizates. As higher values of cross-link density exhibited vulcanizates based on NBR, these vulcanizates showed also higher values of moduli and hardness. The samples of both NBR and also NR based vulcanizates cured only with peroxide system (S0-P1.5) were found to have the highest values of the examined characteristics. The M300 value of peroxide cured vulcanizate (S0-P1.5) based on NBR was not possible to be measured, because the sample was ruptured at the deformation less than 300%. By contrast, superior tensile strength and elongation at break exhibited vulcanizates based on NR (Figs. 10, 11). Mainly, the tensile strength of NR based vulcanizates was much higher compared to the tensile strength of equivalent vulcanizates based on NBR. From Fig. 10 it also becomes clearly evident that the tensile strength of NR based vulcanizates was improved with increasing amount of sulfur or decreasing amount of peroxide in the applied curing systems. The difference between the tensile strength of the sample cured only with peroxide system (S0-P1.5) and the sample cured only with sulfur system (S1.5-P0) was nearly 10 MPa. The similar increasing tendency in dependence on the curing system composition was recorded also in the case of elongation at break (Fig. 11). Compared to the sample cured only with peroxide (S0-P1.5), the elongation at break increased in more the 250% when the amount of sulfur in the applied curing systems increased to its maximum value (sample S1.5-P0). By contrast, the different dependence of both properties on the curing system composition was observed in the case of vulcanizates based on NBR. As seen in Figs. 10, 11, the highest tensile strength and also
Elongation at break was found to have vulcanizate cured with equivalent ratio of sulfur and peroxide (S0.75-P0.75). There was almost no difference in tensile strength of vulcanizates cured either with only sulfur (S1.5-P0) or peroxide system (S0-P1.5). The tensile strength of both samples was kept slightly over 3 MPa. When sulfur curing system was mixed with that of peroxide one at their equivalent ratio, the improvement of tensile strength at about 1 MPa was recorded (for the sample S0.75-P0.75). Although, the improvement is not so significant, this a very promising aspect relating to the preparation of rubber materials with mixed curing systems. Similarly, the elongation at break reached the highest value when sulfur and peroxide systems were used in their equivalent amount. The elongation at break of the sample S0.75-P0.75 was more than 400% higher compared to that of the sample cured only with peroxide (S0-P1.5) and more than 100% higher compared to that of the sample cured only with sulfur system (S1.5-P0) (Fig. 11).

In order to better understand the different values and different dependences of physical-mechanical properties, the strain-stress curves of the prepared rubber materials were investigated (Figs. 12, 13). It becomes evident that both types vulcanizates show different strain-stress behavior. In the early stages of the strain deformation, the curves of vulcanizates based on NR are very similar in their course (Fig. 12). This can be attributed to the similar values of cross-link density of vulcanizates. The highest cross-link density of the sample cured only with peroxide system (S0-P1.5) is reflected in the highest inclination of corresponding strain-stress curve. High stereoregular structure consisting of almost 100% of cis-1,4-isoprene units provides high crystallizing ability to natural rubber. NR can crystallize spontaneously, but also under applied deformation forces (stress-induced crystallization). The crystallization enhances intramolecular attractive forces which subsequently lead to the reinforcement of the polymer. The stress-induced crystallization can be indicated by much steeper slope on the strain-stress curves. The longer are the slopes, the higher crystallization ability it is possible to observe. From Fig. 12 it becomes obvious that the highest crystallization ability shows the sample cured only with sulfur system (S1.5-P0), while the lowest degree of crystallization exhibited the sample cured only with peroxide system (S0-P1.5). The crystallization ability of vulcanizates cured with mixed sulfur/peroxide systems increased with increasing amount of sulfur and decreasing amount of peroxide. The application of peroxide curing systems leads to the forming of more rigid carbon-carbon bonds between macromolecular chain segments, while in sulfur cured elastomers, the macromolecular chains are linked together by longer and more flexible sulfur bridges. Less mobile C-C bonds restrict the mobility and orientation of macromolecular chains in the cross-linked materials when they are stretched and consequently they inhibit, the stress-induced crystallization, which imparts vulcanizates based on NR high values of tensile strength and elongation at break. Moreover, the formed bonds cause increased deformation stiffness, because of less mobility of macromolecular chains, and thus lowered mechanical properties [15]. On the other hand, more flexible
sulfur linkages facilitate the micro-Brown motion of macromolecular chains segments between the cross-links, which improves the elastic properties of vulcanizates. Thus, the elastomer chains segments may more easily achieve the conformation needed for crystallization. Based upon the obtained results it can be stated that the structure of cross-links is main factor determining the mechanical properties of vulcanizates based on NR. It becomes apparent that the higher is the crystallization ability of the polymer, the higher are the tensile strength and elongation at break of vulcanizates (Figs. 10, 11). The crystallization of natural rubber is also the main factor of much higher tensile strength of vulcanizates based on NR compared to that of vulcanizates based on NBR. NBR is statistical copolymer of butadiene (cis, trans-1,4 and 1,2) and acrylonitrile. Due to the irregularity of macromolecular chains, the crystallization does not take place as also becomes evident from the strain-stress behavior illustrated in Fig. 13. As possible to see, the steepest inclination of the strain-stress curve exhibits the sample cured only with peroxide (S0-P1.5). This can be attributed to the highest cross-link density of this sample. The highest cross-link density in combination with the pattern of low mobile C-C cross-links resulted in the lowest elongation at break of that vulcanize. By contrast, lower cross-linking degree and structure of cross-links formed from more mobile and elastic sulfidic bridges reflected in twice as much higher elongation at break of the vulcanize cured only with sulfur system (S1.5-P0). The highest elongation at break showed the vulcanize cured with equivalent sulfur to peroxide ratio (S0.75-P0.75), which was found to have the lowest degree of cross-linking. The lowest cross-link density is responsible for the lowest inclination mode of the corresponding strain-stress curve (Fig. 13). From Fig. 10 it is possible to observe that the dependence of tensile strength on the curing system composition was much less visible, therefore it can be stated the composition of curing system is of minor importance when emphasis is aimed at tensile strength, but of greater importance when emphasis is aimed at the other physical-mechanical properties of the vulcanizates based on NBR. The highest values of tensile strength and elongation at break of the vulcanize cured with the equivalent ratio of sulfur and peroxide can be also attributed to some synergistic effect of both curing systems.

4. Conclusion
In this study, rubber compounds based on NR and NBR were prepared by applying of mixed sulfur and peroxide curing systems. The main goal was to investigate the influence of curing system composition on cross-linking and physical-mechanical properties of prepared materials. The results showed that higher cross-link density exhibited vulcanizates based on NBR, while the sample cured only with peroxide system showed the highest one. The values of both types vulcanizates cured with mixed sulfur/peroxide curing systems were lower compared to corresponding vulcanizates cured only with peroxide or sulfur curing systems. The moduli and hardness of NR and NBR based vulcanizates are in very close correlation with the change of cross-link density. Different character of dependences on curing system composition was recorded in the case of tensile strength and elongation at break. Both characteristics of vulcanizates based on NR were improved with increasing amount of sulfur and decreasing amount of peroxide in the applied curing systems. The strain-stress curves revealed that crystallization ability of NR based vulcanizates decreases with increasing amount of peroxide in the mixed curing systems, as more rigid and less mobile C-C bonds restricts the mobility and orientation of macromolecular chains when they are stretched, subsequently inhibiting crystallization. The more is inhibited crystallization of the polymer, the worse are the tensile strength and elongation at break of vulcanizates. On the other hand, in the case of vulcanizates based on NBR, the highest tensile strength and elongation at break exhibited the sample cured with equivalent ratio of sulfur and peroxide, suggesting some synergistic effect of both curing systems applied in cross-linking of NBR based rubber compounds.

Acknowledgement
This work was supported by the Slovak Research and Development Agency under the contract No. APVV-0694-12

References

Fig. 13: Strain-stress curves of vulcanizates based on NBR.